[O10.1]

YOUNG SCHOLAR AWARD: Expanding the scope of diamond surface chemistry: Stille & Sonogashira cross-coupling reactions

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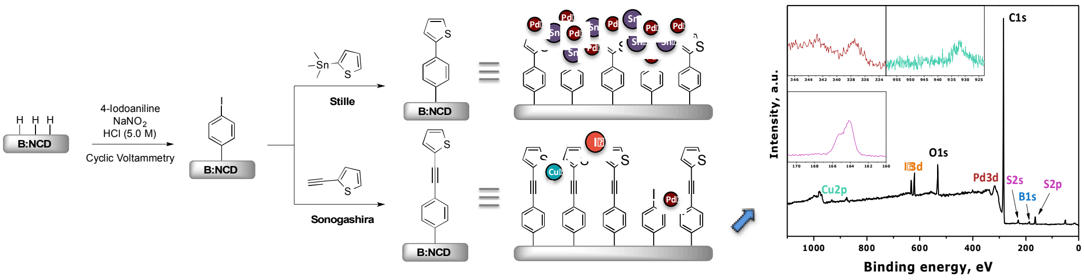
Diamond is an extraordinary material with many appealing properties. This has allowed it to be employed in a large variety of applications, ranging from (bio)chemical sensors to hybrid photovoltaics. Nevertheless, one of diamonds core advantages – a rather inert surface – is also the cause of one of its major limitations, *i.e.* the low reactivity of the diamond surface, complicating direct attachment of functional molecules. H-terminated diamond functionalization generally requires two steps. Initially, a functional handle is introduced via either diazonium/photochemical grafting or direct plasma treatment. Subsequently, the diamond surface can be decorated with a variety of functional moieties using a secondary coupling reaction.

In this work, it is shown that the range of chemical reactions on a H-terminated boron-doped diamond surface can be expanded through a combination of diazonium grafting and Pd-catalyzed cross-coupling reactions, *i.e.* Stille and Sonogashira. This approach enables to couple donor-acceptor type small molecules onto a H-terminated boron-doped nanocrystalline diamond (H-B:NCD) surface toward the realization of p-type dye-sensitized solar cells (DSSCs). By using mainly XPS and FTIR characterization, it was seen that cyclic voltammetry results in efficient diazonium grafting of 4-iodoaniline to H-B:NCD. Further functionalization via Stille cross-coupling provided fundamental insights regarding Pd-catalyzed cross-coupling reactions on diamond thin films and the strong influence of different reagents and employed palladium complexes. The use of organostannyl derivatives typically applied in Stille reactions resulted in severe surface contamination (Pd/Sn). On the other hand, the Sonogashira cross-coupling employing more stable alkynes yielded a higher surface coverage as well as much lower amounts of contaminants, which is of crucial importance when targeting high photon to electron conversion ratios in DSSCs.



Schematic representation of the different diamond functionalization steps and the resulting surface modification.

Keywords: Boron-doped diamond, Surface chemistry, Pd-catalyzed cross-coupling, XPS

[O10.2]

Surface modification of detonation nanodiamonds

L.P. Afonina[1], A.E. Alexenko[1], T.B. Galushko[1], O.A. Kraevaya[2], B.V. Spitsyn*[1]
[1]A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of RAS, Russia, [2]Institute for Problems of Chemical Physics of RAS, Russia

Surface modification of detonation nanodiamonds

L.P. Afonina[1], A.E. Alexenko[1], T.B. Galushko[1], O.A. Kraevaya[2], B.V. Spitsyn[1]

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Nanodiamonds, prepared by explosive techniques, present a novel class of nanomaterials possessing unique surface properties[1].

Due to the very small particle size (2-10 nm), a large percentage of atoms in nanodiamonds are located on the surface of the nanoparticles. Therefore, surface modification of nanodiamonds is an effective method for producing materials with new properties. Among the numerous methods of chemical modification of the nanodiamond surface, fluorination takes a special place as it opens wide possibilities for further surface functionalization with various organic addends, for example, the residues of diamines, amino acids, alkyl radicals[2].

However, the fluorination methods proposed earlier are based on the treatment of nanodiamonds with fluorine gas at temperatures of 150-470 ° C[3], which is rather inconvenient from a preparative point of view. In this paper, we proposed a method for the fluorination of nanodiamonds using liquid antimony pentafluoride at 130^{o}C. The composition and types of the surface groups of the resulting fluorinated nanodiamonds were determined by IR spectrometry, solid state NMR spectroscopy, and elemental analysis. We will also discuss further prospects for using the obtained material as a precursor for the synthesis of new functional derivatives of nanodiamonds.

[1] B.V. Spitsyn *et al*, *Diamond & Related Materials*, 2010, **19**, 123–127

[2] Y. Liu *et al*, *Chem. Mater.*, 2004, **16**, 3924-393

[3] H. Huang *et al*, *Applied Surface Science,* 2012, **258**, 4079–4084

Keywords: nanodiamond, surface, fluorination

[O10.3]

Surface modifications of detonation nanodiamond particles towards radiation-induced hydrated electrons and hydroxyl radicals production

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Abstract: Detonation nanodiamonds (DNDs) have attracted researcher's attention for biomedical fields, specifically, for drug-delivery carriers [1], diagnostic nanotools or even radiosensitizing agents [2] in cancer treatment. Well-controlled mass production provides nanoparticles (NPs) with a primary size of 4-5 nm made of diamond-core and shell-coating containing active surface terminations. Their surface chemistry can be tuned via wet chemistry, thermal treatment or even microwave plasma or methods providing either positively or negatively charged NPs in water suspension.

A few years ago, our team reported on the use of plasma hydrogenated NDs toward radiosensitization of tumor cells [2]. In order to investigate the involved mechanisms, we studied the radicals production under irradiation using a fluorescent probe and we recently reported that plasma-hydrogenated DNDs induce hydroxyl radicals (HO•) overproduction of 40% under X-ray irradiation as detected in aqueous media [3].

The aim of the current study is to further explore the produced species by probing the hydrated electrons in addition to HO•. The effects of surface chemistries and irradiation energies are reported starting from the same DNDs source. For this purpose, DNDs were hydrogenated either by annealing or by plasma. A surface graphitization of DNDs was also achieved by annealing under vacuum to tune the graphitization stage [4]. Oxidized DNDs were used as a reference. For these different surface chemistries, the production of hydrated electrons and hydroxyl radicals under irradiation was compared.

We evidenced the production of hydrated electrons for plasma hydrogenated DNDs for different irradiation energies. Concerning the two hydrogenation approaches, comparable HO• radicals overproduction has been measured. More surprisingly, an overproduction of HO• radicals has also been evidenced on smoothly graphitized DNDs, but with a different evolution versus concentration of DNDs. These results suggest that mechanisms induced by irradiation of DNDs exceed the electronic properties of hydrogenated NDs.

[1] Dean, H. et al., Nanodiamonds: The intersection of nanotechnology, drug development, and personalized medicine, Biomedical Engineering 2015

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[3] Kurzyp, M. et al., *Hydroxyl Radicals Production Induced by Plasma Hydrogenated Nanodiamonds under X-ray Irradiation*, ChemComm 2017

[4] Petit, T. et al., *Early stages of surface graphitization on nanodiamond probed by x-ray photoelectron spectroscopy*, Physical Review B 2011

Keywords: Detonation Nanodiamond, Hydrated electrons, Hydroxyl Radicals, Surface modifications

[O10.4]

Boehm titration for the quantification of oxygen containing surface groups: A critical case study for different carbon materials

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Friedrich Schiller University, Germany

To date, the quantification of oxygen containing groups on carbon materials is still a problem. The analysis methods of the organic chemistry fail because of the insolubility of the material.

H. P. Boehm developed an indirect titration method which allows a quantification of acid oxygen containing groups. Various bases are used to detect different combination of the groups. By subtraction of the values, it is possibly to get the quantity of carbon acids, lactones and phenols (Fig. 1).

With our research, we want to prove that the boehm titration is a valid analysis method with a high reproducibility.

Firstly, we focused on the titration method. We worked with $NaHCO_3$, Na_2CO_3 and NaOH as titrator and analyte solution. The smallest variance of the tested eight aliquotes was reached by the usage of Na_2CO_3 as titrator solution (0.5 Vol%). The titration required only 7 minutes per Aliquote. For that, the reaction bases must be treated with a known excess of HCl. This also eliminates the error of titration which is normally caused by solved CO_2.

After finding the best titration method, we investigated the treatment of different carbon materials with the reaction bases. We tested different aging times and molar concentrations of the reaction base. At CNTs for example one day of aging is sufficient to reach the maximum of conversion (Fig. 1). Moreover, we investigated different ways to remove the carbon from the bases after aging.

Finally, we compared the results of the boehm titration with other typical analysis methods.

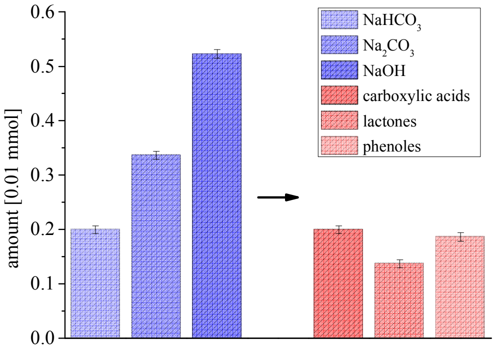

Fig 1: Consumption of reaction base and resulting amounts of oxygen containing groups for oxidized carbon nanotubes by indirect titration method with Na_2CO_3 as titration solution (0.01 M reaction and titrator solutions, 50 ml reaction base on 100 mg CNTs, 4 aliquots (10 ml) for each reaction base)

Keywords: Analysis, Oxygen containing groups, Quantification, Oxidation

[O11A.1]

High purity homoepitaxial diamond (111) film growth

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So far, we have successfully grown high purity homoepitaxial diamond (100) films by utilizing a home-built microwave plasma-assisted chemical vapor deposition (MPCVD) system. Nitrogen concentration of the MPCVD layer is typically less than 1 ppb. By optimizing growth conditions with higher oxygen concentration of 2%, dislocation formation during the MPCVD process was minimized because of efficient etching of the defects at the growth front.

In this study, we applied the growth condition with oxygen addition for (111) film growth. Growth rate was ~ 1 μm h^{-1} at methane concentration of 0.4%. No nitrogen-related luminescence was observed in cathodoluminescence spectra taken from the grown film. By extending the growth time, 400μm-thick homoepitaxial diamond (111) film was deposited on a HPHT type-Ib (111) substrate. Although crack was not formed extensively in the film, film surface became rough with film thickness.

Keywords: homoepitaxial, (111) orientation, purity

[O11A.2]

Mechanism of formation of twins and non-epitaxial inclusions in microwave plasma CVD growth of (001) single-crystalline diamond

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The growth of single-crystalline (SC) CVD diamond with minimized abundance of defects is of paramount importance for the application of this material in various fields. Here we investigated the epitaxial growth processes of (001) SC CVD diamond in order to understand the mechanisms that hinder the growth of thick SC diamond layers, such as the formation of twins and polycrystalline inclusions. Polished (001) HPHT diamond crystals were used as substrates. The epitaxial films were grown in a microwave plasma CVD reactor ARDIS-100 (2.45 GHz) in “hydrogen-methane-nitrogen” gas mixtures (H_2: 460 sccm, CH_4: 20 sccm, N_2:20 sccm) at the substrate temperature of 800 °C with growth rates of up to 40 μm/h. [1]. The deposition time was varied from 5 to 70 min. Our findings show that the major source of twin formation is the (111) surfaces, spontaneously formed during layered CVD growth (Fig. 1a). Such surface may be generated by the intersection of multiple growth fronts of diamond (Fig. 1b). Thus, the effects of off-angles will be discussed. We will also show that dislocations in the substrate tend to form hillocks with non-epitaxial inclusions on the top.

The produced material was studied by the means of photoluminescence and Raman spectroscopy, optical profilometry, X-Ray diffraction, high-resolution scanning electron microscopy, and UV/Vis/IR spectrophotometry. The results can be used to improve growth processes for various applications of diamond, including optical windows and jewelry, cutting tools and substrates for electronic devices.

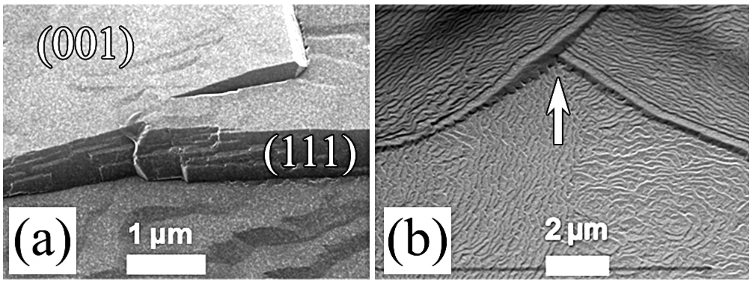

Fig. 1 SEM images of single-crystal epitaxial CVD diamond layers: (a) formation of twins near dislocation-generated non-epitaxial inclusions; (b) generation of defects in the intersection of multiple growth fronts.

References:

1. Ashkinazi, E. E., et al. "Growth of nano-crystalline diamond on single-crystalline diamond by CVD method." *Bulletin of the Lebedev Physics Institute* 43.12 (2016): 378-381.

Keywords: single-crystalline diamond, CVD growth, defects

[O11A.3]

Effect of Ar addition into H2/CH4 source gas mixture on microwave plasma for diamond growth

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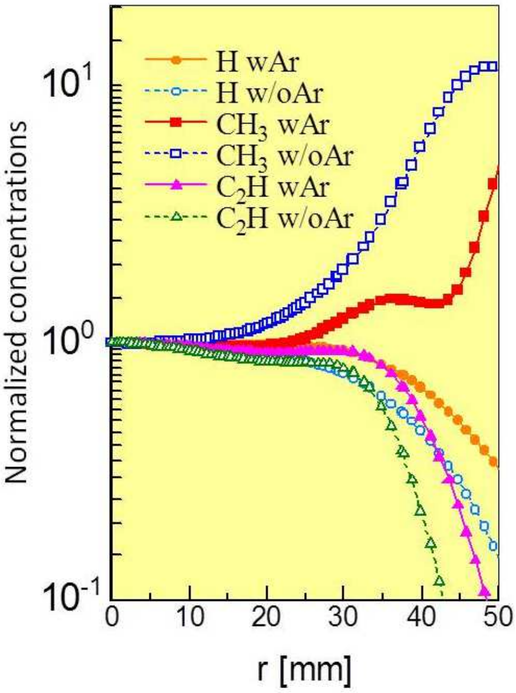
Microwave (MW) plasma chemical vapour deposition (CVD) has been widely adopted for diamond growth especially for the purpose of realization of diamond electronic devices. However, this method still has several draw backs in the growth rate and uniformity. One may apply huge input power to improve these problems, which results in enhancement of wasting power. Ar addition into the microwave plasma discharge is known to realize improved growth rate. However, its effect on the uniformity of the growth and species distributions over the growth area are not clear. In this work, to elucidate changes in the gas phase caused by Ar addition, and its mechanism of the effect on the growth are studied numerically, and compared with the growth experiment.



The right figure shows profiles of several species along with the lateral direction, for the cases with and without Ar, where all species are normalized by the respective magnitude at the centre, r=0. For the case with Ar, its concentration in the source gas mixture was set to 49%. The calculation was conducted under MW power 3kW and the gas pressure 16kPa. Methane concentration in the source gas mixture was fixed to 2%. We obtained increase of the gas temperature several hundred K owing to the Ar introduction (not shown). In addition to increase of the radical densities, we obtained improvement of the uniformity of the hydrocarbon species as shown in the figure. This implies the Ar introduction may contribute to the improvement of uniformity as well as increase of the growth rate.

Keywords: microwave plasma, single crystal, simulation

[O11A.4]

Spectral-resolved video recording of pulsed microwave plasma assisted chemical vapor deposition discharges

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The formation of pulsed microwave discharges in a microwave plasma cavity reactor under single crystalline diamond (SCD) growth conditions was reported for frequencies between 50 and 500 Hz using a frame rate of 5000 fps (200 µs exposure time per frame) [1]. The methane concentration was 5% and the operating pressure was 300 Torr. It has been found that the dynamics of the discharge formation is more complex than previously described with modeling efforts [2]. Several different cases were identified depending on the pulsing conditions (t_{on} and t_{off}): (1) ignition of the discharge nearby its corresponding position at continuous excitation (steady state position), (2) an arc-like ignition on the SCD surface, followed by a detachment when the discharge floats towards its steady state position or (3) the ignition of two separate discharges, one on the SCD surface and a second one halfway between the SCD and the steady state position with the discharges subsequently merge. It was also observed that the second discharge appeared purple instead of green indicating a hydrogen based discharge. Overall, these different dynamics were not expected and cannot be explained by currently accepted models.

In this study, we report on the hydrogen and methane species distribution in the discharge and their dynamic development. This will provide a better explanation why the different ignition patterns occur, how the species densities behave over time and how that correlates with current models. The high-speed camera is equipped with bandpass filters of relevant wavelengths corresponding to the spectral lines to separately analyze the individual species. Videos of the unfiltered discharge are compared with videos showing the development of only one species at a time for all ignition behaviors previously observed. The atomic hydrogen density is of particular importance to explain the nature of the two different discharges observed in (3). Additionally, the data set will be particularly useful to encourage the development of more advanced models at pressures in the 300 Torr regime.

References:

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[2] Brinza et al., Physica Status Solidi (a), 204, 2847 – 2853 (2007)

Keywords: pulsed deposition, video imaging, plasma spectroscopy

[O11A.5]

YOUNG SCHOLAR AWARD: Effect of solvents on boron-doped diamond synthesis by in-liquid microwave plasma CVD process

Y. Harada*[1,2], Y. Sakurai[2], K. Miyasaka[2], C. Terashima[2], H. Uetsuka[1,2], N. Suzuki[2], K. Nakata[2], K. Katsumata[2], T. Kondo[2], M. Yuasa[2] et al

[1]Asahi Diamond Industrial Co., Ltd., Japan, [2]Tokyo University of Science, Japan

Boron-doped diamond (BDD) is a promised material as electrodes for electrolysis and sensing. An in-liquid microwave plasma CVD (IL-MPCVD) method has been applied for diamond growth [1]. Here, we report high speed synthesis of polycrystalline BDD film from organic solvents by IL-MPCVD process.

Fig. 1 shows a schematic of IL-MPCVD system. Vapour of organic solvents was decomposed at the apex of electrode in microwave plasma. Diamond films were grown on Si substrate from several mixtures of organic solvents. B_2O_3 was used as a source of boron. Pressure in the reactor and microwave power were set as 60 kPa and 500 W, respectively.

Composition of the solvents for each experiment is summarized in Table 1. Non-doped diamond from EtOH/MeOH is grown with 160 μm/h (Fig. 2a) by IL-MPCVD method. The growth rate of BDD from EtOH/MeOH + B_2O_3 (B/C = 1.5%) showed much higher value of 287 μm/h. Fig. 3 shows Raman spectrum of the BDD film. The boron concentration of the BDD film was estimated up to 7×10^{21} cm^{-3}. In order to reveal a mechanism of the higher growth rate, effect of H_2O was studied since H_2O is produced by the reaction between MeOH and B_2O_3. As shown in Fig. 2b, diamond did not grow as film from EtOH/MeOH + H_2O, despite the same C : H : O ratio as non-doped diamond. It suggests radicals working as etchant were effectively generated from H_2O. On the other hand, high etching effect from H_2O enabled to grow diamond in carbon rich condition (see Table 1 BDD). This is the mechanism of rapid growth of BDD by IL-MPCVD process. Further investigation using other solvents will be discussed.

Reference

[1] Y. Harada, *et al.* Diamond Relat. Mater. **63** (2016) 12.

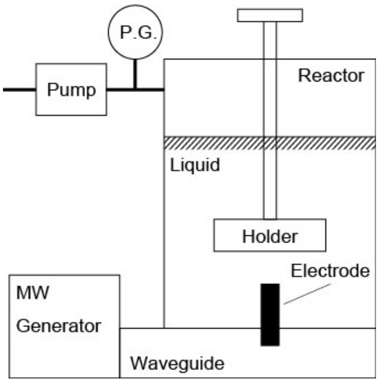

Fig. 1 Schematic of IL-MPCVD system.

Table 1 Composition of the solvents.

System	**MeOH**	**EtOH**	**B_2O_3**	**H_2O**	**C : H : O**

Non-doped	360 cm^3	40 cm^3	-	-	17.2 : 66.7 : 16.1
BDD (B/C = 1.5%)	360 cm^3	130 cm^3	7.14 g	-	18.1 : 66.4 : 15.5
Non-doped with H_2O	360 cm^3	130 cm^3	-	24.05 cm^3	17.2 : 66.7 : 16.1

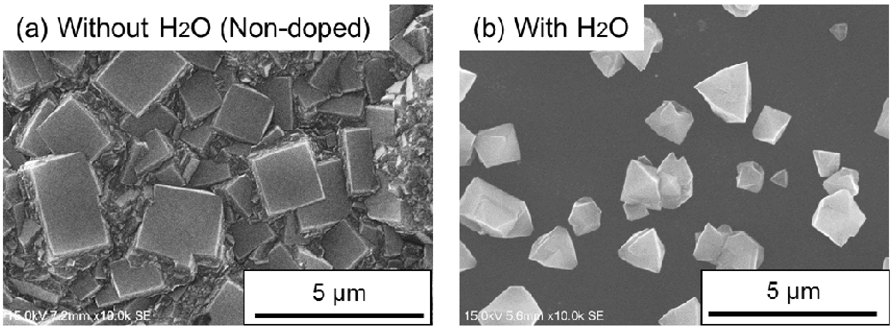

Fig. 2 SEM images of grown diamonds from the same C : H : O ratio.

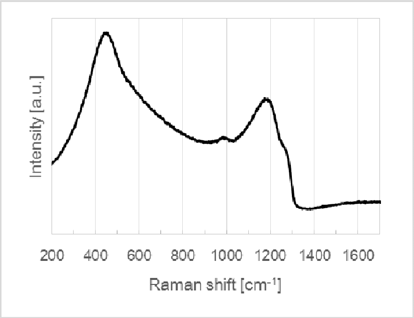

Fig. 3 Raman spectrum of BDD by IL-MPCVD.

Keywords: Boron-doped diamond, High-speed synthesis, In-liquid microwave plasma, CVD

[O11A.6]

Low resistivity phosphorus doped diamond thin films grown on {111} substrates with low off angles

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We characterized the electrical properties of heavily P-doped diamond thin films grown on {111} surface with less than 2 degrees. Growth of {111} P-doped diamond thin films were performed in MPCVD system designed for heavily doping. The growth conditions are as follows, CH_4/H_2: 0.05 %, total gas pressure:100 Torr, PH_3/CH_4: 10,000 ppm and substrate temperature: 900~910 ˚C. The substrate off angles are in the range of 0.5~1.5 degrees to the direction of [$\bar{1}2\bar{1}$]. The electrical properties were characterized by Hall measurements (RT~600 ˚C) and the impurity profiles were measured by SIMS. We confirmed the increase of P incorporation efficiency and the decrease of growth rate as the off angle of the substrate decreases in a good agreement to our previous study [1]. The incorporation efficiency and P concentration were 5% and $8x10^{19}$ cm^{-3}, respectively, at the off angle of 0.7 degree. The sample exhibited clear n-type conductivity at high temperature and hopping conductivity dominated in the regime lower than 500 K as confirmed by Hall measurements. The resistivity of the sample was 50 Ωcm at RT and the value is the lowest one ever reported for P doped n-type diamond. From SIMS analysis, it was also confirmed the low resistivity sample showed lower hydrogen incorporation. This is probably due to higher quality crystal growth obtained on lower off angle substrate surfaces.

[Reference]

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Keywords: Diamond, CVD, n-type

[O11B.1]

Continuous graphene growth by open roll to roll chemical vapour deposition system

J. Robertson*[1], G. Zhong[1], X. Wu[1], S. Zheng[1], L. D'Arsie[1], K. Teo[2], N. Rupersinghe[2], A. Jouvray[2]

[1]*Cambridge University, UK,* [2]*Aixtron Ltd, UK*

We demonstrate the growth of high-quality, continuous monolayer graphene on Cu foils using an open roll-to-roll (R2R) chemical vapor deposition (CVD) reactor with both static and moving foil growth conditions [1]. Previous R2R systems were not truly R2R suitable for pre- or post-growth treatments because they were actually cassette type closed systems. Here a true open, atmospheric pressure system is shown. Reactor over-pressure and slits keep the atmosphere out. No large scale differential pumping is used. N_2 not Ar was used as carrier gas to reduce process cost, and does not cause ‘doping’. The concentrations of H_2 and CH_4 reactants were kept below the lower explosive limit to ensure process safety for reactor ends open to ambient. The carrier mobility of graphene at a Cu foil winding speed of 5 mm/min was 5270-6040 cm^2/V.s at room temperature (on 50 μm x 50 μm Hall devices). Raman 2D/G ratio was over 2.5. These results will enable the in-line integration of graphene CVD for industrial R2R production.

[1] G Zhong et al, App Phys Lett 109 193103 (2016)

[O11B.2]

Hexamethyldisilazane precursor modified onto SiO_2/Si wafer for transferless graphene growth

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[1]BGT Materials, UK, [2]University of Manchester, UK

Transparent electrode has been playing a vital role in consumer electronics, such as touch screens and displays. In current industry, indium tin oxide (ITO) is the mostly used material for transparent electrodes. However, it is expensive as indium (In) is a scarce material, which makes up about 0.2 parts per million of our crust. ITO replacement has been one of top issues of current industry, which we have been looking for ideal solution.

Few-layered graphene sheets associates transparency with conductivity, making it one of the ideal materials for ITO replacement. In order to integrate graphene into current fabrication process, the modification of Hexamethyldisilazane (HMDS) directly onto SiO_2/Si wafer as a reaction precursor can efficiently sort out this issue. This innovative transferless approach successfully demonstrates in-situ growth of large-area graphene sheets on 300-nm-thick SiO_2/Si substrates through low-pressure CVD process. The growth process of HMDS-derived graphene was illustrated in Fig. 1(a). The HMDS was vapor-primed on SiO_2 surface before reaction process, converting the hydrophilic SiO_2 surface into a hydrophobic surface by replacing the hydroxyl end groups with methyl groups as shown in Fig. 1(b). Then, alternating Ni/Cu/Ni layers were sequentially thermo-evaporated onto the HMDS-modified SiO_2 surface to function as catalysts in the CVD reaction. In LPCVD process, carbon atoms, which decomposed from HMDS, diffused into the Ni-Cu alloy originating from pre-deposition of Ni/Cu/Ni layers. After the reaction and the fast cooling process, single- to few-layer HMDS-derived graphene sheets can be obtained at the interface of Ni-Cu alloy and SiO_2 surface. By removing the top layer of Ni-Cu alloy with FeCl3 etchant, the HMDS-derived graphene films grown on the entire SiO_2/Si wafer are ready for subsequent device fabrication without any further transfer. The experimental results are shown in Fig. 2.

This method has great potential for low cost carbon-based circuit and transparent electrodes.

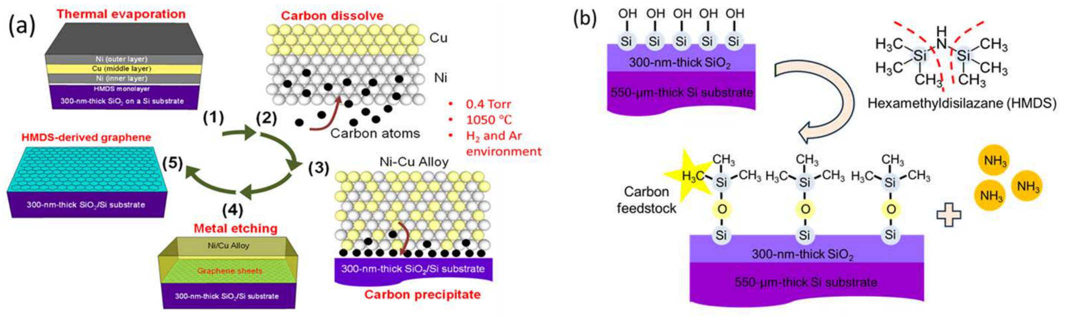

Fig 1.

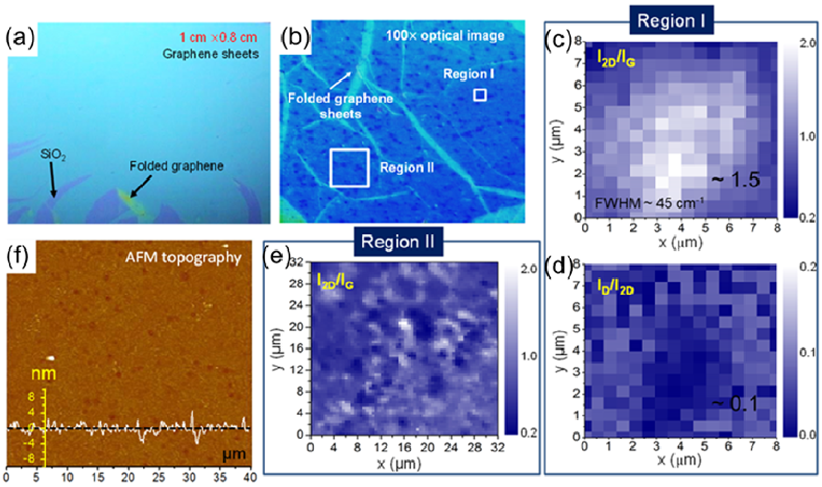

Fig. 2

Keywords: CVD, Hexamethyldisilazane

[O11B.3]

Mechanism of delaminating CVD graphene from its native metal substrate by electrochemical bubbling

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[3]Nanjing University of Posts and Telecommunications, China

Transfer of chemical vapor deposited graphene from metal catalyst e.g. copper [1] and platinum [2] onto insulating substrate is the most critical step for application. Recently, an efficient/non-destructive electrochemical delamination method has been proposed as an alternative to conventional etching transfer, alleviating the problem of cost and environment pollution because it needs not to etch away the metal. Here, the mechanism is for the first time elucidated by studying the effect of various electrolytes on delamination rate. A capacitor-based circuit model is proposed and confirmed by electrochemical impedance spectroscopy [3]. The delamination of graphene can be viewed as the electric “breakdown” of one of the capacitors formed between the electrolyte and sample. A factor of 27 decrease in the time required for complete graphene delamination from platinum cathode is found when increasing the NaOH ratio in the electrolyte solution. The surface screening effect induced by the nonreactive Na^+ ions in the vicinity of electrodes plays a key role in the delamination efficiency. Although Na^+ ions never take part in water electrolysis, many are attracted to the vicinity of the negative electrode and screen out the H^+ from the backside of metal (open surface). This effect offers the main driving force for H_2 bubbles to squeeze into the graphene-metal interface and separate them. If the screening effect is absent, although bubbles are still formed, they are primarily gathered at the backside of the metal foils and can hardly delaminate the graphene from metals at the interface. Our discovery is generic and can be used as a guideline to describe and design the delamination of other 2D materials.

1. J. Sun et al, IEEE Trans. Nanotechnol. 2012, 11, 255.

2. J. Sun et al, Appl. Phys. Lett. 2014, 104, 152107.

3. J. Sun et al, Adv. Mater. Interf. 2016, 3 1500492.

Keywords: Electrochemical bubbling transfer, Chemical vapor deposition, Graphene, 2D materials

[O11B.4]

Characteristics of graphene grown on various metal sputtered on single crystal substrates

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We have examined the optimization of synthesis conditions to obtain large and high quality single crystal graphene by CVD method. Graphene was grown on catalytic metal thin films sputtered onto (100) MgO and c-plane sapphire single crystal substrates. Nickel, platinum and copper were adopted as the catalyst metal. Since these catalytic metals grow heteroepitaxially on the surface of (100) MgO and c-plane sapphire substrates, we expected that single crystal metal thin films can be obtained. When graphene grows on this single crystal metal thin film, we expected that graphene will become a large and high quality single crystal.

The catalytic metal and graphene were synthesized by a RF magnetron sputtering and CVD, respectively. Carbon films on MgO substrate were evaluated by X-ray diffractometer, scanning probe microscope, and laser Raman microscopy system.

Pt thin films of a (111), a mixed of (111) and (100), and a (100) orientation were deposited on a (100) MgO substrates. Next, graphene was grown on these Pt thin films. The intensity ratio I_{2D}/I_G of the G peak and the 2D peak of the carbon on (111) Pt was 2.46, and the full width at half maximum (FWHM) of the 2D peak was narrow. Also, since the D peak was small, crystallinity was high. I_{2D}/I_G of the carbon on (111) (100) Pt and (100) Pt were 0.5 or less, so it was found to be graphite. In addition, it was found that the D peak was observed very strongly and the crystallinity was also low. Since the atomic arrangement of the (111) of Pt are close to the honeycomb structure of graphene, it is considered that graphene is epitaxially grown on the (111) Pt surface.

Results on the sapphire substrate and other metal thin films will be reported on the day.

[O11B.5]

Deposition of 300mm wafer scale amorphous carbon via microwave plasma CVD as a solid phase source for graphene growth at low temperatures

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Graphene exhibits the unusual electrical property of ballistic transport; thus, multilayer graphene is a promising candidate for post-Cu interconnects in next-generation memory devices. Generally, multilayer graphene is grown via chemical vapor deposition (CVD) using a gas-phase hydrocarbon precursor. Multilayer graphene growth via CVD requires the complex parameter control of the total precursor flow, the gas flow rate, and the catalytic reaction rate. Solid-phase carbon-specifically, amorphous carbon (a-C)-is expected to be novel carbon source for the growth of multilayer graphene. Here we demonstrate multilayer graphene growth using an a-C precursor synthesized via microwave plasma enhanced chemical vapor deposition (MW-PECVD). We fabricated a unique sandwich structure, Ni/a-C/Ni, on a 300mm SiO_2/Si wafer. The first Ni layer was formed on the SiO_2/Si wafer via DC magnetron sputtering at room temperature (RT). The deposited Ni was subsequently annealed in two steps, 300°C and 650°C, to crystallize the nickel. The a-C layer was grown on the deposited Ni layer via MW-PECVD at 200°C. Finally, the second Ni layer was formed on the a-C/Ni layers via DC magnetron sputtering at RT. The Ni/a-C/Ni sandwich structure was annealed at 650°C, resulting in multilayer graphene grown on the surface via carbon diffusion into Ni and segregation between the graphene and Ni. The multilayer graphene grown by annealing at 650°C was highly crystalline ($I_G/I_D>34$) and exhibited a large grain size ($L>1$ µm) according to Raman scattering spectroscopy and scanning electron and transmission electron microscopy observations. The results indicated that a-C offers advantages as a novel precursor for low-temperature graphene growth. We further investigated the a-C properties via first-principles molecular dynamics calculations based on the detailed measurement results of density, composition, bonding, and C-H/C-C ratio. This paper is based on results obtained from "Project to develop cross-sectoral technologies for IoT promotion" commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

Keywords: amorphous carbon, graphene, microwave plasma CVD, 300mm wafer scale

[O11B.6]

Formation conditions for epitaxial graphene on diamond substrates

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Graphene has rather recently emerged as a new discovery and has attracted an avalanche attention because of the unique structural, physical and mechanical properties. The availability of samples of graphene has led to extensive exploration of electronic properties and novel transport phenomena in this material. Although several ways of producing graphene have been reported, none of them can be qualified as a high yield method. Efforts on fabrication of epitaxial graphene on SiC have elevated the expectations towards large area homogeneous graphene by applying a high-temperature (2000^{o}C) atmospheric pressure sublimation process [1].

In this paper we present the possibilities for growth of epitaxial graphene on a non-terminated diamond (111) surface under the assumption of a high-temperature sublimation process. We apply annealing experiments at temperatures between 1200 and 1800 ^{o}C of diamond substrates in vaccum and in H2 atmosphere to investigate the formation of grapheme on diamond. The formation of graphene is characterized using local etching in combination with AFM and white light interferrometry to measure the layer thickness. The electronic properties are characterized by contact mode Atomic Force Microscopy (AFM) and the structural properties by confocal Micro-Raman scattering.

These data are compared with results from theoretical modeling, where we have applied ab initio molecular dynamic simulations, including corrections for van der Waals interactions. They show that a temperature dependent graphitization will take place with start from the first C layer on the diamond surface. Graphene-like “bubbles” were initiated at ~500^{o}C, which were fully developed at ~2000^{o}C. Interstitial H within the diamond surface, positioned in the proximity to the surface-“grapheme” bonds did not result in major bond breakage. A higher H concentration led to H-termination of the bare parts of the diamond surface, and the saturation of the sp^{2} carbons in the graphene-like net. On the other hand, a high concentration of substitutional N resulted in a fast conversion to graphene.

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Keywords: Theory, Graphene, Growth

[O12.1]

How bright can be electrically driven single-photon sources on diamond?

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Despite the rapid development of quantum technologies, the absence of efficient bright true single-photon sources (SPSs) operating at room temperature hinders the development and practical implementation of many prospective quantum devices ranging from secure communication lines based on quantum cryptography to quantum computers. Color centers in diamond are considered as the most perspective platform for room temperature SPSs. Although the photoluminescence of these defects in the crystal lattice of diamond is well studied, their prospects for electrically pumped sources are still under question. The semiconducting properties of diamond give the possibility to excite color centers electrically. However, the observed emission rates are much lower than that required for quantum devices of the future. Without an understanding of the electroluminescence process of color centers in diamond, it is not clear to what extent the photon emission rate can be increased.

Here, we present a theoretical model that qualitatively and quantitatively describes single-photon emission from color centers upon electrical injection. Results of self-consistent numerical simulations of the single-photon emitting diode based on the proposed model demonstrate good quantitative agreement with the reported experimental values. Moreover, the revealed mechanism of the electroluminescence process leads to unexpected results. The quantum efficiency does not change appreciably as temperature increases, while the emission rate increases with temperature. In other words, one should heat electrical SPSs based on diamond to improve their performance. It is noticeable that the brightness improvement can achieve three orders of magnitude (Fig. 1) giving the possibility to increase the photon emission rate up to 10^7–10^8 counts/s at 500–600 K. These findings demonstrate the potential of electrically pumped SPSs on diamond and create the backbone for engineering of practical single photon sources.

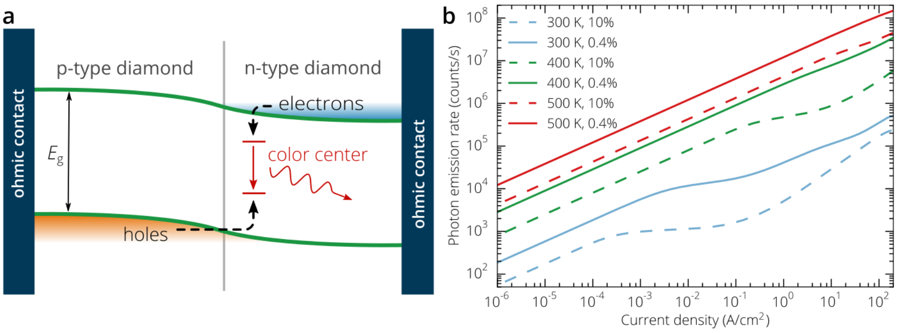

Fig. 1. (a) Schematic of the diamond p-n diode with a color center. (b) Photon count rate versus pump current at different temperatures and compensation ratios of the n-region of the diamond diode.

Keywords: color centers in diamond, electrically driven single-photon source, nitrogen-vacancy (NV) centers, silicon-vacancy (NV) centers

[O12.2]

Cooperatively-enhanced atomic dipole forces in optically trapped nanodiamonds containing NV centres, in liquid

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Nanodiamonds (NDs) containing colour centres are remarkable objects which find applications in a wide range of disciplines, from quantum information technology to quantum metrology and bio-sensing. In life sciences, fluorescent nanodiamonds are implemented as non-toxic biomarkers for biomedical imaging[1] and drug delivery.[2,3] In recent experiments they have been tracked within living cells,[4] and optically manipulated in liquid,[5] yet their manipulation in a 3D biological environment remains beyond reach. Classical optical tweezers cannot trap particles much smaller than ~100 nm. We propose a new approach that stems from cold-atom trapping experiments[6] and addresses this limitation.

We exploit artificial atoms – colour NV centres within the nanodiamond host (~10^3 NVs/particle) – to enhance the trapping of the whole crystal via near-resonant forces acting on them. While holding the nanodiamond (~100 nm) at the focus of classical optical tweezers in liquid,[7] we employ a second near-resonant laser beam, slightly detuned from the dipole transition of the target colour centres.

We measure a change in trap stiffness of ~10%, which is the signature of atomic dipole forces.[8] Most interestingly, we show that our findings can only be ascribed to the existence of collective effects – 'superradiance' (SR) – between colour centres, which has never been reported before at room temperature for a solid-state system archetype of that originally proposed by Dicke in his seminal paper on superradiance.[9]

While the effect of the resonant trapping is limited for NV centers in NDs, we project an increase of at least an order of magnitude for other diamond colour centres, e.g. silicon-vacancy centres. We foresee the ability to trap nanoparticles with sizes (~tens of nm) and forces (~hundreds of pN) currently unattainable with conventional optical tweezers,[10] towards dynamic, single-molecule experiments. Moreover and most importantly, our findings on superradiance offer the prospect of quantum engineering a tailored, room-temperature SR system for applications in quantum metrology[11] and light harvesting.[12]

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Keywords: Nanodiamond, Nitrogen-vacancy NV centre, Optical Trapping, Superradiance

[O12.3]

Doping diamond with Ge and Eu: Understanding the electronic structure

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Within the quantum physics community, diamond is currently the material of choice, as it can contain defects that act as single-photon emitters with long coherence times at room temperature. In this context, the NV centre has been widely studied. Unfortunately, the strong phonon-coupling of this defect gives rise to a weak zero phonon line. The incorporation of Ge and Eu provide interesting alternative luminescent centres.

In this work, we present a density functional theory study of Ge and Eu defect centres in diamond. The contributions to the electronic structure of the different parts of the defect complexes are indicated, and related to the intrinsic different nature of the dopants. The modification of the intrinsic vacancy states [1] is discussed in detail. We also pay attention to the role of the spin configuration of the surrounding C atoms. Charge-transfer between the complexes and the host diamond lattice are investigated using the Hirshfeld-I “atoms-in-molecules” partitioning scheme [2]. This in turn is linked to the calculated stability of the different possible charge states of the Eu and Ge defect complexes.

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Keywords: Density Functional Theory, Electronic band structure, Ge, Eu

[O14.1]

Electrical and optical characterization of diamond 2-D hole-gas with different chemical treatments

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After years of development, AlGaN/GaN 2-D electron-gas FETs have revolutionized the power RF field. With a similar development effort diamond 2-D hole-gas FETs are expected to enable devices with an order of magnitude increase in performance. The two major development challenges are an increased surface conductivity of the 2-D hole-gas, and FET stability at high voltages. At present the surface conductivity of diamond is > 2000 Ω square^{-1} while AlGaN/GaN is ~ 300 Ω square^{-1}.

Hydrogen-terminated diamond, with the appropriate surface treatment, forms a 2-D hole gas at its surface. Electron acceptors generated by treatment with NO_2, O_3, and Cl_2 decreases the resistance to 1000 to 2000 Ω square^{-1}. All these surface dopants are unstable in air with their properties diminishing in time, decreasing carrier density and increasing resistance. We report a doping approach using UV-generated free radicals. These radicals abstract hydrogen from the diamond surface and insert themselves at that site. The resulting surface has increased stability over NO_2 treated diamond with comparable conductivity.

Surface conductivity was measured with a Hall – Van der Pauw system to quantify carrier type, density, and mobility. Further infrared absorption measurements of the surface chemistry after treatment with NO_2, Cl_2, and free radicals implies that these compounds react with the diamond surface to form the 2-D hole gas. The results for this class of compounds are counter to the standard charge transfer model where the NO_2 adsorbs on the diamond surface as a negative ion NO_2^{-}.

This material is based upon work supported by the Assistant Secretary of Defense for Research and Engineering under Air Force Contract No. FA8721-05-C-0002 and/or FA8702-15-D-0001. Any opinions, findings, conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Assistant Secretary of Defense for Research and Engineering.

Keywords: Diamond, surfac conduction, Photo radical, diamond FET

[O14.3]

Improvement on electrical properties of H-terminated diamond FETs using sputter deposition AlN/ atomic layer deposition Al_2O_3 stack gate structure

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A significant enhancement in electrical properties was achieved from AlN/Al_2O_3 stack gate metal-insulator-semiconductor (MIS) field effect transistors (FETs) upon improving the structural quality of the AlN insulating layer. To circumvent the hole channel loss due to thermal sensitivity of hydrogen-terminated (H-terminated) diamond substrate and large leakage current attributed to the large grain size (~100-400 nm) of AlN, herein the AlN layers were deposited at room temperature (RT) by sputter deposition (SD) method under the Ar+N_2 plasma conditions. Upon optimizing the SD parameters, especially Ar and N_2 flow rates, a smooth, transparent, good stoichiometry, and highly insulating AlN layers were obtained (root mean square: 1.1 nm) with columnar grain structure having a smaller average grain size of ~40 nm. Cross-sectional TEM observation confirmed that the grains were oriented along the *c*-axis direction of the substrate. Moreover, the AlN layers were polycrystalline as indicated by the selected area electron diffraction pattern. Then a ~25-nm-thick AlN was used to fabricate the MISFET and MIS diode devices. Prior to SD-AlN, a 5-nm-thick amorphous atomic layer deposition (ALD)-Al_2O_3 was deposited onto H-terminated diamond substrate to prevent surface damage by Ar+N_2 plasma. The measured $C-V$ characteristics indicated a p-type semiconductor, where the accumulation and depletion regions were clearly observed. The drain-source current maximum ($I_{DS,MAX}$) obtained from SD-AlN/ALD-Al_2O_3/H-terminated diamond MISFET with 4 μm gate length is around −65.7 mA/mm with normally-on mode. These improved characteristics were attributed to the quality of the AlN insulating layer due to the smaller AlN grains and good stoichiometry of AlN layer.

Keywords: FET, AlN, Al2O3

[O14.4]

Dual-gate diamond field-effect transistors for electrostatic control of valley polarization

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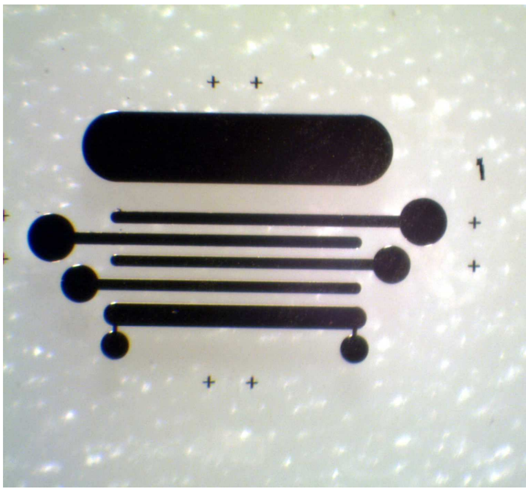
The valley degree of freedom of electrons is attracting growing interest as a possible information carrier in several semiconductor materials, e.g. diamond, graphene and monolayer transition-metal dichalcogenides. As a vision for the future, it will be possible to utilize valley polarization properties to make information processing devices with low power consumption. This fledgling field has been termed “Valleytronics” in analogy with spintronics. During the last few years, there has been an intense effort to generate and detect valley polarized states in several promising materials. M groups have concentrated their efforts to monolayer transition metal dichalgogenides (TMDCs) and valley polarization in e.g. MoS_2 has been reported, albeit with a relaxation lifetime of less than 1 ns.

In 2013 our group reported valley polarization in diamond [1] for the first time, using optical means to inject carriers, and high electric fields to generate valley polarized electron populations. We also showed that the valley polarization could be detected using the Hall effect and that the valley polarization lifetime can exceed 300 ns at 77 K.

Diamond is a unique and unsurpassable platform for studying valley polarized states, for observing spin-orbit interaction phenomena and measuring the interaction of valley polarized states with impurities. To achieve full control of valley polarised states in diamond we have developed dual-gate field effect transistors on intrinsic single-crystalline diamond with an aluminium nitride gate oxide. We show that it is possible to effectively separate conduction band electrons in different states of valley polarization in these devices by utilizing the effective mass anisotropy in different conduction band valleys.



Dual-gated diamond field effect transistor.

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Keywords: Valleytronics, charge transport, field-effect transistors

[O14.5]

Leakspots in diamond power device stack of layers: A TEM investigation

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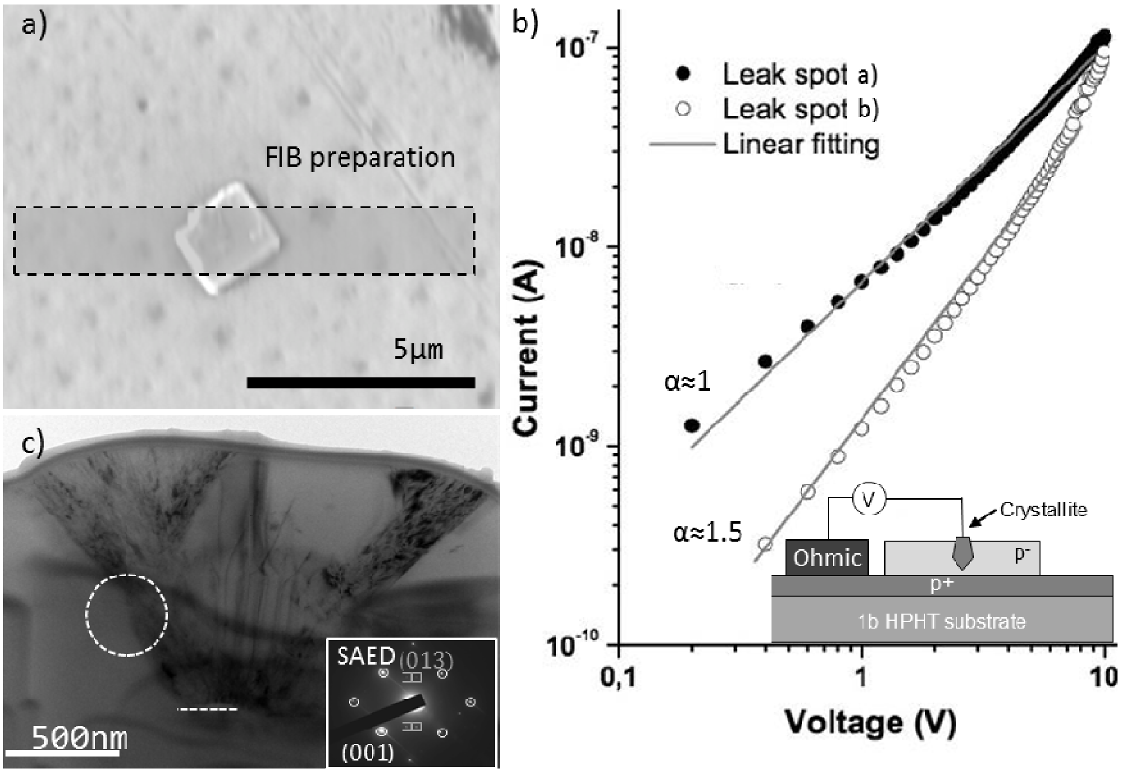
[1]Universidad de Cádiz, Spain, [2]Université Grenoble, France, [3]CNRS,Institut NEÉL, France,
[4]Institut Universitaire de France, France

Diamond power devices development is attractive because its expected high voltage and temperature strength, however some specifics technological aspects still need to be overcome. In particular, homogeneous behaviour among the entire substrate should be improved. Indeed, stacks of layer frequently show undesired forward leakage currents in some sectors of the total substrate surface. The present contribution identifies the origin of this peculiar electrical behaviour. Some defective sites have shown ohmic behaviour when biased in reverse direction. The defective sites correspond, under SEM observations, to crystallites. TEM sample preparations at these sites with a FIB machine allowed observing the crystallite depth configuration in cross sectional view. Dislocation at the crystallite grain boundary and inside explains the electrical behaviour of the layer stack.

Figure: SEM micrography (a) and I/V ohmic characteristics of two leakspots (b). TEM observation of crystallite (c) whose I/V characteristic corresponds with black spots in (b). SAED, obtained in dashed circled region, shows two different and well defined crystalline orientations (see inset). The location of the FIB sample preparation of micrography (c) is shown in (a).



Keywords: Leakspots, TEM, Crystallite

[O14.6]

YOUNG SCHOLAR AWARD: The progress on the investigations of transferred-electron oscillations in diamond

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An unexpected discovery of Negative Differential Mobility (NDM) in diamond was made by our group in 2012. We have since then been seeking different ways to exploit this property for the making of electronical devices. One of the most interesting leads is the Transferred-Electron Oscillator (TEO) that uses NDM to generate the continuous oscillations. By applying an electric field on a diamond sample within the region giving the negative resistance, the internal space charge distribution and the internal electrical field distribution become unstable and cause it to oscillate.

A theoretical investigation of making a TEO has after that been presented by our group[1]. The studies were based on an intrinsic single-crystalline diamond in the temperature range of 110 K to 140 K where NDM had been observed[2]. The results were promising and can be used to map out the parameter space for a specific device geometry in which oscillations are expected to occur. This indicates it to be possible to fabricate diamond based TEO devices and further research of making such a device is in progress.

This theoretical investigation and our most recent findings will be presented at this conference together with our experimental progress.

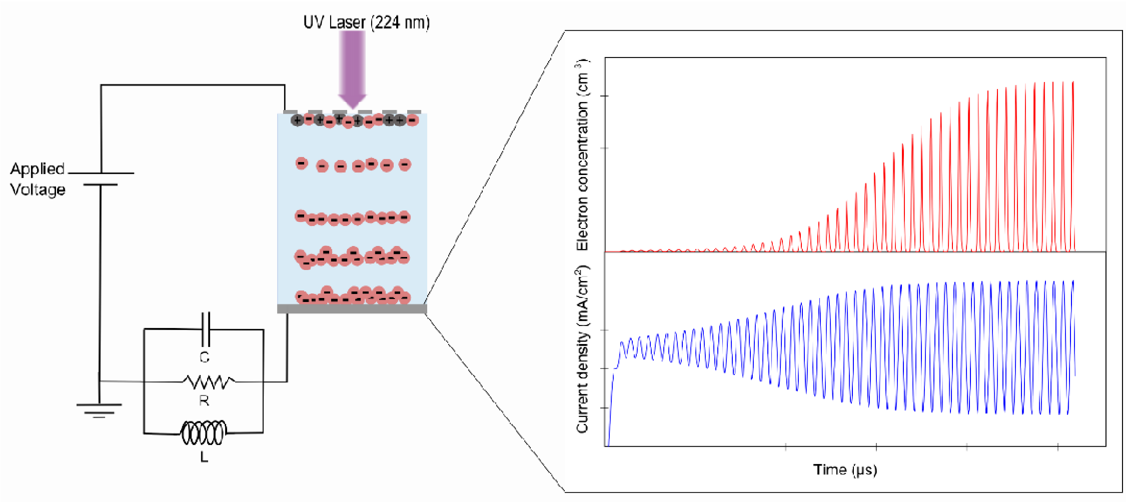

Figure 1 shows a schematic of the TEO together with simulation results of the electron concentration and current density as a function of time.

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Keywords: Transferred-Electron Oscillator, Negative Differential Mobility (NDM), Intrinsic single-crystalline diamond, Negative Differential Resistance (NDR)

[O15.1]

Defect analysis of freestanding diamond substrates and homoepitaxial diamond films

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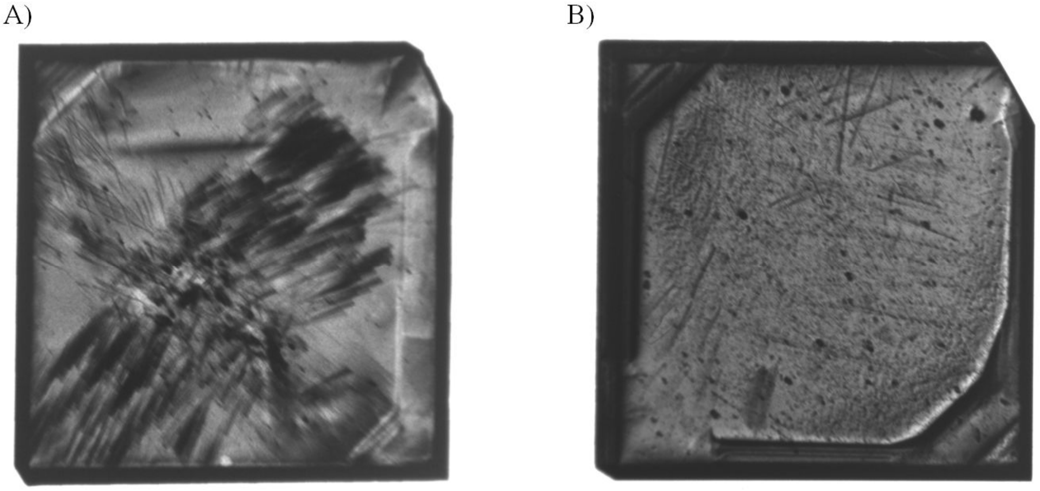
For demanding diamond-based applications like Schottky barrier diodes there is a need for material with outstanding structural perfection, since defects such as dislocations and stacking faults limit the efficiency, performance and lifetime of the devices. Diamond power electronic devices are typically fabricated by chemical vapor deposition (CVD) on freestanding diamond substrates. The defect density of homoepitaxial diamond layers depend besides the CVD growth parameters on the predetermined density of dislocations in the diamond substrates. Another impact on the structural perfection of the CVD layers has the quality of the surface preparation of the diamond substrates in terms of subsurface damage. Significant differences in the defect structure of diamond substrates can be observed in samples obtained from different manufacturers or as a function of the growth technique.

In this work we present a detailed analysis of defect structures of freestanding diamond (001) substrates grown by high-pressure high-temperature method (HPHT) and CVD from different vendors. The quality and improvement of surface preparation of diamond substrates by e.g. various plasma treatments are investigated. Subsequently, the structural quality of homoepitaxial CVD layers is analyzed. X-ray topography (XRT) and high resolution X-ray diffraction (HRXRD) are used for this combined study. HRXRD reciprocal space mappings and omega scans are used for analyses of the subsurface damage and the quality of the homoepitaxial diamond layers. Fig.1 shows an example of 220 reflection topographies of diamond substrates from two different vendors. For substrate A much higher number of threading dislocation becomes visible compared to substrate B.

The combination of these analytical methods allows a detailed statement of the nature, density and distribution of typical defects in diamond bulk substrates and homoepitaxial CVD grown diamond layers with a large field of view.

Fig.1



220 reflection topographies of diamond substrates from two different vendors (A and B). Clear differences in the defect structure are visible.

Keywords: defects, X-ray topography, high resolution X-ray diffraction

[O15.2]

Confocal µ-Raman tomography for the analysis of the interaction between topographic features on diamond surfaces and threading dislocations

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This study analyses the interaction between threading dislocations and distinct topographic features, the so called “V-structures” [1,2], during epitaxial diamond growth. Preceding work [2,3] has already provided direct proof for the tilting of threading dislocations induced by lateral step flow growth specifically by the riser structures formed on off-axis surfaces during growth with nitrogen in the gas phase.

The “V-structures” represent a different phenomenon that occurs during off-axis growth on (001) with off-axis tilt towards [100]. Their characteristic shape including the extraordinary height and steep side faces has been confirmed in several studies. During growth, they move laterally in step flow direction. There have been first indications that the two legs of a “V-structure” redirect the threading dislocations towards its apex. However, many aspects of their formation, the stabilization of their structure and their interaction with threading dislocations are still widely unclear.

In the present work we used µ-Raman tomography to map the width and position of the diamond Raman line laterally and in depth around “V-structures”. The technique required data acquisition with highest spectral resolution and wavelength accuracy. Operating the T64000 Raman spectrometer in the triple mode we achieved a spectral resolution of <0.5 cm^{-1}. Feeding neon calibration lines together with the Raman light into the spectrometer guaranteed an accuracy of 0.1 cm^{-1}.

The Raman line width maps at the surface show a clear correlation with etch pit maps that reveal the lateral distribution of dislocations. Identical maps taken below the surface show how aggregations of dislocations interact with the “V-structures” that apparently enhance strongly the annihilation of dislocations. First measurements also indicate the presence of a large stress dipole around the V-structures. The underlying mechanisms will be discussed. In addition the potential benefit of the V-structures for the targeted reduction of dislocation density will be assessed critically.

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Keywords: heteroepitaxy, iridium, dislocations, stress

[O15.3]

Annealing and lateral migration of intrinsic defects in IIa diamond

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The migration of vacancies in diamond is of considerable fundamental interest and has been widely studied previously [1-2], and there are also a number of theoretical but fewer experimental studies on the migration of self-interstitials in diamond [3]. Recently some progress has been made in the experimental studies on such interstitial- related centers as 3H (503.5nm), 515.8nm, 533.5nm and 580nm as well as single neutral vacancy GR1 defects [4]. In this paper, the annealing and lateral migration of some new interstitial-related centers in type IIa diamond is investigated by low temperature photoluminescence microscopy, and the distributions of interstitial- and vacancy-related centers are also clearly presented and discussed. Results show that the interstitial-related extend considerable lateral depth beyond the limit of the incident beam, while the vacancy distribution is highest near the surface and there is very little lateral spread (see fig.1). After high temperature annealing, the vacancy either aggregates together in the irradiated region or migrates long-distance to find further N centers outside the well-defined irradiated region and the relatively small numbers of isolated N centers are rapidly converted to NV^0 centers while the interstitial-related centers remain concentrated in the irradiated region (see fig.2).

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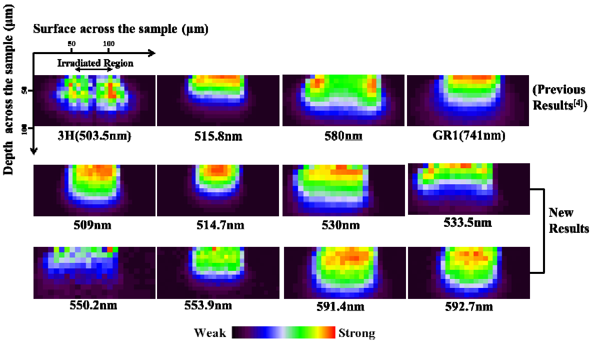

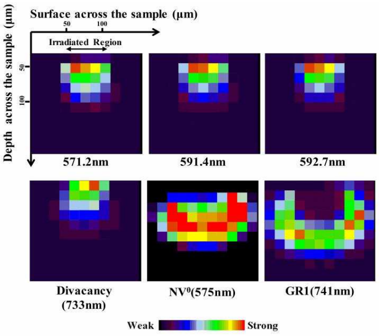

Fig. 1: Distributions of defects on the depth orientation Fig. 2: Distributions of defects on
depth orientation after annealing

Keywords: Diamond, Defect, Photoluminescence, Migration

[O15.4]

FUV photoluminescence of defects in diamond

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Among many and diverse analytical methods established to determine qualitatively or quantitatively the impurities and defects in diamonds, both destructive and non-destructive techniques have been developed to characterize not only natural diamonds but also those from synthesis at great pressure and from deposition of a chemical vapour (CVD). In particular, photoluminescence (PL) emission upon excitation with visible or ultraviolet light provides a sensitive and non-destructive technique for the optical characterization of impurities and defects in diamonds. In this work, we applied the PL technique with excitation from a synchrotron light source in wavelength 125-300 nm to identify sensitively the various defects in diamond materials. The PL excitation (PLE) spectra of natural diamond of type IaAB show four vibrational progressions -- A, B, B′ and N3 related to nitrogen defects in diamond. The vibrational progressions in PL excitation spectra of N2, N3, and N4 centers in diamond of type IaAB at 13 K are identified for the first time. Upon excitation with light at wavelength less than 200 nm, the distinct zero-phonon lines of N3 and N4 centers in diamond at temperature 13 K become prominent at 416.0 and 491.2 nm, respectively. We used PLE spectra to quantitatively analysis of the B center as a N4 nitrogen defect in diamonds; the least detectable concentration of the N4 nitrogen defect is about 13 ppb; the sensitivity of PLE is about 30 times than that practicable with infrared absorption spectra. Associated with nickel defect, prominent spectral PL features were detected at 484.6 and 489.0 nm. During our measurement of PLE spectra of Ni defect in diamond, we observed a distinct PLE line at 215 nm for the first time. In addition, the boron and the NV defects were studied in this work.

Keywords: photoluminescence, nitrogen defect, nickel defect, NV defect

[O16.1]

Synthesis of nanodiamond based energetic composites by means of Spray Flash Evaporation

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Institut franco-allemand de Saint-Louis (ISL), France

Detonation nanodiamonds (NDs) have unique physical and chemical features. Actually they combine high density, good thermal conductivity, a low thermal expansion coefficient and extreme hardness with interesting chemical properties. In this way detonation of RDX/TNT generates 2-5 nm- sized NDs with tremendously high surface area, bearing multiple chemical moieties (-NH, -OH, -COOH…) accessible on the surface [1]. Furthermore well- defined chemical functions can be introduced via an appropriate post-detonation functionalization process [2] that opens up the way to tailor NDs to meet specific needs. The huge amount of possibilities in synthesis and applications thus gave rise in recent times to extensive studies concerning NDs and functionalized NDs in the fields of luminescence imaging, drug delivery, quantum engineering, surface coating, seeding, etc…

Due to their unique properties as well as their entirely gasifiable nature, NDs have soon been recognized as extremely promising in pyrotechnics too [3,4]. The present study deals with the synthesis and characterization of new energetic composites based on NDs coated with a secondary explosive. These core-shell particles are obtained by Spray Flash Evaporation (SFE) [5,6], a patented process invented in our laboratory. Stable colloidal suspensions of bare NDs as well as post-detonation functionalized NDs to which an explosive substance is added are superheated and atomized through a hollow cone nozzle under vacuum. The small size of the droplets and the high evaporation rate of the solvent lead to core-shell particles with less than 100 nm of diameter.

The properties of the resulting core-shell compounds are then compared to those of composite materials prepared by other means. First experiments investigating the interaction between the core and the shell constituents are presented. Moreover, the possibility to elaborate an energetic material that combines enhanced performance with desensitization to impact, friction and electrostatic discharge in order to ensure safer handling is discussed.

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Keywords: detonation nanodiamond, core-shell composite, energetic materials

[O16.2]

Composites based on nanodiamond, carbon onions and carbon xerogels for energy storage applications

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The efficient storage and supply of energy from renewable resources is a worldwide challenge requiring efficient and fast energy storage devices. Technologies such as lithium ion and other battery systems are already widespread. Carbon materials are another promising class of materials for energy storage, e.g. in batteries and supercapacitors. Most of these applications rely on the use of porous carbons as electrode matrix. It is highly desirable to improve their storage characteristics using additives. These can provide enlarged active surface area by increasing the surface roughness, but can also add electrochemical storage capacity.

Carbon xerogel composites with differently terminated diamond nanoparticles embedded in a porous carbon matrix were synthesized via a sol-gel process and investigated as supercapacitor electrodes. Nanodiamonds were incorporated by adding their colloidal dispersions to the aqueous starting solution for resorcinol-formaldehyde (RF) gels. Furthermore, xerogels have been impregnated using stable colloidal solutions of nanodiamond. Surface characteristics and structural properties will be reported.

Using untreated nanodiamond dispersions led to precipitation upon addition to RF sols containing basic catalysts. To prevent this effect resulting in RF-gel composites with a strong gradient we applied surface modified nanodiamond dispersions obtained from oxidized starting material or thermally annealed nanodiamond. With this approach homogeneous composites with diamond nanoparticle concentrations of up to 10 wt% were successfully prepared. The observed impact of the differently treated nanodiamonds on the structure formation upon the sol-gel process was compensated by adjusting the catalyst concentration.

Furthermore, the influence of surface graphitization of nanodiamond was studied. Bucky diamond or carbon onions as composite constituents have been prepared, fully characterized and successfully incorporated into the xerogel composites.

The electrochemical properties of these new electrode materials will be discussed with respect to charge storage applications.

This research was funded by "Bayerisches Staatsministerium für Umwelt und Verbraucherschutz" in the network UMWELTnanoTECH (http://www.umwelt-nanotech.de).

Keywords: supercapacitor, detonation nanodiamond, composite, carbon onions

[O16.3]

Application of boron-doped diamond powder to aqueous supercapacitor

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Electric double-layer capacitors (EDCLs or supercapacitors) with aqueous electrolyte are expected to be useful for an energy storage device with fast charge-discharge. However, the use of aqueous electrolytes causes small working voltage leading to low energy densities. Boron-doped diamond (BDD) is known to show a wide potential window in aqueous electrolytes and should be a suitable electrode material for aqueous EDLCs. In this study, we investigated the electrochemical properties of BDD powder (BDDP) toward the application to aqueous EDLC.

BDDP with a diameter of 150, 350, 3500 nm was fabricated by deposition of BDD layer on the surface of commercial diamond powder substrate with a diameter of 100, 300 and 2500 nm by microwave plasma-assisted CVD. BDDP electrodes were prepared by casting of a BDDP ink onto a current collector substrate, followed by coating with a Nafion layer on the BDDP layer.

In a three-electrode configuration, cyclic voltammetry (CV) in 1 M H_2SO_4 at the BDDP electrodes was found to show a wide potential window as 3 V. In a symmetric two-electrode system in 1 M H_2SO_4, the BDDP electrode exhibited a potential window of 1.5 V, which was wider than that at activated carbon (AC) electrode (0.8 V). Capacitance of the BDDP electrode increased as the BDDP diameter decreased (3.1 F/g for 150 nm BDDP). At fast scan rates, rate of decrease in capacitance was rather small at the BDDP electrode and the calculated energy density was found to be larger at the BDDP electrode than at the AC electrode when the scan rate was 0.5 V/s or faster. Therefore, aqueous EDLC using BDDP as an electrode material is expected to be useful for a high-power energy storage device.

Keywords: Boron-doped diamond powder, electrochemistry, supercapacitor

[O16.4]

Highly fluorescent carbon nanodots from olive mill wastewater

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Olive oil production is a tremendously important agro-industrial activity in the Mediterranean region, with the European Union countries contributing to near 70% of the world quota. Olive oil is typically obtained by two main processes: batch press and continuous centrifugation. Depending on the particular process used, 200-1600 L of olive mill wastewater (OMWW) is produced per ton of processed olives. The OMWW exhibits very low biodegradability parameters which pose serious issues for its treatment. Apparently, none of the researched methods or technological processes developed so far have found a widespread application, probably due to unaffordable economical costs.

In this communication, we will address our proposal to deal with this complex effluent. It will be shown that highly fluorescent carbon nanodots (CND) can be obtained directly from OMWW in excellent yields following expedite and sustainable hydrothermal processes with minimum post-processing. In particular, the photophysical properties of the as-synthetized nanostructured materials will be presented and discussed in regard to several operation variables (viz. reaction temperature, dwell time, carbon source concentration and the use of passivating agents), in addition to their morphology and surface functionality.

The as-prepared CND are highly soluble in water as well as in some protic and non-protic organic solvents, revealing their amphiphilic nature. As a general feature, the synthesized CND present an excitation-dependent fluorescence spanning over the entire visible spectra with a predominance of blue-green emissions.

Such luminescent properties, which can be modulated by synthesis, highlighted by the high quantum yields ($\Phi_F = 0.3$; $\lambda_{exc} = 340$ nm) attained by some of these CND, allied to their easy synthesis and carbon source affordability will likely prompt the use of these carbon nanomaterials in bioimaging, nanomedicine, chemo/biosensing, (photo)catalysis and optoelectronics.

Acknowledgments

We thank IPL (Project Nanolive/IDI&CA/2016) and FCT/MCTES (UID/QUI/00616/2013, COMPETE and FEDER programs) for financial support.

Keywords: Carbon nanodots, Luminescence, Olive mill wastewater

[O16.5]

Towards hierarchical pore structure in Lignin-derived carbons

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Activated carbon materials are used in a variety of sustainable applications, from water filtration and catalysis, to gas separation and energy storage. The performance of the activated carbons in these applications is highly dependent on the size and number of the pores in the material. Lignin, a naturally occurring polymer, has received increasing interest as a precursor for such materials. The abundance, as a by-product of the paper pulping industry, and high carbon content of lignin makes it a promising precursor for producing nanoporous carbons. It also possesses a similar aromatic backbone to phenolic resins, and thus may be used as a sustainable and cheap alternative as phenolic resins are typically derived from crude oil. The structure of lignin is highly dependent on the plant species it is isolated from. It is well known that lignins extracted from different feedstocks but using the same isolation method differ primarily in the ratio of their aromatic monomers S, G, and H. However, the effect of the lignin structure on the resulting activated carbon porosity has not been studied in detail.

This research presents an in-depth characterisation of four lignins extracted from different feedstocks using the organosolv process. The structure of the extracted lignin was carefully characterised using gel permeation chromatography, 2D-NMR, thermogravimetric analysis and other advanced techniques. Our systematic investigation examined the effect of lignin structure on the thermal behaviour, and structure of resulting activated carbons. We found a correlation between the S/G ratio and type of carbon produced. Carbons from lignins with a high S/G ratio displayed a pronounced foaming behaviour (Figure 1), resulting in a macroporous char. These results were validated on a commercial organosolv lignin to demonstrate how careful selection of the feedstock may be used to control porosity of the resulting carbon material. Subsequent activation of the carbon foams introduced micropores, resulting in a high surface area (>1000 $m^2\ g^{-1}$) porous carbon with a hierarchical structure. This work indicates that there may be scope for control of the structure of lignin-derived activated carbons through careful selection of the initial feedstock.

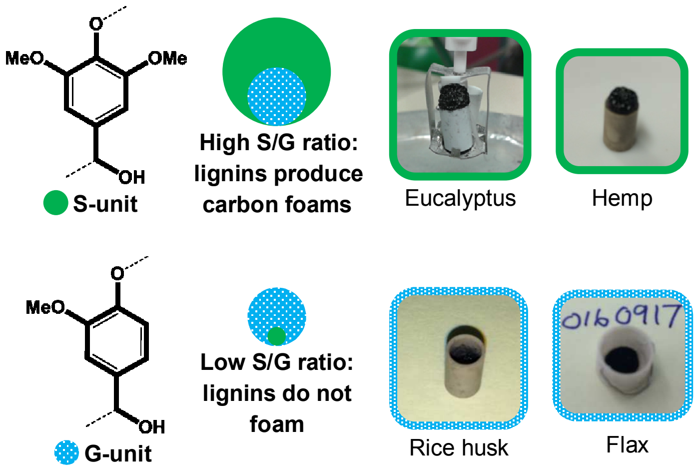

Figure 1. The ratio of syringyl (S) to guaiacyl (G) aromatic units in the lignin polymer affects its thermal behaviour and the resultant carbon structure.

[O16.6]

Investigation of synthetic route for the new carbon allotrope

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[1]*Hokkaido University, Japan,* [2]*Institute for Material Science, Japan*

Introduction: Theoretical calculations suggested many types of sp^3-carbon allotropes such as M-carbon, Z-carbon and so on in recent years. However, there is no experimental evidence for these theoretical prospects due to the difficulty of the actual synthesis. It is known that nanodiamond (<5 nm) is thermodynamically stable product due to the size effect. We suggest in this pater that nanosize poly(hydridorcarbyne) which is consist of only sp^3-carbon and hydrogen can be used as a precursor to open a synthetic route for the sp^3-carbon allotropes.

Methods: Poly(hydridocarbyne) ($[CH]_n$) was chemically synthesized with Wurtz coupling: NaK + $CHBr_3 \rightarrow [CH]_n$ + Na(K)Br. We have successfully reduced the C=C bonds which can be formed by side reactions. NMR (^{1}H and ^{13}C) and FTIR clearly showed the backbone framework of the polymer is mainly consisted of sp^3-carbon.

In order to convert the poly(hydridocarbyne), it was annealed with two different conditions: (i) in a sealed tube (1000 ºC) (ii) under high pressure (7.7 GPa, 1500 ºC).

Results: In the condition (i), the local ordered structure was confirmed by electron diffraction pattern and TEM-EDS revealed that the annealed solid was carbon. The lattice constant was not identical to one of the graphite and diamond, which implies that the new carbon allotrope can be synthesized under low pressure if one uses a suitable precursor (poly(hydridocarbyne)).

In the condition (ii), Raman spectra and electron diffraction pattern showed that the obtained solid was the mixture of the new carbon allotrope and diamond. It is noticeable that poly(hydoridocarbyne) can be directly converted into the diamond without any transition metal under the condition of 7.7 GPa and 1500 ºC because more than 8.5 GPa and 3000 ºC is necessary to directly convert a graphite into a diamond.

Discussion: We suggested the new synthetic route for the synthesis of sp^3-carbon allotropes. Poly(hydridocarbyne) is a good potential precursor to synthesized them due to the backbone framework of sp^3-carbon. Further improvement of the synthesis of poly(hydridocarbyne) can reduce the required pressure to make the new carbon allotrope and diamond. One possible way to improve the quality of the polymer is hydrogenation with tris(trimethylsilyl)silane and azobis(isobutyronitrile) in order to completely remove the C=C bonds and unreacted Br.

Keywords: polymer precursor, carbon allotrope

[O17.1]

Progress in black diamond technology for solar energy conversion

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High-temperature solar cells are possible by exploiting the Photon-enhanced Thermionic Emission (PETE) concept, which represents a novel and very attractive mechanism for the exploitation of solar radiation, especially if concentrated, and characterized by promisingly high conversion efficiency (>50%). PETE converters rely on the concept that engineered semiconductor photocathodes can provide a very efficient electron emission, induced by hot-electrons produced by photons with sufficient energy, combined to a thermionic emission, sustained by the high temperatures induced by every other thermalization process.

Ultrashort pulse laser-assisted surface nanotexturing combined to surface-hydrogenation, aimed at achieving negative electron affinity conditions and a work function as low as 1.7 eV with a nitrogen-doping of the emitting-layer, are here proposed as a radically new and potential effective PETE cathode completely based on chemical-vapour-deposited (CVD) diamond, able to operate up to temperatures of 800 °C. CVD diamond is transparent to solar radiation due to its wide bandgap, consequently black diamond technology was developed for drastically increase its absorption coefficient and photogeneration capability under sunlight irradiation [1]. The final p/i/n structure merges the technologies of surface texturing by fs-laser [2], boron-implantation for formation of buried p-type layer [3], and laser-induced graphitic microchannels [4], to form an innovative defect-engineered black diamond cathode for the conversion of concentrated solar radiation operating at high temperature.

Results under high-flux solar simulator will be reported and discussed by demonstrating for the first time the PETE effect at temperatures from 350 to 550 °C.

Ongoing extension of the technology to polycrystalline films for large area scale-up and to thin single crystal films for an optimized performance will be discussed.

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[4] M. Girolami et al., Carbon 111 (2017) 48.

Keywords: Solar energy conversion, Thermionic energy conversion, Photocathode, Black diamond

[O17.2]

Vertically aligned diamond-graphite hybrid nanorods for thermionic and field electron emission applications

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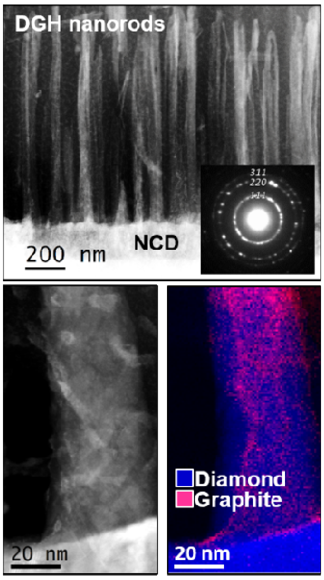
Diamond is a good candidate for solid-state electronics emitters because of its negative electron affinity (NEA) surface in addition to superior properties such as mechanical hardness, chemical inertness and high thermal conductivity. Significant applications may be enabled with the development of a stable electron emission source that operates at low applied fields or a thermionic source that would operate at low temperatures. Specifically, the development of high current field emission cathodes would be important for microwave systems which would exhibit effectively instant-on characteristics, and a gated cathode structure enabling highly compact designs. Low temperature thermionic emission could enable the development of compact and highly efficient heat to electrical energy conversion systems. These systems could prove important for large scale commercial energy systems and remotely operated compact systems.

The focus of this work is on field electron emission behavior of diamond-graphite hybrid (DGH) nanorods and adapting them in the thermionic behavior of the materials. Vertically aligned DGH nanorods were fabricated from nanocrystalline diamond (NCD) films by reactive ion etching using nanodiamond particles serving as a hard mask. The resulting nanorods have diameter and height in ranges ~15̃20 nm and ~800̃1200 respectively. The superior field emission behaviors of the nanorod arrays resulting in low turn-on field (5.26 V/□m), long lifetime stability (700 min) and large field enhancement factor (3270) can be advantageous in a thermionic energy converter. The thermionic emission measurements from nanorods resulted in a high current density of 16 mA/cm^2 at a temperature of 550° C. The enhanced field/thermionic emission properties are attributed to the nanocomposite nature of the nanorods composed of sp^2-graphitic phases in the boundaries of nano-sized diamond grains. The simplicity in fabrication process of the DGH nanorods may have greater potential for the cathode applications in field emission displays and thermionic energy converters.



Keywords: Diamond-graphite hybrid, Nanorods, field electron emission, thermionic electron emission

[O17.3]

Elucidating degradation mechanism of field electron emission from carbon nanotubes in fully vacuum-sealed x-ray tubes

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Carbon nanotube (CNT) has attracted a great deal of attention as the most promising field electron emitter due to its geometric high aspect ratio with a nano meter-sized diameter and high chemical inertness [1]. However, the stability and reliability of CNT field emitters is a still big problem in vacuum electronic device applications like field emission x-ray sources. In this report, we elucidate degradation mechanism of field electron emission from CNTs in fully vacuum-sealed x-ray tubes.

The CNT emitters were printed from the optimized paste consisting of multi-walled CNTs, carbide fillers, and an organic binder on a metal substrate [2]. The field emission x-ray tubes have a gate electrode to control field emission from the CNT emitters independently of the anode voltage and are completely vacuum-sealed by brazing of a CNT emitter cathode, an anode with W target, and a ceramic of Al_2O_3 at an elevated temperature. Here, we note that the vacuum level of the sealed x-ray tubes is maintained with only a non-evaporable getter.

Figure 1 shows a fully vacuum-sealed x-ray tube and its cathode currents with time during the aging procedure. Just after sealing of x-ray tubes, electron emission largely degrades even at a low cathode current. A proper aging gives stable and reliable electron emission, guaranteeing the lifetime of x-ray tubes for medical imaging. Electron emission more than the aging current level again induces degradation in the cathode current. We conclude, from the systematic study on aging of x-ray tubes, that adsorbate or residue on CNT emitters strongly deteriorates electron emission through chemical attacks on CNTs.

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Acknowledgements: This work was supported by ICT and Future Planning, Korea through the R&D programs of NST (B551179-12-04-00) and NRF (2015M3A9E2066999), and ETRI R&D program (17ZE1110).

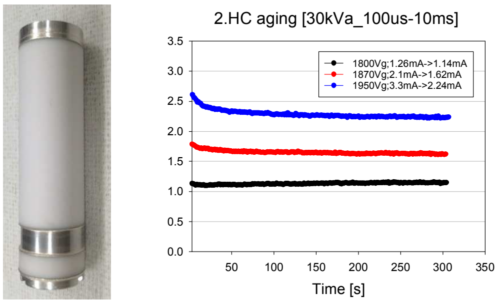

Figure 1. Fully vacuum-sealed x-ray tube and its cathode currents with time

Keywords: carbon nanotube, field electron emission, x-ray tube

[O17.4]

Compact field emission device using directly grown carbon nanotube for x-ray imaging

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[1]Kyung Hee University, Republic of Korea, [2]Asan Medical Center, Republic of Korea, [3]CAT Beam Tech. Co. Ltd., Republic of Korea

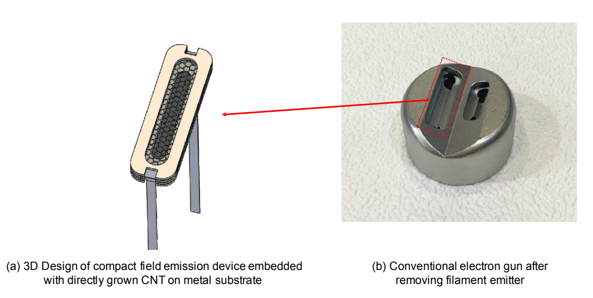
Introduction

CNTs as electron emitters in x-ray generation have superior properties such as compact structure, reduction of power consumption and active control function. A minimum focal spot size and high anode current of electron beam in the anode target can obtain a high-resolution image with a low dose.

In this paper, we obtained the x-ray image from compact field emission device (CFED) embedded with directly grown CNT on metal substrate by replacing thermionic emitter (TE) in conventional electron gun (CEG).

Methods

CFED can be used to make multi, single x-ray source and emission lamp. The device is designed (fig.1a) to replace the TE in CEG (b). We can use the CEG without changing its structure and size. It consists of cathode and gate electrode. The emission area is 11.5 x 1.5 mm2 focused at anode to produce isotropic emission.


(a) 3D Design of compact field emission device embedded with directly grown CNT on metal substrate

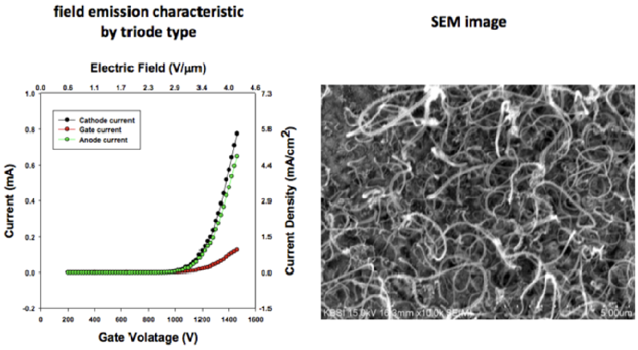
(b) Conventional electron gun after removing filament emitter

Fig. 1. Concept of CNT based electron gun

CNTs were grown using a dc-PECVD system. The NH_3 plasma pre-treatment time was 10 min. The substrate electrode was maintained at −300 V with the top electrode grounded. C_2H_2 and NH_3 gases were used and the gas pressure was maintained at 4.2 Torr for 20 min at 900 C temperature.

Results

Figure 2 shows the electron field emission properties of the CNT emitters. The obtained emission current on DC mode is 0.6 mA at 1400 V (4.0 V/μm). The anode current was measured by adjusting the gate electrode in the dc mode. The transmission rate to anode target was ~84% from elliptical emitter.



Specification

- Real emission area : 0.1377 cm^2
- Anode net current : 0.65 mA @ 4.17 V/μm
- Operation electric field : < 8 V/μm
- Leakage current ratio : < 16 %
- Emitter pattern : Non patterned

Fig. 2. Characteristics of CNT field emitter

Discussion

An x-ray source with CFED has been demonstrated. The CNT emitter replacing the TE in CEG can enhance the response time. This enhanced emission with the ability to control emitter density can produce high resolution images helpful in industrial and medical field.

Keywords: carbon nanotube, field emission device, X-ray

[O17.5]

Surface effect and improvement of the quality factor of single crystal diamond NEMS resonators

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National Institute for Materials Science, Japan

The authors report surface effect and the marked improvement of the quality factor (Q-factor) of single crystal diamond (SCD) nanomechanical system (NEMS) resonators through annealing in oxygen ambient. The NEMS SCD resonators were fabricated by ion implantation assisted lift-off technique. The annealing experiments were performed at 430 ^{o}C firstly and then at 500 ^{o}C for different durations. The resonance frequency followed well the inverse power law relationship with the length of the cantilevers despite of the annealing. It was observed that there was little modification in the resonance frequency and Q-factor at 430 ^{o}C, while an obvious red-shift in the resonance frequency occurred at 500 ^{o}C. Meanwhile, a marked improvement in the Q-factor from around 4000 to 8000 was observed at 500 ^{o}C. The frequency red shift is due to the etching of diamond with a rate of 0.4-0.5 nm/hour at 500 ^{o}C. The analysis of the energy dissipation discloses the surface effect dominates the energy loss mechanism for the SCD NEMS resonator. The improvement of the Q-factor is thus attributed to the elimination of the surface defects.

Keywords: MEMS/NEMS, Single crystal diamond

[O17.6]

ON AN INDUSTRIALLY FEASIBLE PRESSURE SENSOR WITH DIAMOND DIAPHRAGM AND RESISTORS

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[1]CIS FORSCHUNGSINSTITUT FÜR MIKROSENSORIK GMBH, GERMANY, [2]UNIVERSITY OF ULM, GERMANY

Purpose of the work, approach, scientific innovation and relevance:

Pressure sensors are used in many different applications in our daily life, but main applications can be found in industrial environments. To protect such sensor devices from aggressive substances, either complicated technologies have to be used (stainless steel protection membrane in combination with oil filling) or limited precision due to drift and reduced lifetime has to be agreed to. In any case, a compromise between price and performance has to be found. Many consumers from different branches (automotive, chemical and medical engineering) need robust sensor devices that can overcome problems in pressure measurements due to degradation of the sensor.

Diamond has many outstanding material properties, which were investigated in depth for several years. Amongst others the chemical resistance and piezo-resistivity[1] are highly interesting for the preparation of diaphragm-based pressure sensors that can be used in aggressive media as corrosive fluids or exhaust gases. In the past, only few concepts have been published[2,3,4]. Meanwhile much progress was achieved in understanding synthesis, doping and processing of diamond layers[5]. Nevertheless, up to now there is no pressure sensor with active or passive diamond layers commercially available (to the knowledge of the authors).

Results and conclusions:

In the paper a route for fabrication of a piezoresistive pressure sensor is demonstrated featuring all-CVD-diamond layers acting as diaphragm as well as resistive elements (Figure 4). Special emphasis was put to the industrial feasibility of the device: A nanocrystalline diamond (NCD) layer with a thickness of 15 µm was synthesized on silicon wafers. After removing of the silicon the diamond acts as intrinsic diaphragm – only a supporting frame of Silicon was not removed. Further, a thin, electrically conductive ultrananocrystalline diamond (UNCD) layer of ~ 1 µm was synthesized on top of the intrinsic layer, leading to a sheet resistance of ~ 250 □/sq. After deposition and structuring of a metal mask (AlSi), the separation of the resistors on top of diamond diaphragm was done by reactive ion etching. To provide ohmic contacts, metallization was deposited using a sputtering sequence of the metals Ti, Pt and Au, followed by a subsequent photolithography step. All processing was done on 4” silicon wafer substrates, making the separation by wafer dicing necessary. The final sensor devices had lateral dimensions of 10×10 mm². To allow sensitivity measurements of the device, a further assembly to a printed circuit board (PCB) and wirebonding to the contact pads was performed. A Wheatstone bridge out of four resistors was built, to increase the sensitivity. Such devices were characterized regarding the structural and electrical properties:

- The device was tested in a pressure range between -1 and +1 bar (Figure 1). The data set shows nearly-linear behavior over the entire range with a sensitivity of ~ 2 mV/V·bar. Detailed measurements showed a linear homogeneity between 0 and -10 mbar (pressure from backside of the device) with a sensitivity of 5.7 mV/V·bar (Figure 2). From

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[2] Otterbach, R., & Hilleringmann, U. (2002). Diamond and related materials, 11(3), 841–844.

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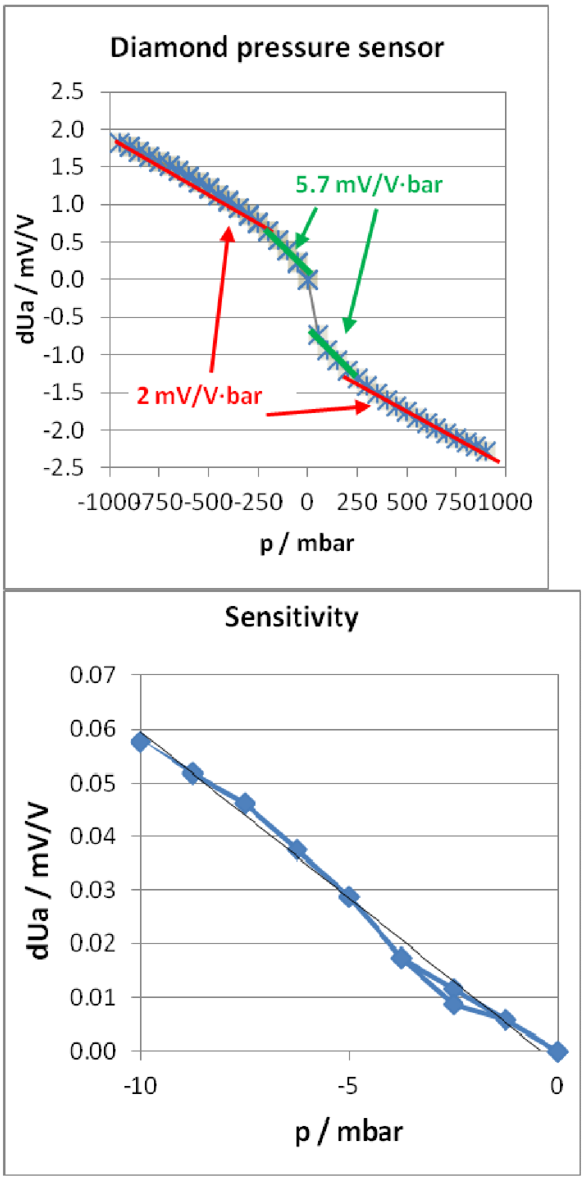
[5] e.g. Wiora, N., Mertens, M., Mohr, M., Brühne, K., Fecht, H.-J., (2016), Diamond and Related Materials 70, 145–150.

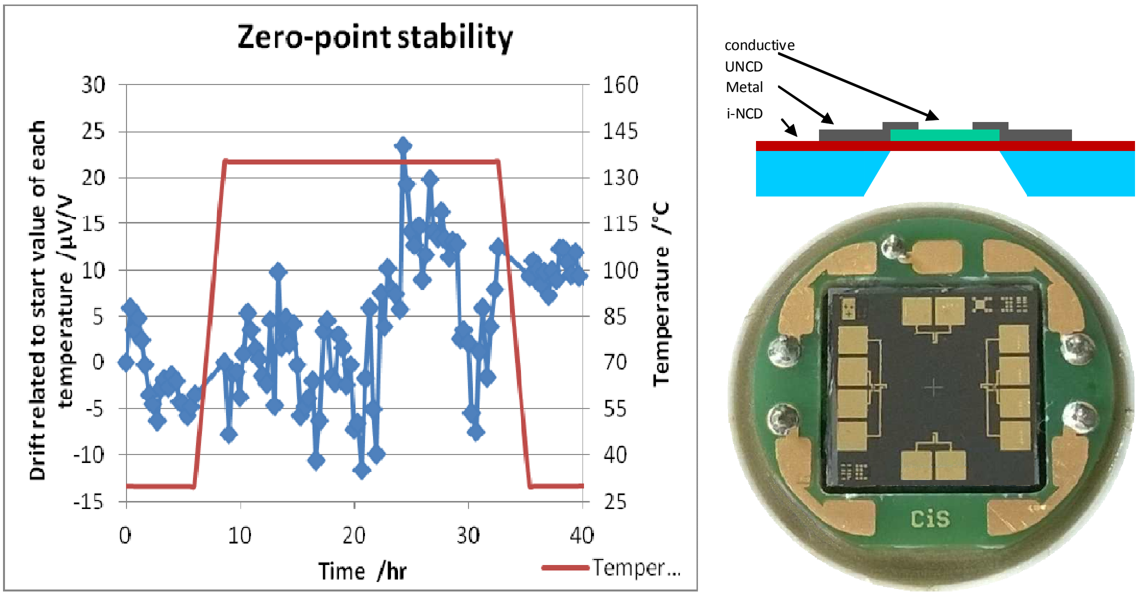
measurements (Figure 1) a linear range between 0 and -100 mbar can be assumed, pointing out, that this certain device geometry can be applied in this pressure range. By adapting the geometry (thickness and area of the membrane, setup of resistors) another sensitivity and linear regime can be addressed.

The increased gradient in the zero-crossing suggests mechanical strain in the membrane.

- Temperature dependence of the bridge-offset was measured in a temperature regime between room temperature and 135°C, for 25 hours. A homogeneous offset stability of (-15/+25) µV/V was measured during the elevated temperatures (Figure 3).



Figures 1, 2: Left: Homogeneity of the electrical signal of a representative sensor device for a large pressure range. An average sensitivity of 2 mV/V·bar is obtained (red lines). The step at the zero-crossing suggests strain in the membrane. Right: Hysteresis measurements for a representative device between 0 and 10 mbar, leading to an average sensitivity of 5.7 mV/V·bar and negligible hysteresis.



Figures 3, 4: Left: Device performance (offset stability) during 135°C cycle test. Data point deviations from the start value of each set temperature are plotted as function of time, and additionally the set temperature.

Right: Sketch of the cross section and photograph of the pressure sensor (photograph: mounted on PCB). The inner device (grey with golden metal structures) has dimensions of 10x10 mm².

Keywords: Pressure sensor, piezo-resistance, nano crystalline diamond, industry

[O2.1]

Selective optical detection of diamond nanoparticles within complex matrices using optically detected magnetic resonance full-frame imaging

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One major challenge in environmental science is to identify nanoparticles within complex environmental and biological matrices. Surace-oxidized nanodiamonds are stable in water but the Nv center fluorescence is broad, making it difficult to separate Nv-center fluorescence from background signals such as autofluorescence from biological matrices or environmental contaminants. We demonstrate the ability to selectively image small, surface-oxidized Nv-nanodiamonds within complex matrices by combining optically detected magnetic resonance (ODMR) with full-frame imaging. Application of a weak microwave field at the Nv center resonance modulates the intensity of the Nv center fluorescence, while leaving fluorescence from other background signals unaffected. By performing digital subtraction of full-frame images on and off resonance, the fluorescence from the Nv centers can be selectively identified in the presence of background fluorescence.

Methods: we use a custom-built apparatus to perform full-frame imaging of nanodiamond, linked to a custom-made microwave antenna for Nv center modulation. Surface-oxidized nanodiamond samples ranging in size from 15 microns to 10 nm in diameter were investigated.

Results: As diamond nanoparticle size decreases <100 nm, the fractional contrast in ODMR decreases due to non-radiative surface processes that compete with optical spin-pumping. In addition, the charge state distribution shifts from Nv^- to largely Nv^0, decreasing the lifetime and intensity of emission from Nv-. Despite these factors, ODMR contrast can be observed in <40 nm nanodiamond. We demonstrate the ability to selectively identify Nv- nanodiamond in the presence of other competing background fluorescence by digitally subtracting CCD images obtained on-resonance and off-resonance;

Discussion: Spatial identification of Nv nanodiamonds withing complex matrices solves a difficult problem in environmental science by revealing the location of nanodiamond even in the presence of competing autofluorescence. Understanding the factors controlling the signal-to-noise ratio of Nv-ODMR imaging experiments provides insights into the use of Nv nanodiamond in biological and environmental imaging.

Keywords: ODMR, Nanodiamond, Imaging, Nv center

[O2.2]

Nanodiamond nitrogen vacancy centres for quantum sensing applications

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Diamond nitrogen vacancy (NV) centres have attracted much attention as sensitive nanoscale quantum sensors. NV centres possess electron spins in diamond lattice, which can measure multiple physical quantities (magnetic field, electric field, temperature) of the nanoscale local environment. However, this multi-functionality of NV centres complicates the analysis in cellular environment. The electron spin properties may be affected by many parameters in physiological conditions, like local heat generation around mitochondria, local pH change around ion channels. It is therefore important to clarify the effect of all possible factors to the spin properties of NV centres in nanodiamonds, prior to biological experiments.

Here we report effect of pH change to the spin decoherence of single NV centres in nanodiamonds [1]. It is known that pH can change the charge state of NV centres. The pH change, in principle, should not affect the electron spin decoherence if the diamond surface is completely terminated by oxygen. However the surface oxidation of nanodiamonds is not perfect as that of bulk diamonds due to the inhomogeneity of morphology and surface. It is therefore necessary to characterize the spin property of surface-oxidized nanodiamonds for various pH.

We characterize the same single nanodiamonds in the course of pH change and measure the spin decoherence time. The results show spin coherence time fluctuates between 1.5 and 3.1 us. Continuous-wave ODMR spectra and Rabi oscillations also show dynamic fluctuations as shown in Fig. 1. The effect of oxidation is also investigated. T_2 coherence time of NV are measured for different nanodiamonds which are oxidized by several oxidation techniques. The surface oxidation extends the T_2 time, but not significantly compared to bulk diamonds.

This work is partially supported by JSPS-KAKENHI (Nos. 25620001, 26706007, 26610077, 16K13646, and 26220602) and MEXT-LEADER program.

[1] Fujiwara et al., manuscript in preparation.

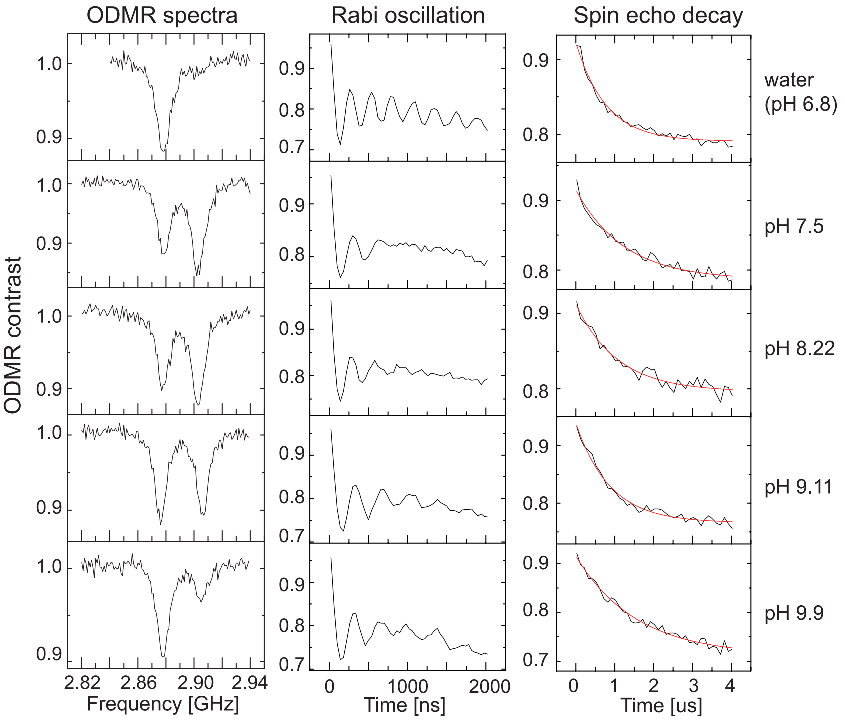

Figure 1: From left to right, continuous-wave ODMR spectra, Rabi oscillation profiles, and spin-echo decay curves of the same single NV centre in different pH buffer solutions.

Keywords: sensing, magnetometry, coherence time, surface treatment

[O2.3]

Electrical spin readout of NV$^-$ centres in diamond

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The nitrogen vacancy (NV) centre in diamond is a promising candidate for quantum applications such as the sensing of magnetic fields and temperatures. To date, the state of the NV spin is generally read out optically via fluorescence detection. This approach, however, has severe drawbacks: it is highly inefficient, requiring several 100 repetitions for a single spin readout, and cumbersome to implement in many cases. In contrast, electrical spin readout could surmount some of these limitations.

To achieve this, we have extended a recent study [1], which had demonstrated electrical detection of NV centres via spin-to-charge conversion [2] and spin-dependent photoionization of the centre, by pulsed spin manipulation and pulsed optical excitation. We demonstrate that this approach enables us to truly read out the spin state via electrical measurements using coherent control (Rabi oscillations) and Hahn echo experiments as elementary examples for quantum sensing protocols [3]. We further quantify the efficiency of electrical readout by identifying and optimizing the decisive experimental parameters and find that spin readout with a contrast as high as 17% and an effective count rate of close to 10^7 electrons/s can be reached experimentally already by simple pulsed protocols [3]. These values compare favourably with optical fluorescence detection (where typical numbers are a 30% contrast at 10^5 photons/s). To understand the complicated dynamics of the electrical readout, which is expected to require a total of four optical transitions per mobile electron generated, we use both extended Monte-Carlo simulations as well as multi-colour optical excitation experiments.

[1] E. Bourgeois et al., Nat. Commun. **6**, 8577 (2015), Phys. Rev. B **95**, 041402 (2017).

[2] B. J. Shields et al., Phys. Rev. Lett. **114**, 136402 (2015).

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[O2.4]

Photo-electric transitions under NV electron spin resonance conditions: Modeling and experiments

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Hybrid photoelectric readout of NV spin states opens important promises for developing scalable NV diamond quantum chips for room temperature operation. Building on our previous work [1,2,3], we discuss the photo-excitation, photoionization and recombination traffic associated with the NV centre energy levels in diamond. Interestingly, we found that the Magnetic Resonance (MR) contrast can be changed from a positive to negative, depending on the laser power density and conditions of the light focus. Here we present a detail modeling of this phenomenon by solving the rate equations combined with the expression for 2 –photon and 1-photon ionization and the laser power density. The modeling is compared with experimental data. Considering the current limit of NV electron spin resonance being 30%, an understanding about a positive and tunable MR contrast on NV centre would progress significantly the photoelectric detection of magnetic resonances (PDMR) field.

[1] E. Bourgeois *et al.*, Nat. Comm. 6, 8577 (2015).

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[3] M. Gulka *et al.*, Phys. Rev. Applied **7**, 044032, (2017)

[O2.5]

Quantitative sensing of the electric-field in diamond power devices using NV centers

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Electric-field in power devices is an important physical parameter which determines the device performance. Especially, high electric-fields are generated inside wide band-gap devices such as 4H-SiC, GaN, and diamond. However, it has been difficult to quantitatively sense the internal electric-field in operating devices in high spatial resolution. In this study, we demonstrate the internal electric-field sensing inside diamond power devices by using nitrogen-vacancy (NV) centers [1].

Diamond pin diodes were fabricated on a (111) substrate. NV centers were formed in the devices by ion implantation and subsequent annealing. When the electric-field is applied to the NV center, the ground state levels of the NV center change due to the Stark effect [2,3]. Optically detected magnetic resonance (ODMR) technique enables us to detect the change of the ground states and thus to quantitatively estimate the internal electric-field.

Figure 1a shows ODMR spectra of a single NV center while applying reverse voltages up to 150 V. We clearly see the split width of the two dips increase as increasing the voltage. This indicates that the electric-field perpendicular to the N-V axis is detected. The estimated electric-field is summarized in Fig. 1b. At a reverse voltage of 150 V, the electric-field reaches approximately 350 kV/cm. Importantly, the experimentally obtained values are in good agreement with those by device simulation. Moreover, we utilized ensemble NV centers to sense electric-fields over 1 MV/cm, which is the highest value detected by the NV center. Here, we realized the quantitative sensing of the electric-field in operating power devices by using atomic-level structure with an electron spin.

This work was supported by TEPCO Memorial Foundation and JST-CREST.

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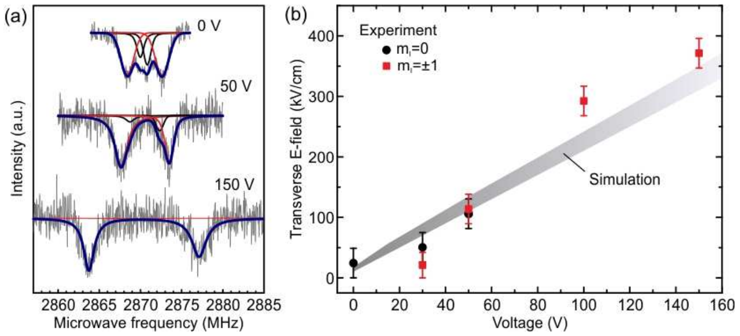

Figure 1 Electric-field sensing in operating diamond power device using NV center. (a) ODMR spectra with reverse voltages up to 150 V. (b) Estimation of electric-fields, compared with device simulation.

Keywords: Diamond, Power device, Electric-field sensing, NV center

[O2.6]

DC noise reduction of the magnetometer system with NV- centers in diamond for IoT applications

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Nitrogen-vacancy (NV) centres in diamond have been proposed as a promising quantum sensor. DC noise reduction technologies for the magnetic sensor device are crucial, especially for IoT applications, where <nT/Hz$^{1/2}$ sensitivity is required without shielding. For this purpose, the detected fluorescence intensity is fed back to the microwave frequency. In Ref. [1], both high-frequency feedback for magnetic signal detection and low-frequency feedback for drift compensation is provided through data acquisition system (DAQ). We propose another scheme that does not require DAQ and is suitable for portable applications.

We carried out (i) the low-frequency feedback to the digital frequency setting at the microwave synthesizer along with (ii) the high-frequency feedback through the analog circuit path to its frequency modulation input (Fig. 1). The feedback amplitudes of (i) and (ii) were measured for many hours (Fig. 2). The standard deviation (S.D.) of (i) over the whole period was c.a. 4 μT/Hz$^{1/2}$ in terms of magnetometer drift noise, mostly caused by temperature fluctuation. The S.D. of (ii) over the whole period was c.a. 6 nT/Hz$^{1/2}$. A minimum value of 2.3 nT/Hz$^{1/2}$ in (ii) was obtained when (i) is stable. We will attain a lower value if the surrounding noise can be reduced.

We used a diamond crystal of 1 mm^2 in area, and the NV centres were produced by 10^{18}/cm^2 EB radiation. Its shot noise is estimated to be in pT/Hz$^{1/2}$ range, and thus the measured noise seems to be limited by surrounding noise. The perfectly aligned ensemble NV centres in diamond obtained by CVD [2] also have a shot noise below nT/Hz$^{1/2}$ and would show a similar performance.

In summary, we have demonstrated that a new scheme can reduces the noise to nT/Hz$^{1/2}$ range using a simple analog circuit, which is advantageous for IoT applications.

This work was supported by JST CREST.

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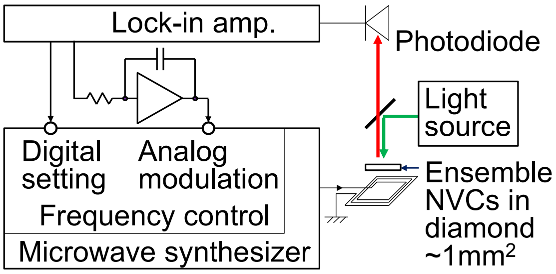

Fig.1 Proposed noise-reduced sensor system with ensemble NVCs in diamond

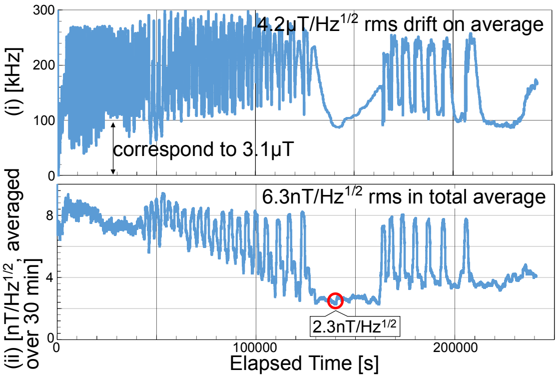

Fig.2 Measured (i) low-frequency digital and (ii) high-frequency analog feedbacks

Keywords: NV center, magnetometer, noise, optically detected magnetic resonance

[O3.1]

Operating temperature as a trade-off parameter for designing drift region of diamond power devices

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Diamond is considered as the ultimate semiconductor for power electronics applications, especially thanks to its ability to withstand high voltage and to operate at high temperature. In unipolar power devices such as schottky barrier diode or field effect transistor, the breakdown voltage is linked to the design of the drift layer but also to the physical properties of the material used. For instance, due to the specificity of diamond (temperature carrier and mobility dependence), for a given breakdown voltage value, only one drift layer design (doping level and thickness) will offer the lowest ON-state resistance at a specific operating temperature.

Based on the ionization integral calculation with impact ionization coefficients adapted to diamond, we performed an accurate analysis of the drift layer design as function of the breakdown voltage in which the doping level, the thickness and the operating temperature are considered as tunable parameter.

We will first give the optimal designs for few typical classical breakdown voltage values and show the importance of the operating temperature. For instance we found an optimum operating temperature of 495 K for BV=10 kV while it is 575 K for BV= 3 kV. Our analysis also points out that thicknesses and doping levels required to achieve such structures are quite challenging for crystal growth in the context of high voltage power devices.

Then, using these results we will show how some small trade-off on the ON-state resistance and a judiciously chosen operating temperature can allow growing drift layer with achievable design while keeping rather good performances at device and system levels.

These results will allow proposing preliminary design rules to fabricate efficient unipolar diamond power devices, which are necessary to convince power electronics community about the interest of diamond.

Keywords: Power electronics, Drift layer, Design, Unipolar

[O3.2]

High temperature characteristics of diamond PIN diodes and BJTs using phosphorus doping

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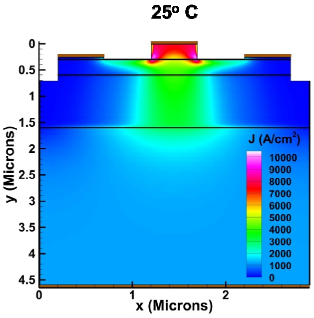
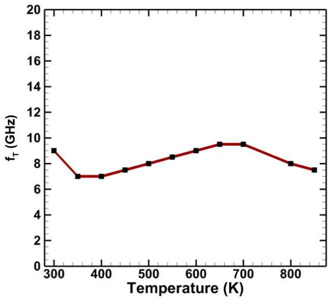
The achievement of n-type doping of diamond using phosphorus incorporation during epitaxial growth has enabled development of bipolar PIN diodes and bipolar junction transistors (BJT). The operation of these devices is dependent on epitaxial diamond-diamond interfaces and metal contacts which are potentially stable at temperatures > 500°C. These devices can open unique applications including space based electronics for exploration near the sun or on the 450°C surface of Venus or deep underground exploration for geothermal energy sources.



A crucial aspect of fabricating these devices is precise control of phosphorus incorporation during homoepitaxial growth. In our system phosphorus doping is achieved using trimethylphosphine (TMP) in a microwave plasma CVD system. However, BJT devices require a thin (~200 nm) base layer with carefully controlled P-doping. Results are presented that show the doping concentration can be controlled by varying the substrate temperature (while holding the relative TMP gas phase concentration constant). Utilization of a dual-wavelength pyrometer accurately resolved the surface temperature of the diamond substrate that was heated by plasma discharge only under exploitation of plasma focusing effects. With 350 sccm hydrogen, 0.5 sccm methane and 50sccm of a 200 ppm TMP/H_2 phosphorus source a substrate temperature of ~890°C was achieved at a microwave power of 2000W and a chamber pressure of 65 Torr. A controlled phosphorus incorporation from ~5×10^{16}cm^{-3} to ~6×10^{19} cm^{-3} was obtained for an accurately controlled growth temperature where a positive temperature gradient of ~2°C/min established an average growth rate of ~15nm/min. This finely tuned growth process was effected through a small increase in the deposition pressure with a gradient of typically 0.1-0.2 Torr/min.



The temperature dependence of PIN diodes have been measured to 300°C. The measurements showed that in (100) diodes the n-type layer is fully depleted and transport is limited by thermionic emission, whereas on (111) the n-type nature and bipolar transport is confirmed with the observation of continuous light emission at forward bias. The properties were simulated using a custom Silvaco model that includes both band and hopping transport of both electrons and holes. The temperature dependence of the resistivity of phosphorus and boron doped diamond were fit with experimental data for a wide range of temperatures. The diodes showed a strong increase in the saturation current density as the temperature was increased due to the increase in the ionization of the dopants.

The simulation program has been used to project the high frequency operation of a BJT. The current density was simulated for a vertical BJT as shown in the figure, and the results were extended to 500°C. The device showed a nearly constant f_t of ~8 GHz as a function of temperature. Devices are being fabricated to verify the predictions of the simulations.

Research supported by ARPA-E through the SWITCHES program.

Keywords: phosphorus doping, high temperature electronics, bipolar devices, device simulation

[O3.3]

Electrical properties of diamond p$^+$in$^+$ junction at forward bias region

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We discuss electrical properties of diamond p$^+$in$^+$ junction at forward bias region through spatial distribution of excitonic emission in the i-layer.

Diamond is expected to be a promising semiconductor for electronic applications, because of the excellent material properties of high breakdown electric field, high thermal conductivity, and so on. When we apply the diamond to the semiconductor electric devices, pin junction is the important base structure. However, pin junction has an issue, such as high specific on-resistance at the forward bias region, which is originated from the high resistance of the p- and n-layers due to deep dopant levels of impurities.

To overcome this issue, in this work, we have fabricated diamond p$^+$in$^+$ junction (i-layer thickness is 7.5 □m) using heavily boron- (phosphorus-) doped p$^+$ (n$^+$) layers with the impurity concentration of the order of 10^{20} cm^{-3}, which shows hopping conduction (inset of Fig. 1). Figure 1 shows the electrical property of the p$^+$in$^+$ junction at room temperature. We realized higher forward current compared to that of the conventional pin junction by decreasing the series resistance of p- and n-layers.

Moreover, in order to study the carrier distributions in the i-layer at forward bias region, we make a cross-section of the p$^+$in$^+$ junction by laser-cutting, and observed the distribution of the electroluminescence due to excitonic emission. As shown in Fig. 2, it was found that the excitonic emission was clearly observed in the i-layer. This result indicates that both electrons and holes are injected into the i-layer, and then the actual resistance of the i-layer becomes low, so-called “conductivity modulation”. Also, from this measurement, it was found that the excitonic emission-intensity is not uniform in the i-layer under the low forward current condition, and becomes more uniform by increasing the forward current.

This work was partially supported by SIP (NEDO).

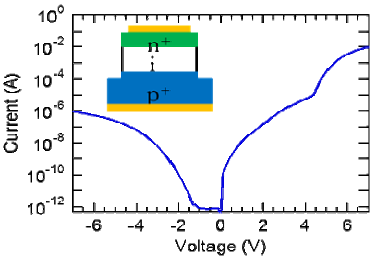

Fig.1 Electrical property of diamond p$^-$in$^-$ junction. Inset is schematic structure of diamond p$^-$in$^-$ junction.

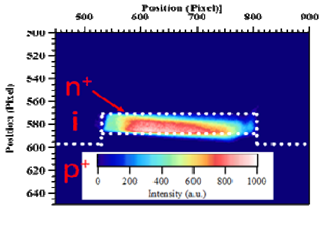

Fig.2 Distribution image of excitonic emission at forward current of 10 mA at room temperature.

Keywords: diamond, pin junction, electrical property, exciton

[O3.4]

Charge collection properties of drift layer in diamond vertical pin diode

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Diamond is hoped to be utilized as ultimate power electronics devices. To verify high breakdown field of diamond, it is important to characterize impact ionization coefficient in the simple device structures such as pin junction. In the point of view of precise characterization, charge loss in the drift layer is important. Nonetheless, there is no report on charge collection properties of diamond pin diode. In this study, we evaluated charge collection efficiency(CCE) in the drift layer of diamond vertical pin diodes by alpha-particle induced charge distribution measurement.

We formed vertical pin diodes grown on {111} (sample#1) and {100} (sample#2) heavily boron doped single crystal diamond substrates. Thickness of intrinsic layers are 40 and 70 microns, respectively. Ohmic contacts were formed by EB deposition of Ti/Pt/Au both on mesa structures of n^+ epilayer and on the back side of p-type substrate. The contacts were connected using gold wire bonding to the SMA coaxial cable and Al housing. 5.486 MeV alpha particles from ^{241}Am radioactive source were injected into pin diode from the n^+ contact. A conventional Silicon pin photo diode (S3590; Hamamatsu) was used as the standard for the induced charge calibration. Average e-h pair creation energy of Silicon and diamond were 3.62 and 12.8 eV, respectively.

Figure 1 shows induced charge distribution of each sample. The CCE was 98.1 ± 0.6 % for sample#1 and 96.9 ± 0.6 % for sample#2, which means almost all generated charges are collected accordingly equivalent to Si pin photodiode. Mean free path λ deduced by equation (1)

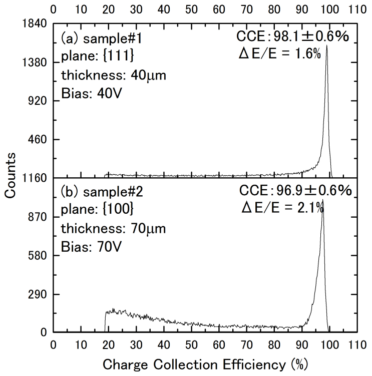

Fig. 1. Induced charge distribution

$$CCE = \exp(-(w-d)/\lambda) \times 100 \quad \ldots (1)$$

were larger than several hundred microns. Where, *w* and *d*(= 13μm) denote thickness of drift layer and range of alpha particles. The results showed charge loss is negligible when the drift layer thickness is within several tens of microns.

Keywords: charge collection efficiency, impact ionization coefficient, mean free path

[O4.1]

Diamond-based detector for a multi-sensing approach in neuronal cells investigation

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Action potentials generation and synaptic quantal release of neurotransmitter molecules are key mechanisms of brain activity, which are at the basis of information transmission and signal communication in neuronal microcircuits. Their detection is therefore a prominent research field in neuroscience.

In the present work, we report about the systematic employment of a diamond-based multi-functional sensor, which represents a novel tool to investigate both quantal exocytic events and action potential firing from cultured cells or tissue slices.

The multi-electrode-array device was fabricated using a broad 1.1 MeV He ion beam on a type-IIa monocrystalline diamond sample ($4.5\times4.5\times0.5$ mm^3) creating up to 60 graphitic active electrodes.

Taking advantage of diamond biocompatibility, we were able to grow neuroendocrine cells over the device surface for several week and detect stable amperometric signals (quantal release of catecholamines) without any functional deterioration, thus demonstrating the long-term chemical/physical stability of the sensor.

The collected data allowed the full investigation of quantal secretory events during stimulated or spontaneous activity of isolated chromaffin cells [1 - 3], slices of the intact adrenal gland or *substantia nigra* neuronal network [4].

Moreover, the versatility of our diamond-based sensor allows revealing potentiometric events (synchronous Action Potentials) from tissue slices such as the sinoatrial node, and from neuronal networks.

Our diamond-based sensors allow the simultaneous recording of action potential waveforms (neuronal firing) and release of neurotransmitters (pre-post synaptic activity): the recording of these key parameters in living neurons furnishes a complete framework of the functional or pathological state of the cells.

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Keywords: Ion-beam lithography, Multi Electrode Array, Neuronal cell, electrochemical sensing

[O4.2]

Black diamond as a bactericidal surface

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‘Black silicon’ (bSi) is a synthetic nanostructured material that contains high-aspect-ratio nanoprotrusions, such as spikes or needles, on its surface produced through a simple plasma etching technique. We show that coating a bSi surface conformably with CVD diamond produces a robust, sensitive electrode with high electroactive surface area. Due to its near 100% absorbance of visible light we have named this nanostructured composite material ‘black diamond’.

The nanostructured surface of bSi has recently been found to generate a mechanical bactericidal effect, killing both Gram-negative and Gram-positive bacteria at high rates. We now show that black diamond also acts as an effective antibacterial surface, with the added advantage that it is far more robust and less likely to become damaged than Si. Three different types of black diamond have been fabricated, with needle lengths 0.5, 5 and 20 μm, and their efficacy at mechanically killing various common bacteria types has been evaluated. Other factors which contribute to increased bacteria death rates, such as diamond crystallite size, doping level, needle density and bacteria type (Gram positive or negative) will be discussed.

Using nanostructured diamond as a bactericidal surface is potentially an exciting new area of research for diamond, with many applications in healthcare, medical implants, and biotechnology.

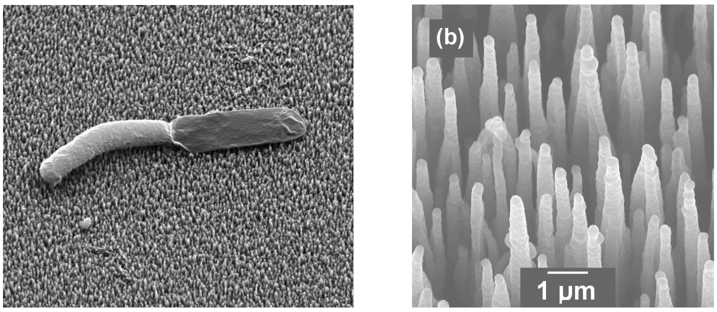

Fig.1. (a) A live (left) and dead (right) bacterium lying on top of a black diamond surface.

(b) High magnification SEM image of a black diamond surface with 20 μm needles.

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Keywords: black diamond, nanostructured surface, bactericidal surface

[O4.3]

Direct fabrication of the graphene-based composite for cancer phototherapy through graphite exfoliation with a photosensitizer

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We report on the application of pristine graphene as a drug carrier for phototherapy (PT).

The loading of a photosensitizer, chlorin e6 (Ce6), was achieved simply by sonication of Ce6 and graphite in an aqueous solution. During the loading process, graphite was gradually exfoliated to graphene to give its composite with Ce6 (G–Ce6). This one-step approach is considered to be superior to the graphene oxide (GO)-based composites, which required pretreatment of graphite by strong oxidation.

Additionally, the directly exfoliated graphene ensured a high drug loading capacity, 160 wt %, which is about 10 times larger than that of the functionalized GO. Furthermore, the Ce6 concentration for killing cells by G–Ce6 is 6–75 times less than that of the other Ce6 composites including GO–Ce6.

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Keywords: phototherapy, cancer, exfoliation

[O4.4]

Carbon quantum dot - photosensitizer conjugates in photodynamic therapy

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Photodynamic therapy (PDT) has seen wide clinical application for treatment of skin cancers using photosensitizers (PS) to produce singlet oxygen leading to cell death. However, effectiveness is limited by low solubility and inefficient accumulation in target tissue. Carbon quantum dots (CQDs) can increase uptake and feature efficient energy transfer towards conjugated photosensitizers. CQDs have been found to have high biocompatibility and no photobleaching.

In this work, PDT was carried out using CQD-PS conjugates excited via laser irradiation. CQDs were synthesized through microwave-assisted pyrolysis of sucrose and ethane-1,2-diamine. Carbodiimide-based crosslinking was used to fabricate CQD-PS conjugates, which were purified through dialysis and characterized by UV/Vis spectroscopy, fluorescence spectroscopy, FTIR, dynamic light scattering and TEM. Intracellular delivery of CQD-PS was confirmed by confocal and two photon microscopy using C8161 melanoma, co-staining with DAPI. Toxicity was evaluated using resazurin cell viability assay after varying incubation time intervals in concentrations from 1 - 100 ug/ml. Clonogenic survival was also utilised to further study long term toxicity.

The CQD-PS conjugate was confirmed with changes in the absorption and emission spectra of the CQD. Cell viability assays focused on dark toxicity indicate CQD-PS conjugates are less toxic than unbound photosensitizer, though the conjugate shows increased toxicity compared to unbound nanoparticles. Although solubility was increased, aggregation can still be seen in the CQD-PS solution, which limits the concentrations of CQD-PS conjugates to around 25 ug/ml, compared to ~50% viability with 2.5 ug/ml of free photosensitizer stated in literature. Cells were also exposed to light using an LED lamp to produce the phototoxic effect via FRET activation of the compound which resulted in loss of viability. In summary, the use of CQDs as carriers for photosensitizers allows higher drug concentrations without compromising cell viability before photoactivation, improving the efficiency of treatment.

Keywords: Carbon dot, Toxicity, Photodynamic therapy, Protoporphyrin IX

[O4.5]

YOUNG SCHOLAR AWARD: Fluorescent nanodiamonds as multi-purpose labels for (electron) microscopy

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Introduction

Nanodiamonds containing fluorescent nitrogen vacancy centers (FNDs) are increasingly attracting interest as a probe in biological microscopy. This interest stems from (i) strong resistance to photobleaching allowing prolonged fluorescence observation times; (ii) the possibility to excite fluorescence using a focused electron beam (cathodoluminescence; CL) for high-resolution localization; and (iii) the potential use for nanoscale sensing. For all these schemes, the development of versatile molecular labeling using relatively small diamonds is essential. We show the direct targeting of biological molecules with FNDs as small as 70nm using a streptavidin conjugation and standard antibody labelling approach. We also show internalization of 40nm sized FNDs.

Methods

40nm FNDs were incubated with J774 mouse macrophages and processed for (electron) microscopy. Streptavidin conjugated 70nm FNDs were used to imunnohistochemically identify the extracellular EpCAM domain in HT29 GFP-EpCAM cells and compared to proper controls (e.g. quantum dots). All samples were processed for confocal microscopy using a Zeiss LSM780 microscope and a homebuilt magnetometry-enabled confocal microscope. Samples were embedded in epon resin, sectioned and analyzed with a confocal integrated SEM, where simultaneously secondary electrons and electron generated photons were monitored.

Results

Fluorescence from nanodiamonds survives osmium-fixation and plastic embedding, making them suited for correlative light and electron microscopy. We show that unlike other biocompatible molecules, CL can be observed after epon-embedding, while surface-exposed nanoparticles also stand out in secondary electron (SE) signal due to the exceptionally high diamond SE yield. Finally, we demonstrate the magnetic read-out using fluorescence from diamonds prior to embedding.

Conclusions

Our results firmly establish nanodiamonds containing nitrogen-vacancy centers as unique, versatile probes for combining and correlating different types of microscopy, from fluorescence imaging and magnetometry to ultrastructural investigation using electron microscopy. The combination of immunohistochemical staining with cathodoluminescence results in an easy and durable method to identify molecular structures in electron microscopy.

Keywords: Fluorescent Nanodiamonds, Cathodoluminescence, Immunohistochemistry, Magnetometry

[O6A.1]

XAS spectra of functionalized carbonaceous materials simulated from first principles

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Carbonaceous materials are potential electrode materials for electrochemical detection of neurotransmitters, for instance dopamine [1–3]. Measuring physiologically meaningful dopamine levels *in vivo* could help to understand several neurological disorders such as Parkinson's disease, schizophrenia and depression. In addition to biocompatibility and resistance to bacterial adhesion, amorphous carbon in particular, possess characteristics that can improve selectivity and sensitivity of the biosensors. It is known that the oxidation/reduction behaviour of dopamine strongly depends on the electrode surface chemistry, and thus these carbon-based materials have been characterized in detail [2, 4–8] and their electrochemistry has been widely studied [1, 2, 4, 7]. However, profound understanding of the relationship between structural characteristics and electrochemical properties of these materials is still lacking, because, considering the complexity of the materials discussed here, interpretation of the experimental results obtained e.g. with XAS (X-ray Absorption Spectroscopy) is very difficult. In this work we employ density functional theory-based simulations of XAS spectra of carbonaceous materials in order to rationalize the experimental results.

Carbon can be bonded in various ways (sp^1 , sp^2 and sp^3) and form several different kinds of ring structures in amorphous carbon [5, 6]. In addition, the electrode materials always contain also other elements than carbon, such as hydrogen and oxygen. These elements are present as functional groups on the surface and have a profound effect on the electrochemistry of these materials [7]. To examine the roles of differently bonded carbon, three types of carbon materials were included in this study: graphene, diamond and amorphous carbon. Furthermore, these surfaces were functionalized with hydrogen, oxygen, hydroxyl group and carboxylic acid. Finally, the simulation outcome is compared with the experimental XAS results to provide more in depth knowledge of the effects of these groups on XAS spectrum. Possible implications of surface characteristics to electrochemical detection of dopamine are also provided.

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Keywords: DFT, XAS, amorphous carbon, dopamine

[O6A.2]

High resolution absorption spectroscopy of isotopically enriched boron acceptor centers in high quality IIb-type HPHT diamond.

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Understanding of optical properties of IIb diamond requires knowledge of fundamental structure of electronic states of acceptor centers formed by substitutional boron atoms. To date, known and commonly accepted are: boron binding energy and rich and complicated spectrum of boron-mediated lines falling in the infrared (IR) wavelength range. Exact assignment of the boron-related IR transitions is still under dispute. The reasons are first of all different line broadening mechanisms, such as concentration, isotopic content, as well as correlation of some boron-mediated bands with strong lattice bands in diamond.

Here we present the results aimed to identification of structure of excited boron states by high resolution low-temperature IR absorption spectroscopy of high-quality boron-doped diamond samples. We cut (001) plates by laser from IIb-type HPHT diamond crystals. Two different boron sources were used for doping: amorphous natural boron and isotopically enriched oxide with at least 99% of ^{11}B. Plates were double-side polished with wedge of ~ 1° to avoid interference. For each samples shadow masks were produced to obtain absorption from the single growth sector with uniform boron content, which was varied from 50 ppb to 1 ppm for different samples.

For diamond doped by natural boron we clearly distinguish more than 50 absorption lines. Analysis of IR spectra obtained at different lattice temperatures allows select thermally induced transitions, which correspond to population changes of spin-orbit split ground state. Reduced number of transitions in C:^{11}B reveal on significant isotopic splitting of 0.7 meV for ^{10}B and ^{11}B. Thus, the absorption spectra can be significantly simplified by using isotopically pure samples and applying temperatures lower than 5K. It gives an opportunity for further investigation of the excited state symmetry and a hint on natural linewidth of transitions in lowest doped samples.

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Keywords: boron-doped diamond, infrared spectroscopy, acceptor excited states, isotopically enriched diamond

[O6A.3]

Refined analysis of Raman spectra from boron doped diamond

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Raman spectroscopy is a simple and non-destructive technique which is widely used for the characterisation of diamond layers obtained using microwave plasma enhanced chemical vapour deposition and in particular, for boron doped diamond layers. The features of Raman spectra from boron doped diamond with metallic conduction are well described. They exhibit the typical Fano shaped diamond peak and several other characteristic peaks. However, the origin of these peaks is still of some controversy and are not understood well.

In this work, Raman spectra of boron doped epitaxial diamond layers are studied experimentally and discussed with the inclusion of extensive literature data in order to understand the origin of characteristic features. Characteristic Raman peaks have been examined as a function of boron concentration, electrical conductivity, isotopic composition and temperature in order to determine their origin. Despite the evidence that the main Raman bands are mostly characteristic of carbon vibration modes, we observe proportionality of Raman peak positions with boron concentration. Analysis of reduced Raman spectra unambiguously reveals electronic Raman scattering at the origin of the Fano shape of the diamond line and the 1200 cm^{-1} band. Detailed analysis of the diamond peak's Fano fitting parameters demonstrates that the downshift and broadening of the diamond line are due to lattice expansion, a phonon confinement effect cause by the high boron impurity concentration, and finally to electronic Raman interaction.

This work was financially supported by the project 13-31783S of Czech Science Foundation, the French-Czech Project Barrande 35785SC - 7AMB16FR004 of the Czech Ministry of Education, Youth and Sports and the J.E. Purkyne□ fellowship awarded to V. Mortet by the Czech Academy of Sciences.

Keywords: Diamond, Raman spectroscopy, Boron doping

[O6A.4]

Determination of nanocrystalline diamond thin film thermal conductivity by combining spectroscopic ellipsometry and thermoreflectance microscopy

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Many thermal and electrical applications of diamond require large-area layers deposited at temperature compatible with various substrates [1]. In particular, NanoCrystalline Diamond (NCD) grown by Distributed Antenna Array (DAA) low-temperature microwave process [2] is a good candidate for thermal management of electronics devices, since it could allow depositing a high thermal conductivity diamond layer at the top surface of the device, in the closest vicinity of the active region, at a temperature compatible with the processing steps of the GaN HEMT technology (200-400°C) [3]. However, the measurement of thermal properties of very thin diamond layers is difficult owing to the impossibility to distinguish the contribution of the film, substrate and interfaces.

The thermal properties of 4-inch NCD films grown on silicon in a DAA system at temperature below 400°C was investigated by a robust and reproducible method combining both spectroscopic ellipsometry (SE) and thermoreflectance microscopy (TRM) [4]. SE permits to determine a multilayer model of the film/substrate system and to emphasize the layers and interfaces involved in the thermal measurements. This multilayer structure is introduced in a thermal model in order to fit experimental data of TRM, which permits to reach NCD film thermal conductivity.

Whatever NCD film thermal properties, which depend on growth conditions, the diamond layer is bounded between two strong resistive interfaces of 2×10^{-8} and 0.5×10^{-8} $K.m^{-2}.W^{-1}$, corresponding to the growing surface and the nucleation side, respectively. It shows the necessity to control both the film surface roughness and the film/substrate interface to improve the thermal performances of NCD films.

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Keywords: Nanocrystalline, Diamond film, Plasma CVD, Thermal properties

[O6B.1]

Doped nanodiamonds produced from organic compounds

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Diamond nanoparticles doped with nitrogen, boron, silicon, and other impurity atoms are promising material platform for implementation of new generation of nanomagnetometers, conducting biosensors, and single-photon emitters. A “top-down” approach is commonly used for production of doped NDs. It consists of mechanical grinding of bulk diamond obtained by CVD or HPHT techniques.

In this work our progress in production of boron- and nitrogen- doped nanodiamonds (NDs) from organic compounds at high pressure are reported. The B-doped NDs were synthesized from the 9-borabicyclo[3,3,1] nonane dimer $C_{16}H_{30}B_2$ at a pressure of 8–9 GPa. At the temperatures ranging from 800 to 1250 ^{o}C we succeeded in obtaining the smallest of the so far known boron-doped NDs, as small as 3 nm to 10 nm. Such nanoparticles were found to demonstrate intense heating of surrounding water under visible laser irradiation. This opens prospects for using the boron-doped NDs as nanoagents in local hyperthermia. The high quality nanodiamonds were synthesized from adamantane $C_{10}H_{16}$ and adamantanecarbonitrile $C_{11}H_{15}N$. Intensive decomposition of the compounds took place above 700-800 ^{o}C at 8-9 GPa. At temperatures up to 1300 ^{o}C, predominant formation of graphitic phase was detected. Further Increase in temperature up to 1400-1500 ^{o}C stabilizes diamond formation, while dispersion of ND sizes was quite large: from 50 to 1000 nm. The ability to control content of nitrogen and NV centers in the synthesized diamonds varying $C_{10}H_{16}/C_{11}H_{15}N$ mass ratio in the precursor mixture was demonstrated. Individual diamond crystallites of 300-400 nm in size containing NV centers can be used as microcavities for their own NV emission.

This work was supported by Russian Science Foundation, grant No 14-12-01329.

[O6B.2]

Salt-assisted ultrasonic deaggregation of nanodiamond

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Detonation nanodiamond particles (nanodiamonds, NDs) are particularly known to form agglomerates that are notoriously difficult to destroy by traditional means such as sonication, milling, etc. This is generally explained by rich surface chemistry of ND. The presence of diverse functional groups on ND surface, such as carboxyl, hydroxyl, lactone, etc., may result in formation of multiple hydrogen and even covalent bonds between the adjacent ND particles, making it difficult to separate them. Strong agglomeration severely limits potential of NDs in many applications. We present a new facile, inexpensive, and contaminant-free technique of salt-assisted ultrasonic deaggregation (SAUD) of nanodiamond into single-digit particles stable in aqueous colloidal solution in a wide pH range [1]. The technique utilizes the energy of ultrasound to break apart nanodiamond aggregates in sodium chloride aqueous slurry. In contrast to current deaggregation techniques, which introduce zirconia contaminants into nanodiamond, the single-digit nanodiamond colloids produced by SAUD have no toxic or difficult-to-remove impurities and are therefore well-suited to produce nanodiamonds for numerous applications, including theranostics, composites, lubrication, etc. Requiring only aqueous slurry of sodium chloride and standard horn sonicator and yielding highly pure well dispersed nanodiamond colloids, the technique is an attractive alternative to current nanodiamond deaggregation protocols and can be easily implemented in any lab or scaled up for industrial use.

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Keywords: nanodiamond, deaggregation, colloid, biomedical applications

[O6B.3]

Thermal phase transition on facets of detonation nanodiamond particles for formation of diamond hydrosols

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Over a couple of decades the application area of detonation nanodiamond (DND) was essentially restricted. The main problem consisted in extreme hardness of agglomerates formed by its particles. Recently developed methods for deagglomeration of DND and obtaining the stable hydrosols based on thermal treatment in air or in hydrogen [1, 2] opened new application areas for this promising material. Nevertheless, the reason for unusual hardness of its agglomerates and the nature of deagglomeration process remained unrevealed. In this presentation the results of the comprehensive study of the structure of DND agglomerates and their transformations under thermal treatment as well as subsequent forming the hydrosols of separate 4-nm particles are reported. We have shown that a key factor of deagglomeration is the sp3-sp2 phase transition on facets of diamond nanocrystals. Details of the phase transition have been studied by number of complimentary methods including TEM, AFM, XPS, Raman scattering, X-ray diffraction and dynamic light scattering. The model based on the results of study giving the complete explanation for the processes taking place at thermal treatment and forming the stable hydrosols of 4-5 nm DND particles is submitted. The model also shows the new ways for obtaining sols of separate 4-5 nm DND particles in various solvents. This work was supported by the RSF (project 14-13-00795)

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Keywords: phase transition, nanodiamond, hydrosol, surface modification

[O6B.4]

Introducing DAICEL's activities related to detonation nanodiamonds, unique surface modification and application development

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DAICEL Corporation, Japan

Daicel is a Japanese chemical company, which was formed through the merger of eight celluloid producers in 1919. As a part of our effort to create new business domains, we started developing the detonation nanodiamond, and have already established semi-commercial production capacity for the detonation, as well as for purification, of the detonation soot to provide nanodiamonds (ND).
We have been investing our R&D resources mainly on two areas. One is to exploit unique and original functions of the nanodiamonds to develop profitable applications. The other is to create unique and original nanodiamonds themselves to pursue even higher values. In the talk, we will introduce DAICEL's unique nanodiamonds that we have recently started introducing to markets as well as some of recent topics about commercial applications we've been working on.
Unique nanodiamonds
Nanodiamonds can be dispersed very stably in water due to their hydrophilicity and high zeta potential to earn repulsion between the particles. There are single digit nano-dispersions of nanodiamonds in water available in the market including ours. However, as long as one depends on the zeta potential to obtain stable dispersions, it is difficult to achieve the same stability in water-base formulas in which various chemical components coexist especially at high concentration. For instance, in a solution for metal plating, nanodiamonds are no longer able to maintain nano-dispersion due to high ionic strength. DAICEL has a surface modification technology to make nanodiamonds water-soluble, regardless of surrounding conditions such as ionic strength of the solution. In the talk, we will introduce some of its properties and possible applications.
In addition to above, we will show performances of nanodiamonds for commercial applications, such as tribological behaviour in water and as a thermal stabilizer for polymers.

[O6B.5]

Positive zeta potential of nanodiamonds

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It is well known that diamond nanoparticles' surface charges play a determining role in view of its subsequent material characteristics. Surface charges are determined by the surface functional groups present in the diamond nanoparticles, and can be controlled through different cleaning methods, annealing treatments or surface functionalization. The manipulation of these surface charges will be deeply important for a wide range of applications and will have an important influence over colour centres fluorescence.

However, for most applications, diamond nanoparticles have to exhibit stability in colloidal systems to prevent particles' aggregation. The key indicator of a colloid stability is known as zeta potential and is defined as absolute zeta potential values greater than 30mV.□Diamond nanoparticles usually exhibit negative zeta potentials due to oxygen based surface functional groups, but hydrogenated diamond nanoparticles were proved to have a positive zeta potential although the origin was uncertain.

In this work, the positive zeta potential of commercial 50 nm size diamond nanoparticles after vacuum annealing treatments at 1000°C is explained. At this temperature, a graphitic layer is created around the diamond core of the diamond nanoparticles. Positive zeta potential in nano-structured carbons is explained due to the presence of basal planes in graphite, which leaves oxygen-free Lewis sites and so promotes the suppression of acidic functional groups. At the same time, sp^2 carbon creation on diamond nanoparticles surface eases low temperature (500°C) diamond nanoparticles hydrogenation, previously demonstrated for detonation diamond (5nm).

Keywords: zeta potential, colloidal stability, sp2

[O6B.6]

Understanding the surface of hydrogenated detonation nanodiamond using isotopic labelling

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Nowadays, diamond nanoparticles are developed and used in many application fields including composite materials, lubricants, catalysis and medicine.[1] Among the different synthetic methods, nanoparticles synthesized by detonation are considered in the present study.[2] Detonation nanodiamonds (DNDs), obtained by explosion of carbonated charges, combine outstanding properties like hardness, low friction coefficient, chemical resilience, thermal conductivity, colloidal stability and biocompatibility with a 5 nm diameter core. When looking at the interaction of the DNDs with their surroundings like proteins, biological targets catalysts, dyes, matrix polymer for example, controlling and understanding the surface properties of DNDs is essential.[3]

Many efforts were done in order to obtain before functionalization, homogeneous surface functions. Among all the investigated methods, hydrogenation is of great interest[4], due to combine removal of non-diamond carbon, reduction of oxygen groups and the formation of C-H groups. Despite recent progress in the understanding of the hydrogenation of DNDs, the development of techniques for quantitative analysis of the surface termination remains challenging. Radioactive labeling of the DNDs appears to be a promising tool for this purpose. Indeed tritium, thanks to its radioactivity, can be easily detected with a high sensitivity by standard liquid scintillation counting and autoradiography.[5]

The aim of this work is to understand better the surface chemistry of DNDs after hydrogenation using isotopes of hydrogen. We applied the two main methods for hydrogenation: micro-wave assisted plasma and annealing in presence of hydrogen, deuterium or tritium gas while keeping strictly the same experimental conditions. Thanks to the presence of isotopes, advanced characterization have been performed onto the treated nanoparticles such as solid state NMR (^{2}H, ^{3}H), Raman and FTIR. For instance, C-D terminations can be evidence by FTIR while the efficiency of the treatments in terms of loading can be quantified and compared with ^{3}H.

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Keywords: detonation nanodiamonds, isotopic labelling, annealing, plasma

[O7A.1]

Electric field distribution using floating metal guard rings edge-termination for diamond Schottky diodes

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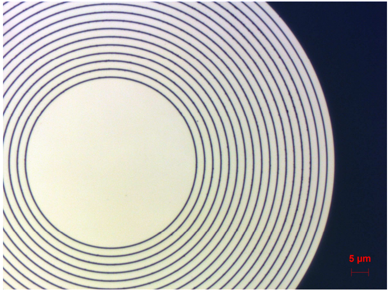
Exceptional properties such as high critical field, high carrier mobility and high thermal conductivity, make diamond an attractive material for power devices. In particular, this extremely high critical field strength leads to high breakdown voltages of the devices. Unfortunately, diamond devices showed breakdown characteristics lower than those predicted. One reason for these low breakdown voltages is the electric field crowding at the edge of the main junction, which causes premature avalanche breakdown.

To obtain better performance of power devices for high-voltage application, one needs to reduce the field concentration using edge termination technique such as oxide field-plate, junction-termination extension or floating metal guard rings [1-2]. Among them, floating metal guard ring termination is the easiest and the most suitable architecture for diamond Schottky diodes [3].

In this work, diamond diodes with boron doping levels of 3×10^{15} and 1×10^{16} cm^{-3} were fabricated with Mo/Pt/Au Schottky contacts in a pseudo-vertical structure. Floating metal guard rings were fabricated using the same metal deposition, as shown in the figure below. Influence of the number and the distance between rings were investigated, and compared with devices without guard rings. Devices were measured by Electron Beam Induced Current (EBIC), in order to observe the electric field distribution.



Diamond Schottky barrier diode with floating metal guard rings

The results clearly spread out the effective spatial distribution of the electric field induced by the integration of the guard rings. An Optimized layout will be proposed for high voltage Schottky diodes.

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Keywords: Schottky diode, Edge termination, Electric field, Diamond

[O7A.2]

Transport mechanism of diamond Schottky-pn diode

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We clarify the transport mechanism causing ultra-low specific on-resistance ($R_{on}S$) of the diamond Schottky-pn diode (SPND) by measuring the *I*-*V* characteristics as a parameter of n-type layer thickness and measurement temperature.

Diamond SPND can be an ideal power diode [1, 2]; low $R_{on}S$, high breakdown voltage, and fast switching time. SPND is composed of a fully depleted n-type active layer, sandwiched between a highly boron-doped p^+-type layer and a Schottky metal, as shown in Fig.1. When the forward bias is applied, the potential barrier (ΔE) for holes decreases. At a certain forward bias, where the electric field at the interface between p^+-type and n-type layer becomes around zero, the free holes start to flow into the n-type layer. The holes are instantly accelerated by the strong internal electric field in the n-type layer. This situation brings low $R_{on}S$ for SPND while the limitation of $R_{on}S$ in SPND is still unclear.

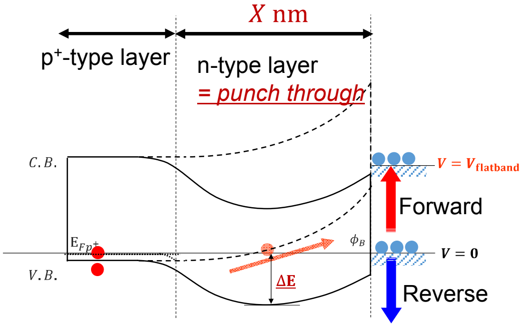

Fig. 1. The band structure of SPND. Solid line; thermal equilibrium. Dashed line; flat-band voltage.

The schematic structure and optical microscope image are shown in Figs. 2 (a) and (b). We prepared four kinds of n-type layer thickness for the same substrate; X =70, 155, 245, 330 nm. The phosphorus concentration were evaluated as around 3×10^{16} cm^{-3} from SIMS analysis. From *I*-*V* characteristics, we found that the $R_{on}S$ increases with increasing the n-type layer thickness. It was thought that the $R_{on}S$ is determined by the p^+-type layer's resistivity. However, our results indicate that there exists another $R_{on}S$ component related with n-layer thickness (Fig.2 (c)), like space charge limited current and an imperfection of device designing or processing, etc. In the presentation, we will also discuss the transport mechanism of SPND derived from the temperature dependence of *I*-*V* characteristics.

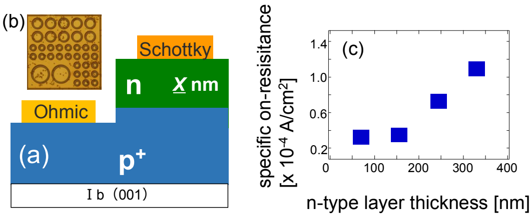

Fig. 2. (a) The schematic structure, (b) optical microscope image of SPND and (c) n-type layer thickness dependence of the specific on-resistance

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Keywords: switching diode, power device, on-resistance, blocking voltage

[O7A.3]

Electrical properties of Schottky barrier diodes fabricated on diamond substrate

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Diamond is a promising semiconductor for future high-voltage high-temperature applications due to its excellent properties, such as high breakdown field, wide band-gap and high carrier mobility, etc. These attract researchers' attention to investigate high power diamond devices. Although highly doped substrates are used to fabricate power devices, such as Schottky barrier diodes (SBDs), these substrates by high-pressure high-temperature (HPHT) are very limited. In order to meet the need to develop high power electron devices, some groups used lateral structure to fabricate high voltage diamond SBDs. However, their forward and reverse characteristics of diamond SBDs are lower than the expected value due to the non-optimum device geometry.

In this research, a pseudo vertical structure was fabricated to improve SBD's forward and reverse characteristics, as shown in Fig.1. The first epitaxial layer was grown on HPHT Ib (001) diamond substrate through microwave plasma chemical vapor deposition method, on which ohmic electrodes were patterned by photolithography and magnetron sputtering technique. Then, second epitaxial layer was grown on the window area. Finally, Schottky electrodes were deposited on center diamond surface. This geometry SBDs were evaluated and the results will be presented on the conference.

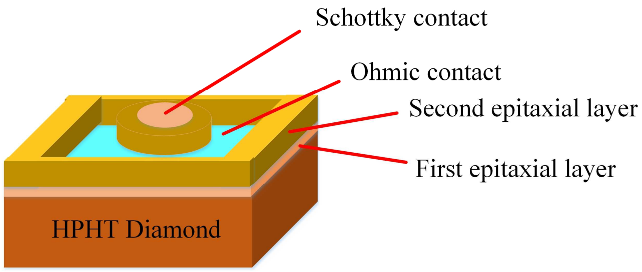

Fig.1

Reference

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Keywords: Diamond, Schottky barrier diode, Electronic properties, Pseudo vertical structure

[O7A.4]

Ohmic metal-graphite contacts on lightly boron-doped diamonds

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In the last years there has been a large increase in interest in diamond devices due to their properties, such as high carrier mobility, high thermal conductivity and high breakdown field. In addition, doped diamond devices appear to be very functional for power electronic technologies, like p-n junctions and Schottky diodes. If on one side the n-type doping of diamond materials presents several critic points and limits for applications, on the other side the p-type doping, which is obtained by addition of boron impurities, show interesting perspectives. For example, heavily boron-doped diamond devices are widely studied in literature, for pseudo-vertical Schottky diodes technology and vertical power devices [1, 2].

Anyway a crucial point for boron-doped diamond devices is again opened: the production of ohmic and stable electrodes [3]. Traditionally, the diamond contacting is performed by metallic layer deposition, for example Ti/Au, and an ohmic behaviour is obtained for heavy boron-doped diamonds. Nevertheless, decreasing the doping level, the electrode ohmic behaviour is compromised [4, 5].

In this work, we study the contact electrical conduction of several CVD single crystalline diamond samples, grown with different boron doping levels (from 10^20 to 10^16 cm^-3) and contacted by metallization processes. In particular, after having determined which samples show a not ohmic behaviour and individuated critic doping levels, the contacts are removed and replaced after an additional treatment: a graphitic layer is induced by He ion implantation before of a new metallic deposition. Structural and morphological characterizations of the graphitic layer by micro-Raman and Scanning Electron Microscopy, respectively, were carried out, in addition to the electrical analyses performed by the transmission line model (TLM) in order to evaluate improvements obtained.

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Keywords: ohimc contacts, boron-doped diamonds

[O7B.1]

Scaled-up process for producing longer carbon nanotubes and carbon cotton by macro-spools

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Carbon nanotube-based materials exhibit properties far below theoretical predictions and even much lower than those for some conventional carbon materials. So it is one of the most challenging targets to translate outstanding properties of carbon nanotubes into macroscopic composite or fiber features. One can suggest rather obvious idea that the synthesis of longer nanotubes would help. Recently, some works like [1, 2] showed that it works and brings better properties. Although there are several methods discovered for synthesizing millimeter- and centimeter-long nanotubes, the macroscopic material requires the nanotubes in quantities, which are difficult or impossible to produce in laboratory bench scale. So it is necessary to scale up, which is a difficult chemical engineering problem for any process, and is especially difficult for such a delicate topochemical reaction.

This work reports a scaled up process of the longer carbon nanotube synthesis. A suspended-bed synthesis rig is reported capable of producing carbon nanotube cotton in spools or piles in kilogram amounts. A possibility to produce free-standing non-woven nanotube thin films is demonstrated. The embryonation and initial growth periods are recorded.

The carbon nanotube cotton was investigated by electron microscopy (SEM/TEM), Raman spectroscopy, thermal analysis and XPS. It was shown that the material is dominated by double-walled nanotubes. It was also shown that the carbon nanotube cotton is electrically conductive and shows more that 1 kS/cm even in loose form with multiplication if densified.

Opportunities of combing, roving and spinning the carbon nanotube cotton are discussed. In conclusion this successful scale-up development paves the way for intensification of the development in macroscopic carbon nanotube-based fibers and composite materials.

Figure. A macro-spool of nanotube cotton, manufactured during 15 min.

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Keywords: Scale up, carbon nanotube, catalyst, cotton

[O7B.2]

Atomic-scale simulations of hydrocarbon effects in the nucleation of carbon nanotubes

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Atomic scale simulations of the nucleation and growth of carbon nanotubes (CNTs) provide access to a microscopic understanding of their growth mechanism. Nevertheless, and in spite of over two decades of simulation efforts in this area, virtually no progress has so far been made on addressing the role of the hydrocarbon precursor on the growth process. Especially, the onset of CNT formation using hydrocarbons remains unclear [1].

We here address the Ni-catalysed CNT nucleation from hydrocarbons (C_2H_2, C_6H_6, CH_2O, C_2H_6O, etc.) at temperatures 1000 K - 2000 K using hybrid molecular dynamics / Monte Carlo (MD/MC) simulations.

We found that in the incubation stage, impinging molecules contribute to initial ring formation after supersaturation, in addition to earlier suggested mechanisms [1,2]. Also, the formation of polyyne chains before the cap nucleation depends on the particular hydrocarbon species. Furthermore, C atoms may either diffuse into the cluster after full dehydrogenation, or diffuse over the surface in the case of partial dehydrogenation. In either case, they are found to eventually incorporate into the carbon network on the cluster. Moreover, the formation of free-standing graphene nanowalls and a horizontal carbon nanosheet is observed on the catalyst cluster due to a competition between (re)hydrogenation and dehydrogenation processes. The etching effect of adsorbed/desorbed H species in the nucleation stage is also carefully discussed [3,4].

Overall, our investigations reveal that dehydrogenation, rehydrogenation, and H-etching can clarify a number of experimental observations: (i) the appearance of unstable carbon protrusions in in-situ TEM-observations; (ii) the onset of MWNT nucleation in the case of low-temperature and high H-flux; (iii) the lower growth rate.

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Keywords: CNT nucleation, hydrocarbons, etching, MD/MC simulation

[O7B.3]

Mechanical properties of high temperature treated carbon nanotube fibers

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Notable progress has been made recently on the mechanical properties of carbon nanotube (CNT) in the development of fibers. CNT fibers are composed of tightly packed and uniformly twisted CNTs, and produced by dry spinning directly of densely and relatively long vertically aligned CNT (VA-CNT) array. However, it is yet to investigate how temperature treatments govern the mechanical properties of CNT fibers.

The VA-CNT array on Si coated with Fe was synthesized by the thermal chemical vapor deposition method with hydrogen as the process gas and acetylene as the carbon source at 680 – 700°C. CNT fibers were heated by applying bias voltage to CNT fibers under vacuum. The temperatures of CNT fibers varied up to 2000°C. The mechanical properties were analysed by a tensile strength tester. The Raman intensity ratio between the graphite-like G-band at 1590 cm^{-1} and the disorder induced D-band at 1350 cm^{-1} (I_G/I_D ratio) was evaluated.

The diameter and number of walls of CNTs were 4-6 nm and 2-5 layers, respectively. We have successfully obtained high percentage of double-walled CNTs. Typical twisting angle of CNT fibres were between 20-25°. The tensile strengths and Young's modulus of pristine CNT fiber were 620MPa and 34GPa, respectively. By heat treatments (HT) at 100 and 2000°C, the tensile strengths and Young's modulus improved up to 0.96/0.97GPa and 70/180GPa, respectively. It is worth noticing and reporting that we achieve extremely high Young's modulus, which is 6 times higher than that of the pristine one. The I_G/I_D ratio for the pristine CNT fiber, the HT treated CNT fibers at 1600 and 2000°C were measured to be 0.95, 1.1, and 8.2, respectively. The graphite component in CNT fiber was increased with increase of applied temperature may be due to decrease of the defects and increase of the graphite component.

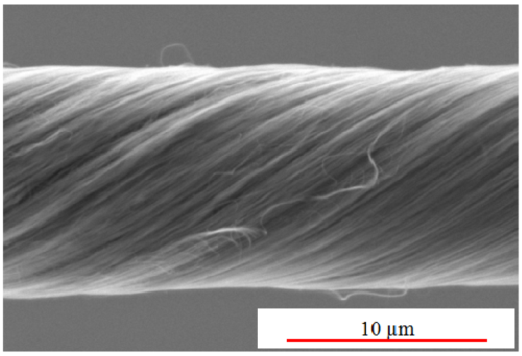

Fig.ure 1. SEM image of CNT fiber with diameter of 11µm and twisting angle of

Table 1. Mechanical properties of CNT fibers

	Tensile Strength (GPa)	Young's Modulus (GPa)
Pristine	0.62	34
HT at 1600°C	0.96	70
HT at 2000°C	0.97	180

Keywords: c properties,
Raman char

[O7B.4]

Carbon nanotubes for CubeSat radiometric sensors

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[1]National Institute of Standards and Technology, USA, [2]University of Colorado, USA

Vertically aligned carbon nanotubes (VACNTs) have been shown to be excellent broadband absorbers of light exhibiting quite possibly the lowest reflectance for a sub-millimetre thick planar coating. As a result, VACNTs are appealing for radiometric applications not only because of their low reflectance but for their potential to replace black body absorbing cavities traditionally used in radiometers. Currently at NIST, we are developing a variety of chip-scale radiometers for room-temperature, cryogenic and CubeSat applications - all of which utilize VACNTs as the black body absorber. We will present hemispherical reflectance and water contact angle measurements for VACNTs treated with CF_4 and O_2 radicals. Our as-grown VACNTs display low reflectance and are hydrophobic, but additional plasma treatments can further lower the reflectance by up to a factor of five while maintaining hydrophobicity. In addition, I will give an overview of radiometric detectors utilizing VACNTs which we are developing in collaboration with LASP, scheduled for launch.

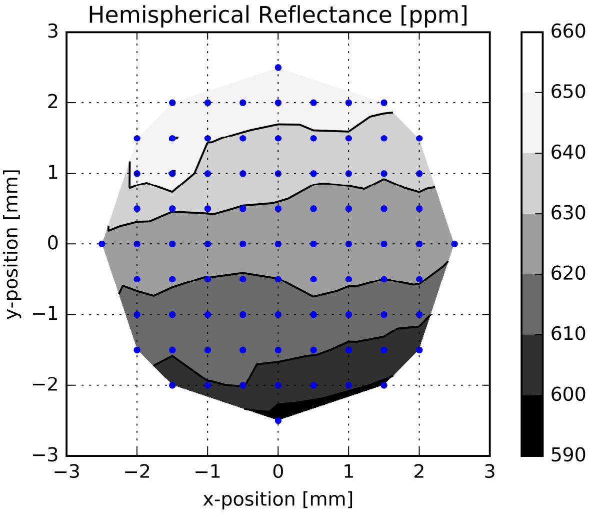

Figure 1. Hemispherical reflectance of a 5 mm diameter circle of as-grown VACNTs measured at 520 nm. Median hemispherical reflectance is 624 parts per million. Blue dots are reflectance measurement positions and the gray-scale contours are linearly interpolated from the individual points.

Keywords: reflectance, radiometer, hydrophobic, cubesat

[O8A.1]

YOUNG SCHOLAR AWARD: Internal structure and electrical properties of laser-induced wires in diamond bulk

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[1]General Physics Institute of RAS, Russia, [2]National Research Nuclear University “MEPhI”, Russia

Laser processing is successfully used for fabrication of buried conductive wires in diamond bulk applying local phase transition of diamond into graphenic carbon (sp^2 phase). Here we report on investigation with nanometer spatial resolution of the interior of laser-induced wires in diamond bulk and correlation between the internal structure of the wires and their electrical properties.

A set of conductive wires was fabricated inside a CVD single-crystal diamond varying velocity of focus movement and energy of laser pulses emitted by a Ti:sapphire-laser (λ=800nm, *f*=1KHz, t=5ps). High-quality longitudinal cross-sections of the wires were prepared via precise mechanical polishing. The cross-section surfaces were examined by means of scanning electron microscopy (SEM) and scanning spreading resistance microscopy (SSRM). The electrical characterization of the wires was carried out by standard I-V measurements.

It was found out that only small part of diamond is altered into the sp^2-phase in the region of laser irradiation. The sp^2-phase is localized within numerous cracks forming a conductive net of graphenic nanosheets separated from each other by diamond interlayers. The nanosheets are clustered in segments of a few microns in size, which are spread along the wires quasi-periodically (see Fig.1). We have found that the integrated conductivity of the wires is the higher, the more segments per a length unit and vice versa.

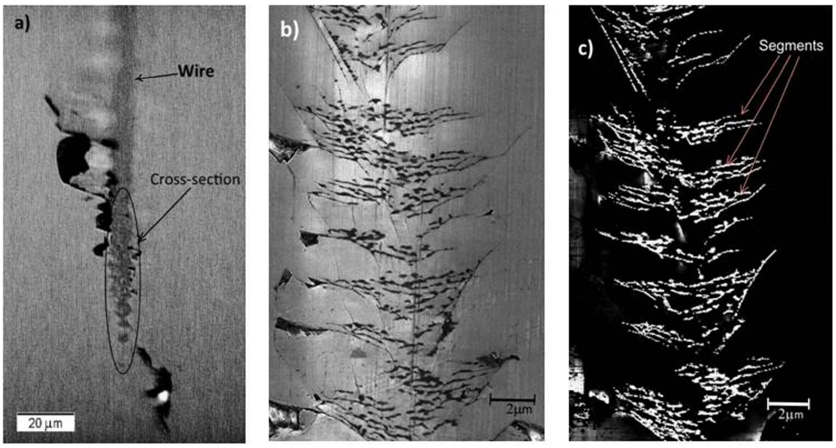

Fig.1 Cross-section surface of the wire: general view in optical microscope (a) and the magnified image of a small area obtained with SEM (b) and SSRM (c). The last presents a map of the local conductivity.

Thus, the laser-induced wires are a mixture of two carbon phases having a sophisticated spatial structure. Further investigations are needed to clarify relationship between the 3D-configuration of graphenic nanosheets and electrical characteristics of the wires.

The work was supported by the Russian Ministry of Education and Science (grant №3.2608.2017/ПЧ).

Keywords: laser-induced phase transition, diamond, grapnenic carbon, internal structure

[O8A.2]

Radiation hardness of three-dimensional sensors fabricated on different CVD diamond materials

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[1]INFN, Italy, [2]University of Florence, Italy, [3]INO-CNR, Italy, [4]Jozef Stefan Institut, Slovenia, [5]LENS, Italy, [6]University of Perugia, Italy, [7]INFN, Perugia, Italy, [8]GSI, Darmstadt, Germany, [9]University of Augsburg, Germany

Three-dimensional (3D) diamond detectors are intensively investigated at present as radiation detectors and dosimeters due to the appealing intrinsic properties of the diamond material (radiation tolerance, very low leakage currents, tissue-equivalence) combined with the advantages of the 3D architecture (smaller distance between electrodes, low operating voltage bias, well defined active volume). Moreover, recent progress on heteroepitaxial chemical vapor deposition (CVD) of diamond on iridium substrates (DOI) makes interesting a comparison of this new material with the more standard polycrystalline (pCVD) and single-crystal material (scCVD).

We present here the outcome of an investigation on radiation hardness of 3D-sensors fabricated on DOI, scCVD and pCVD plates by laser irradiation.

We have fabricated 3D sensors on three scCVD, four pCVD plates and a DOI sample.

Conductive electrodes of different density per unit surface were grown along the plate thickness (columns) by laser irradiation with an 800 nm Ti:Sa femtosecond laser. The pulse width ranged from 30 to 65 fs. The energy per pulse was of the order of 1 μJ. The columns were electrically connected at each opposite face of the plates by graphitic paths engraved on the diamond surface by irradiation with a ns laser.

A reference planar detector was also fabricated in each sample, with the sole surface structure.

We performed six neutron irradiations up to the fluence level of $10^{16}/\text{cm}^2$ (1-MeV neutron equivalent fluences), at the Jozef Stefan Institute in Ljubljana.

The charge collection efficiencies of the sensors have been simulated and measured before and after irradiation by means of a standard setup with a 1.6 μs shaping time.

Our results demonstrate a major improvement of the radiation tolerance of diamond sensors with the implementation of the 3D concept. Moreover we have assessed that the DOI material is well fitted in the same general framework describing the standard material.

Keywords: diamond sensors, 3D sensors, radiation hardness, charge collection

[O8A.3]

YOUNG SCHOLAR AWARD: Demonstration of V-groove diffraction gratings in single crystal diamond

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EPFL, Switzerland

We report for the first time on the fabrication and characterization of V-groove optical diffraction gratings etched into a single crystal diamond substrate. The gratings are fabricated by means of standard hard mask deposition and lithography techniques, followed by an inductively coupled oxygen plasma with zero platen power. The etch process is selective to the characteristic {111} crystal planes (Fig. 1), resulting in smooth grating surfaces.

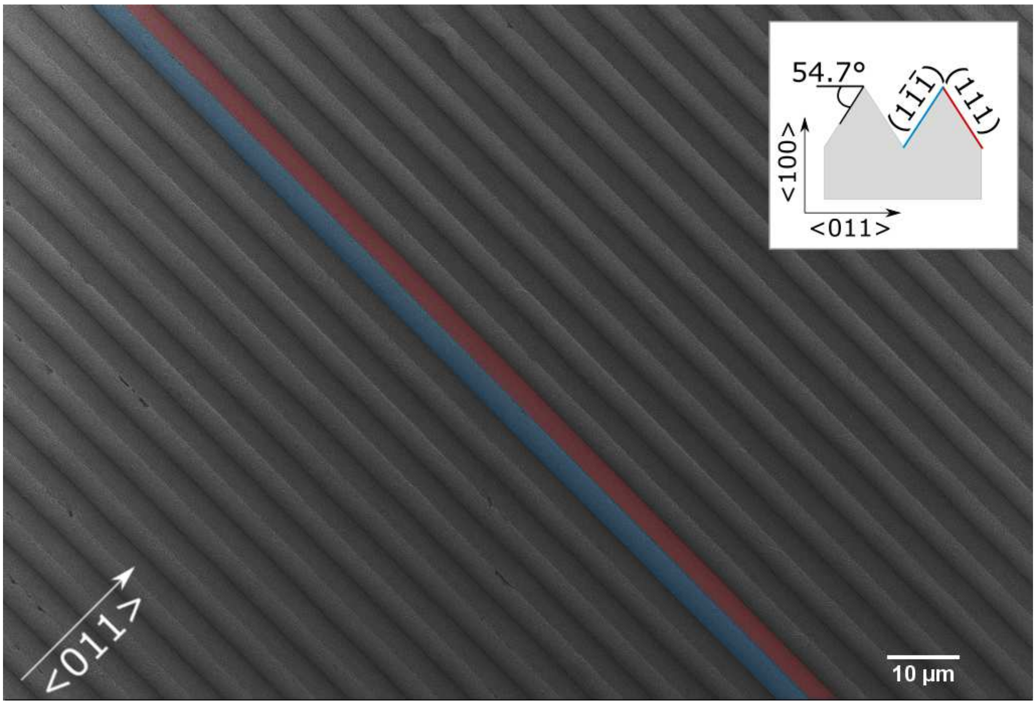

Figure 1 SEM top view of the fabricated grating, revealing the characteristic crystal {111} planes (inset: cross-section showing the orientation of the crystal planes)

We fabricated V shaped gratings with a characteristic angle of 54.7° with respect to the diamond surface and a pitch of 6 µm, 8 µm and 10 µm, corresponding to grating densities of 166.6, 125, and 100 g/mm, respectively, fully covering the surface of a <100> single crystal 2.6mm x 2.6mm x 0.3mm CVD diamond plate (Fig. 2). We characterize the gratings in transmission (Fig. 3) using a broadband measurement setup to evaluate the uniformity of the grooves and the surface roughness.

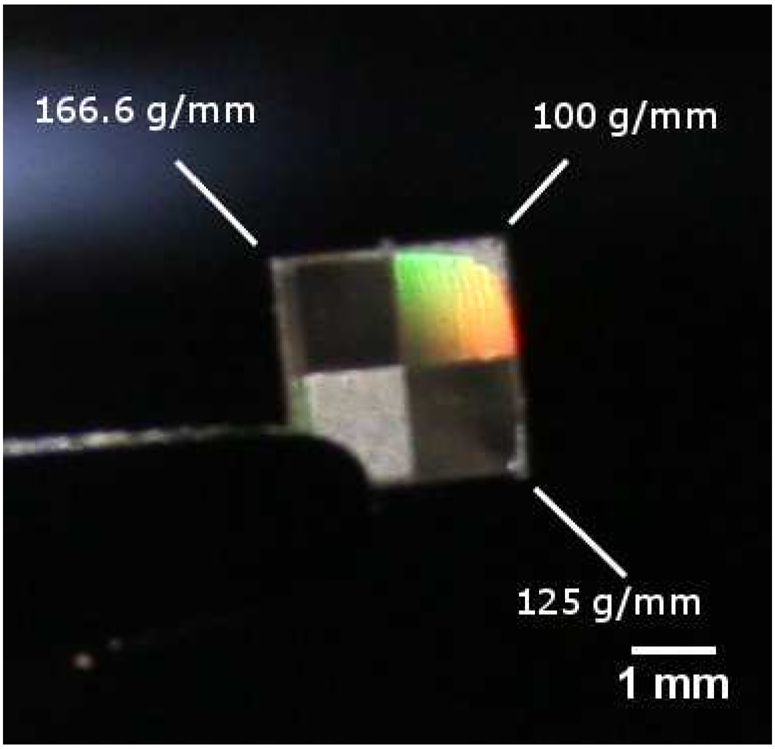

Figure 2 Photograph of a single crystal diamond plate with three grating regions of different density. The incident white light is separated in transmission, causing the color gradient

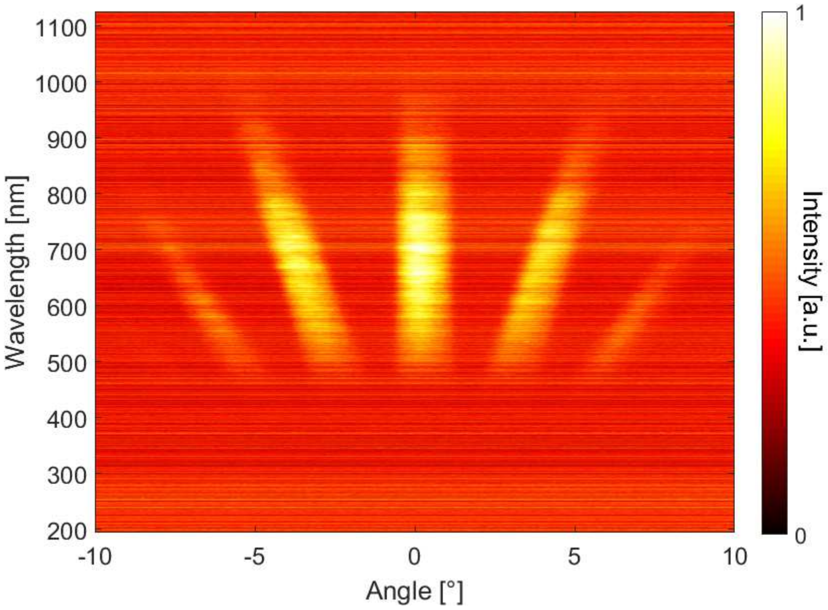

Figure 3 Measured spectral response of the single crystal diamond grating (100 g/mm) in transmission as a function of angle

To our knowledge, this is the first demonstration of V-groove gratings in single crystal diamond. The fabrication process will equally enable reflective and transmission blazed gratings for high power and visible spectroscopy applications.

Keywords: grating, microoptics, microfabrication

[O8A.4]

Fabrication of high quality thin single-crystal CVD diamond membranes with back support SiO2 frame windows

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High quality single crystal (SC) CVD grown diamond membranes with micron range thicknesses are ideal for applications ranging from radiation detectors, photonics, optical components, quantum sensing, and N/MEMS. However, self-supported thin SC CVD membranes are challenging to process, handle and scale-up. Here, we developed high quality, defect free, smooth thin SC CVD membranes bonded to back-support SiO_2 windows over large areas of up to 5 × 5 mm. The method enables fabrication of membranes without deformations such as breakage, bowing or bending. The fabrication process utilizes ion beam implantation in depth of crystal to create buried graphitized layer that can chemically be etched releasing the top thin film with single crystal quality. Since the membrane is very thin a process of wafer bonding is developed to fuse the membrane to back support Si wafer with open windows. The final step of RIE etching removes the remaining damage and as-grown diamond is revealed. The process fabrication allows flexibility in designs and thicknesses for membranes and easy to handle making them adoptable to manufacturing of optical, electrical and mechanical devices. We demonstrate arrays of single crystal diamond membrane windows, each up to 1 × 1 mm in dimension and as thin as □500 nm, supported by a diamond frame as thick as □300 µm. The membranes were characterized using birefringence, Raman, Infrared (IR), photoluminescence spectroscopies. The fabrication method is robust, reproducible, scalable and cost effective. Figure 1 shows the schematic diagram of etching setup and the membrane structural design for easy handling[1]. The membrane windows were investigated at each processing stage with Raman spectroscopy using 532 nm laser to measure the diamond quality during fabrication. Raman peak at 1333 cm^{-1} observed from membrane shows similar characteristic of as-received SCCVD substrate.

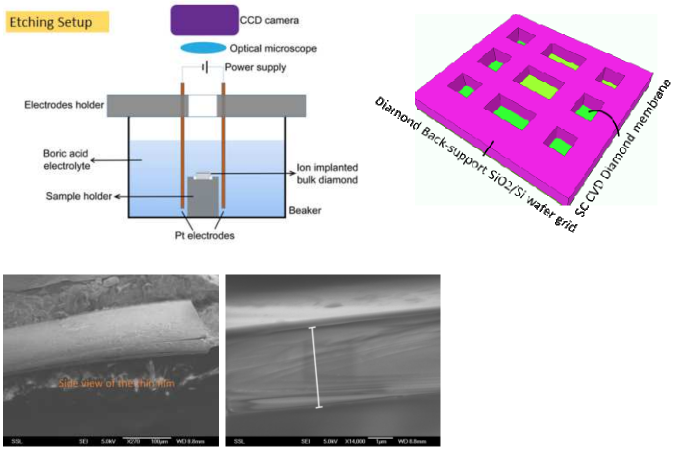

Figure 1. Schematic diagram of a) etching set up b) membrane design c) SEM of side view of membrane thin films

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Keywords: Single crystal CVD diamond, membrane, thin film, detector

[O8A.5]

Diamond etching mechanism by solid-solution reaction of carbon into nickel

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Diamond is very promising as semiconductor for next-generation high-power and high-frequency applications due to its excellent properties such as high breakdown electric field, high mobility, and high thermal conductivity. Recently, we reported about an inversion channel diamond MOSFET with normally off characteristics [1]. For this device, the development of novel etching techniques is of highest importance as we need damage-free diamond surfaces, which are atomically smooth and alight to crystallographic orientations. This aims towards the realization of vertical trench diamond MOSFET structures which will show higher blocking voltages and lower specific on-resistances. In our previous reports, we reported anisotropic diamond etching using Ni catalytic etching in Ar or H_2 gas atmospheres [2, 3]. In this study, we try to elucidate the Ni-based etching mechanism and optimize this mechanism for device fabrication.

In this presentation, we report about Ni catalytic etching, using diamond substrates with atomically flat surfaces which were selectively etched by applying the solid-solution reaction of $C_{diamond}$ atoms into a Ni film as shown in Fig. 1. We use high-pressure and high-temperature(HTHP) synthetic Ib-type single-crystal diamond (100) substrates. The Ni films were deposited by a vacuum evaporation method with a thickness of approximately 400 nm. The diamond samples were annealed at 900 °C for 15 min under Ar gas atmosphere with 99.99995 % purity. We observe anisotropic etching of the diamond surface during the annealing in Ar gas atmosphere. The results suggest that the etching process progresses as follows: 1) The diamond surface around defects is preferentially etched, 2) the surface is preferentially etched toward the directions parallel to the surface, 3) smooth diamond (100) surface without defects is achieved. The results of the etching under an atmosphere containing H_2 gas will be presented for comparison.

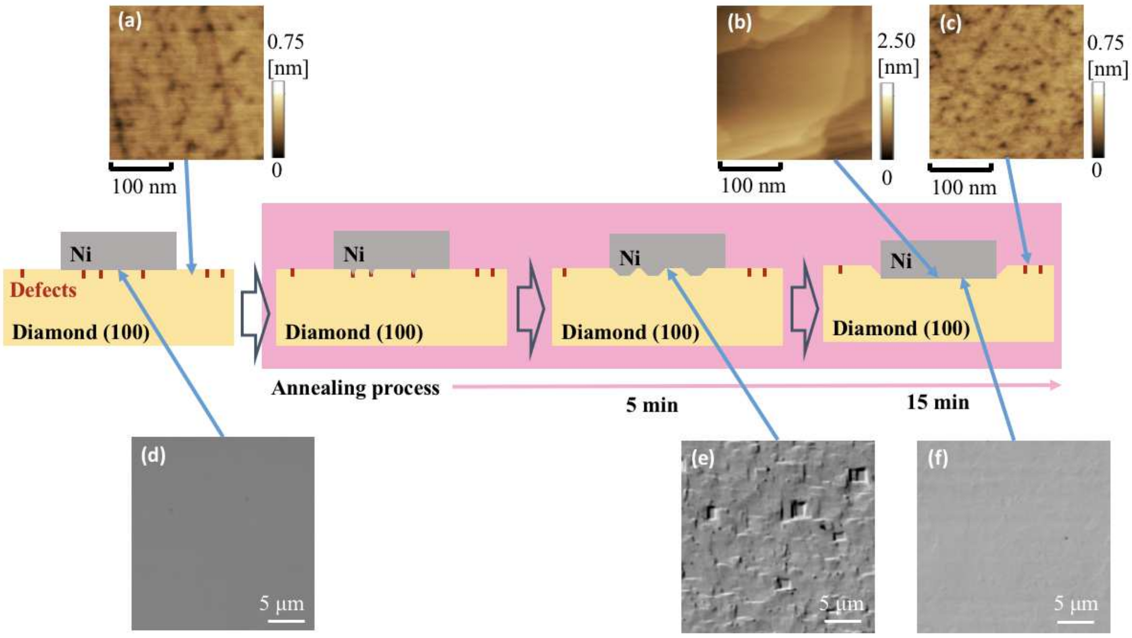

Fig.1. Process of diamond by solid-solution reaction of C into Ni.

AFM images of the diamond (100) surface (a) before and (b) after annealing for 5 min and (c) 15 min.

LM-DIC images of the diamond (100) surface (d) before and (e) after annealing for 5 min and (f) 15 min.

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Keywords: diamond, etching, Ni

[O8B.1]

Analysis of microstructure and surface morphology of a-C:H films deposited on a trench target

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Recently, the bipolar-type plasma-based ion implantation and deposition (bipolar PBII&D) method has attracted large attention owing to its non-line-of-sight coating technique. In particular, bipolar PBII&D is beneficial in coating a hydrogenated amorphous carbon (a-C:H) film on a three-dimensional target. In response to these advantages, we previously prepared a-C:H films onto a complex-shaped three-dimensional target called “macrotrench” (pitch: 20 mm, aspect ratio: 1.0) by using bipolar PBII&D, and the film properties were evaluated. With regard to the mechanical properties, the film thickness and hardness were evaluated using a scanning electron microscope (SEM) and nanoindentation measurements, respectively, and with regard to the structural properties, the microstructure of the films was evaluated by Raman spectroscopy. Subsequently, these mechanical and structural properties were compared with each other to reveal the coating mechanism. As a results, we found that mechanical and structural properties of a-C:H films on the sidewall surface were quite different as compared to that of coated on the plain, top or bottom surface, e.g. hardness and adhesive force became much smaller, and more, stripes were diagonally formed in the cross section of the film as shown like the below figure. According to the plasma simulation, these film deteriorations were mainly due to the ununiform incident behavior of plasma particle on each surface, but it still hasn't reached a basic resolution. In this study, to investigate causes of deterioration more, we measured the microstructure and surface morphology of the a-C:H films on the sidewall surface by using the SEM, AFM, FTIR, XPS, TOF-SIMS and so on. These experimental results will lead to reveal the coating mechanism and to find the optimum coating conditions for improve the film properties.

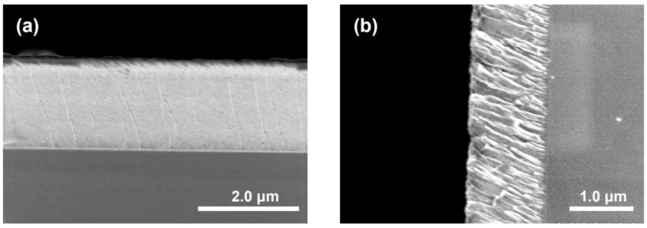

Figure Cross sectional SEM image of a-C:H films coated (a) on the plain and (b) on the sidewall surfaces

Keywords: Hydrogenated amorphous carbon film, bipolar PBII&D, macrotrench, surface morphology

[O8B.2]

High-speed preparation of DLC films using high-repetition nano-second pulsed glow discharge plasmas under sub-atmospheric pressure

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Diamond-like carbon (DLC) films have a lot of superior characteristics such as high wear resistance, high hardness, low friction coefficient, high electrical resistance, optical transparency, and chemical inertness. In general, DLC films have been prepared by physical vapor deposition (PVD) and chemical vapor deposition (CVD) under low gas pressure, typically below 10 Pa. However, the conventional plasma-assisted CVD process resulted in a low deposition rate of DLC film due to use of a low density plasma.

The present study demonstrated a new plasma process under sub-atmospheric pressure to obtain a DLC film with a high-deposition rate. In particular, the present technique employs a recently developed novel technology of an SiC-MOSFET inverter power supply for the plasma generation which enables to produce bipolar and unipolar nano-second voltage pulses with a high-repetition frequency (adjustable up to 300 kHz). Then, a high-repetition nanosecond pulsed glow discharge plasma was achieved with a pair of parallel electrodes under sub-atmospheric pressure. In this study, a mixed gas of helium and methane with the gas pressure of 1 kPa was used as a process gas for the DLC preparation. Silicon wafers were used as substrates.

The results showed that the deposition rate was 0.1 □m/min that was five times larger than that in conventional plasma CVD processes. It was also found that the hardness of the DLC film was strongly affected by the repetition frequency of the pulsed voltage. As a result, the DLC film with the hardness of 13 GPa was successfully prepared with the repetition frequency of 200 kHz. Raman spectroscopy indicated the hydrogen content in the DLC film decreased with increasing the repetition frequency. With the high-repetition frequency operation, the increase in the ion flux to the substrate could enhance hydrogen release from the DLC film, leading to the increase in the film hardness.

Keywords: Diamond-like carbon, Sub-atmospheric pressure plasma CVD process, High-speed preparation of DLC film, Hydrogen content in DLC film

[O8B.3]

Towards realistic lifetime estimation of carbon coated articulatingimplants

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Empa, Switzerland

In vitro lifetime estimations of carbon coated articulated implants may not accurately represent their in vivo performance within the human body, leading to premature replacement surgeries. The aim of our studies is to develop an experimental methodology to better predict the lifetime of implants by mimicking the performance in the human body. The strategy deals with the study and characterization of time dependent corrosion and fatigue processes at the interface, accelerated by reciprocating sliding tests performed in simulated body working conditions. Considering that carbon coating wear overcomes the requested lifetime, this research focuses on the study of the few atomic rows of reactively formed material between the adhesion promoting interlayer and the substrate, which play a crucial role in corrosion-enhanced delayed delamination processes [1].

We tested several controlled oxygen contaminant concentrations in the Silicon containing hydrogenated amorphous carbon adhesion promoting interlayer, Si-a-C:H. The interlayer and the 4 µm a-C:H coating were deposited from Tetramethylsilane (TMS), and acetylene (C_2H_2), respectively, by Radio Frequency Plasma Assisted Chemical Vapor Deposition (RF-PACVD). The interlayer was characterized by X-Ray Photon Spectroscopy as well as by a novel technique developed to expand the few nanometers thicknesses to a few microns by low angle cross-section polishing, which enables both the compositional (by Auger Spectroscopy) and electrochemical characterization of the interlayer (by microcapillary technique).

The results show a correlation between small amounts of contaminants at the interface and increased delamination after the tribological test performed in corrosive media, which are connected with the electrochemical behaviour of the interlayer.

These fatigue and corrosion stability studies significantly contribute to arrive at advanced experimental procedure for reliable life-time estimation of carbon coated implants.

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Keywords: DLC coated implants, Interfaces, Crevice & Fatigue corrosion

[O8B.4]

Friction force microscopy of micro and nano-patterned diamond-like nanocomposite films

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We report the effects of surface micro/nanostructuring on nanofriction properties of diamond-like nanocomposite (DLN) films investigated with lateral force microscopy (LFM) technique. For the surface modifications of DLN (a-C:H,Si:O) films on the micro and nanoscale, the techniques of laser micropatterning and scanning probe microscopy (SPM)-based nanolithography are applied. DLN films of various thickness (from 100 nm to 3 μm), doped with metals (W, Ti) are studied. Laser microstructuring of 3-μm-thick metal-doped DLN films was performed with ultrashort pulses to produce various patterns under conditions of surface graphitization, spallation and developing ablation. The LFM studies evidenced that nanofriction properties of laser-irradiated regions depended on the irradiation conditions, metal doping, and modified film structure, showing both the decrease and increase in the friction forces within the produced micropatterns. In addition, attention was paid to the effect of relative humidity on the nanofriction behavior revealed in our recent study of the DLN films [1]. The SPM nanopatterning was performed on the surface of ultrathin DLN films (of ~100 nm thick), with LFM examination of the produced nanopatterns being applied directly after the nanolithographic process. It was found that the film structure, relative humidity, and magnitude of the applied voltage pulses were the main factors to influence the appearance and growth of unique dendrite-like nanostructures, characterized mostly by higher nanoscale friction compared to the original film. The obtained data are discussed in comparison with the LFM data recently reported for SPM-nanopatterned ta-C films [2].

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Keywords: DLC, laser micropatterning, scanning probe nanolithography, friction force microscopy

Keywords: DLC, laser micropatterning, scanning probe nanolithography, friction force microscopy

[O8B.5]

From mechanical properties to evaluation of biological effect - comparison of doped diamond-like carbon coatings synthesized by multitarget DC-RF magnetron sputtering on metallic substrates

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Diamond like carbon (DLC) coatings are one of the possible answers to the need of global market of metallic implants to secure mechanical properties and positively affect the biological response of the human's organism [1]. Nevertheless the requirements set against films are different depending on the designated specificity of applications. Promisingly, further adjustment of properties of DLC is possible via its doping with various elements.

From the comparison of different methods of deposition of DLC coatings for biomedical applications, the best results were obtained for films synthesized by means of magnetron sputtering [2]. Taking it into account, pure DLC coatings and their derivatives incorporated with e.g. Si, Ti and Cu in amounts that do not exceed 25 at.% were synthesized by means of multi-target DC-RF magnetron sputtering.

Regardless of the coatings' composition, the improvement of hardness in comparison to pure

substrate materials (AISI 316 LVM and Ti6Al7Nb) was observed for all the investigated films. By varying the type of dopant and synthesis parameters it was possible to improve the hardness of coatings to over 15 GPa for Si-DLC, and more than 3 times the adhesion of Ti-DLC.

The corrosion resistance of the films was evaluated with salt spray technique. The biological investigation involved short and long term microbiological test with use of *E. coli* strains and viability/cytotoxicity examination on osteosarcoma (Saos-2) and endothelial (EA.hy 926) mammalian cells.

This research has been supported under the grant no. LIDER/040/707/L-4/12/NCBR/2013 entitled „MOBIOMED: Modified BIOmaterials – MEDicine future".

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Keywords: Doping, Biomaterials, Magnetron Sputtering, Biological evaluation

[O8B.6]

Synthesis of amorphous diamond under high pressure and temperature

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Diamond has many unparalleled properties due to its extremely strong sp^3 C-C bonding. The search for the same sp^3-bonded tetrahedral amorphous carbon which would have properties complementary to diamond has been a long-sought after yet elusive goal.

By combining high pressure with *in situ* laser heating at a specific temperature window, we successfully synthesized a completely sp^3-bonded tetrahedral amorphous carbon, i.e., “amorphous diamond”, for the first time. Moreover, this amorphous diamond obtained under high pressure can be recovered to ambient conditions. We preformed comprehensive studies including x-ray diffraction, high-resolution transmission electron microscopy, electron energy-loss spectroscopy experiments and *ab initio* molecular dynamics simulations on the amorphous diamond. The results suggest the amorphous diamond has a three dimensional sp^3-bonded network structure similar to crystalline diamond, except no long-range order. In our *in situ* high pressure x-ray diffraction experiment, this amorphous diamond showed ultrahigh incompressibility (bulk modulus) comparable to diamond.

The three important Group-14 elements C, Si and Ge all have sp^3-bonded crystalline phases with the same diamond-cubic structure. Si and Ge also have well-known sp^3-bonded tetrahedral amorphous forms which have widespread applications. However, the counterpart in C, an amorphous form of diamond, was conspicuously missing and remained a puzzle, until now. Our high pressure study finds this missing member of the carbon allotrope family, and demonstrates that it can be maintained at ambient conditions. These results enhance our fundamental understanding of carbon materials and will trigger follow-up studies on the mechanical, thermal, optical, electrical, and chemical properties of amorphous diamond for potential applications.

Keywords: high pressure, tetrahedral amorphous carbon, sp3 bonding, bulk modulus

[O9A.1]

Diamond on GaN: Extraction of 2DEG and thermal properties of HEMT layers after diamond growth

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Power devices based on monolithic diamond devices or having hybrid power devices integrating diamond with other wide bandgap materials is the ultimate goal for achieving high reliability under high frequency high power operation while keeping the devices cool (minimizing thermal hotspots and withstanding large break down electric fields). Devices with diamond layers can be made reliable to perform under high temperature, high pressure and high radiation exposed environments.

In this specific study, we consider the case of diamond grown on GaN based high electron mobility transistor heterostructures (HEMT) layers. Little attention has been paid to understand the effect of diamond grown directly on passivated HEMT structures and their interfacial electronic and thermal properties. In this study, we examine using cross-sectional TEM, approaches to extract the built in electronic carrier concentration arising due to the intrinsic polarization between AlGaN/GaN layers.

Diamond layers were grown up to a thickness of 2µm and cross-sectional TEM and EELS mapping of the sample specimens are employed to extract possible changes in composition in the underlying SiN/AlGaN/GaN interfacial layers. For extracting the 2DEG properties, three different possible approaches are evaluated to determine the electron concentration of HEMT layers before and after diamond growth. For comparison, an effort is made to pattern Hall contacts prior and post diamond growth and the direct electrical characterization of the layers is made. In addition, evaluation of effective thermal conductivity of diamond layer and the interfacial thermal boundary(TBR) resistance of Diamond on GaN is extracted using the time-domain thermo-reflectance technique. We find that the effective maximum thermal conductivity (k) reaches a maximum of 200 W/mK for films of 1-2 µm thickness. Diamond layers grown at high temperature(650°C) show a TBRDiamond/GaN ranging from 50-90 m2 K/GW while low temperature growth (350-400°C) results in a TBR drop to 10-20 m2 K/GW range.

Keywords: AlGaN/GaN, Strain, 2DEG, Thermal conductivity

[O9A.2]

Diamond growth on GaN for thermal management in high power devices

S. Mandal*[1], E. Thomas[1], C. Middleton[2], L. Gines[1], D. Wallis[3], S. Novikov[4], S. Lynch[1], M. Kuball[2], O. Williams[1]

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With the high breakdown voltage and current handling ability of GaN, AlGaN/GaN on SiC HEMT structures are the current benchmark for high-power, high-frequency applications[1]. However, in such devices the GaN epilayer and particularly the SiC substrate, with thermal conductivity of around 400 W/mK, limit the heat extraction leading to de-rating of the maximum power dissipation[2]. Through replacement of the substrate and capping of the transistor channel with diamond of thermal conductivity of up to 2000 W/mK, large decreases in the thermal resistance should therefore be achievable[3].

The growth of pinhole free, thin film diamond on non-diamond substrates requires the use of a nucleation enhancement step. One of the most commonly used techniques involves seeding the substrate with nanodiamond particles, resulting in high nucleation densities of the order of 10^{11} cm^{-2}[4]. As attachment of the particle to the substrate is dependent on both the zeta potential of the surface and the particles, it is essential to measure the zeta potential of the surface and tailor the surface groups of the seeds to reach such nucleation densities. In the present study, we have measured the surface zeta potential of the GaN surface. Using such knowledge, diamond films have been successfully grown atop GaN on sapphire wafers, without the addition of a thermally resistant intermediate dielectric layer to aid growth as used within previous studies[1]. Raman and SEM characterization of the resulting samples revealed continuous films over the 15 by 15 mm samples with uniform lateral grain size of 100—150 nm.

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Keywords: Diamond, Chemical Vapour deposition, GaN, Thermal properties

[O9A.3]

Large scale coated and patterned diamond layers by coating and printing of diamond seeds for „heater” applications

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[1]Institute for Materials Research (IMO), Belgium, [2]IMOMEC, Belgium, [3]Flanders Make vzw, Belgium

Patterning of diamond films often requires laborious after growth processing techniques, such as reactive ion etching, to reach the desired features. Straightforward pre-growth patterning techniques via selective seeding methods are therefore highly valuable as they reduce processing time tremendously. Moreover, with increasing reactor sizes novel deposition methods for large area substrates gain more and more attention.

This work shows the possibilities of large-scale deposition techniques such as ultrasonic spray coating and Drop-on-Demand (DoD) inkjet printing for nanodiamond particle seeding, enabling coating and patterning techniques for diamond films on various substrates. Specifically we focus on the deposition of a suspension of nanoseeds on various large area substrates and selective deposition of nanoseeds via drop-on-demand inkjet printing.

With ultrasonic spray coating and subsequent low temperature growth in a linear antenna microwave CVD system we were able to grow closed diamond films on flat and curved substrates, thereby displaying a scalable, novel, fast and easy seeding method for large area substrates.

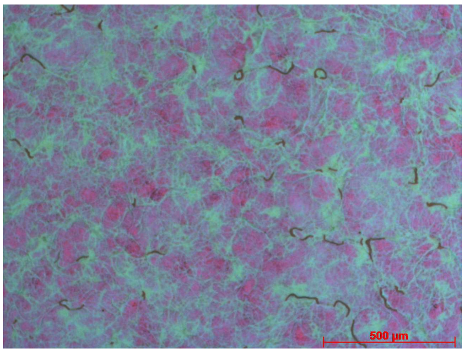

Figure 1 - Ultrasonic spraycoated microscopy slide after growth in a linear antenna microwave CVD system

In a second set of experiments, we started patterning diamond films from a bottom up method using DoD inkjet printing. By tuning the substrate surface properties we were able to reach feature sizes down to 60 micrometer, while removing any coffee ring effect usually attributed to nanoparticle-based inks.

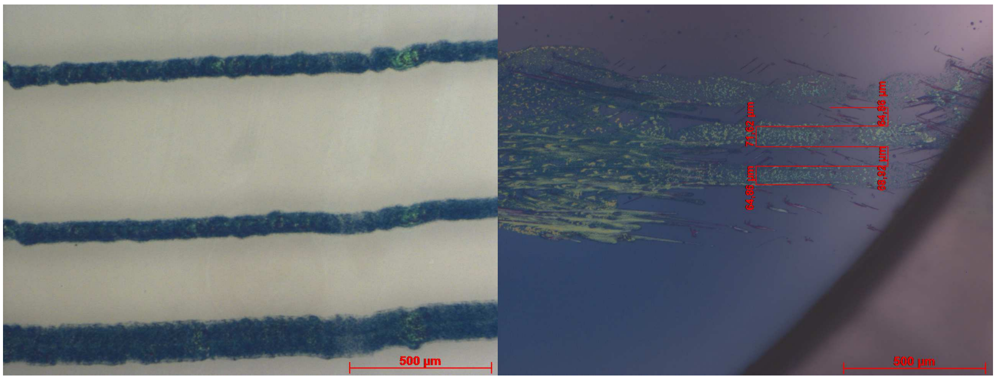

Figure 2 - Optical microscopy images of drop on demand printing of nanoseeds and growth in a linear antenna microwave CVD system (A) and an ASTeX resonant cavity system (B)

By applying the pattern via DoD inkjet printing and a subsequent growth step fully closed diamond features were achieved. A next step will consist out of the production of diamond heaters without any subtractive or lithographic steps. Therefore we can conclude that this work not only shows the possibility of coating full layers on large and curved substrates but that also patterning of diamond structures can be achieved and applied for heater (and other diamond based) applications.

Acknowledgements: PP is a Postdoctoral Fellow of the Research Foundation – Flanders (FWO).

Keywords: Drop-on-Demand ink jet printing, Ultrasonic spray coating, pre-growth patterning, single digit nanodiamond

[O9A.4]

Diamond heteroepitaxy on Ir/SrTiO3/Si (001) substrates: From nucleation to thick films characterizations

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The up-scaling of heteroepitaxial diamond remains one challenge for the technological development of power electronics. One option is to consider heterosubstrates compatible with silicon based technologies, such as Ir / YSZ / Si multilayers [1]. We have developed diamond heteroepitaxy on iridium buffer layers grown on SrTiO$_3$ / Si (001) substrates [2]. The SrTiO$_3$ has a low lattice mismatch with Ir (1.7 %) whereas the silicon substrate ensures a closer thermal expansion mismatch with diamond.

The present study provides an extended characterization of each step of the heteroepitaxial process applied to SrTiO$_3$ / Si (001) substrates: from the iridium deposition, to the bias enhanced nucleation (BEN) and the growth of heteroepitaxial diamond films (200 nm up to 240 μm thick).

High quality iridium buffer layers were grown on SrTiO$_3$ / Si (001) substrates with mosaicities of 0.3° (polar) and 0.1° (azimuthal) as measured by XRD. After the BEN step, the surface and the interfaces of Ir / SrTiO$_3$ / Si (001) multilayer were investigated by SEM and HRTEM in cross-section. The morphology and the crystalline quality of a 200 nm thick heteroepitaxial diamond film were characterized using SEM and UV Raman. Moreover, a cross-section of this film was investigated by High Resolution TEM.

Thicker diamond films were grown under dense MPCVD plasma with growth conditions close to homoepitaxy [3]. Structural and chemical characterizations of diamond heteroepitaxial films grown on Ir / SrTiO$_3$ / Si (001) were performed by XRD, Raman and Cathodoluminescence.

The obtained results demonstrate the potential of Ir / SrTiO$_3$ / Si (001) substrates to achieve heteroepitaxial diamond films with characteristics at the state-of-the-art. The up-scaling has already proved successful allowing the size of the substrates produced to be increased from 5x5 to 7x7 mm^2.

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Keywords: heteroepitaxy, interfaces, BEN, chemical and structural characterizations

[O9B.1]

Plasmonic diamond films: synthesis, electron emission, and photocatalytic activity

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Since diamond is an indirect-bandgap material, even above-bandgap light is absorbed only weakly. For some applications such as photocathodes and/or photocatalytic applications, stronger absorption is desired. The integration of plasmonic nanoparticles with diamond films provides one way to enhance diamond's optical properties, both by providing new optical resonances that can provide new pathways to electronic excitation, and by providing non-lossy scattering centers within the film to increase absorption in the near-surface region. Here, we describe the formation of plasmonic diamond films and the influence on diamond's optical, photoemissive and photocatalytic properties.

Diamond films with embedded <50 nm diameter nanoparticles exhibit strong optical plasmonic features. Fig. 1 shows two examples such films, consisting of plasmonic diamonds film grown on a silicon substrate, and photographed using ambient lighting. Measurements of the optical reflection properties of these films using an integrating sphere show strong optical resonances characteristic of plasmonic films, as evidenced by the optical absorption spectrum in Fig. 1. Changes in processing conditions can be used to alter the optical response. We demonstrate that the plasmonic films provide enhanced photocatalytic properties both using sub-bandgap and above-bandgap light.

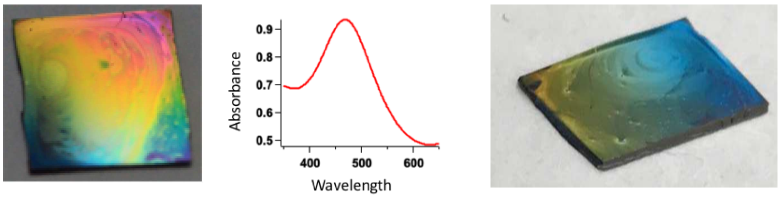

Fig. 1: Plasmonic diamond films. The center panel shows a representative optical absorption spectrum measured in reflection mode using an integrating sphere, exhibiting a clear mid-visible resonance. Samples at left and right were photographed using ambient white light illumination.

The integration of diamond with plasmonics provides a way to provide controlled optical response. While demonstrated here for photocatalytic and photoemissive properties, this work could be extended to diamond optical filters and the formation of colored diamond films for a wide range of applications.

Keywords: plasmonic, photocatalytic, photoresponse, absorption

[O9B.2]

Multiwalled carbon nanotubes as full catalyst for oxidative dehydrogenation reaction of ethylbenzene

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The dehydrogenation of ethylbenzene to styrene is one of the ten largest production processes in the petrol chemistry. More than 25 million tons are produced every year. The strong endothermic process is carried out on an iron catalyst. It has been found that carbon deposits are deactivation agents for this reaction. With addition of oxygen, the deposit appears as active material for the oxidative dehydrogenation of ethylbenzene to styrene. Compared to the dehydrogenation, this oxidative reaction is exothermic. Furthermore, it can be carried out at lower temperatures and a complete conversion is theoretically reachable.

To investigate the performance of carbon materials as catalysts for this reaction, we choose multiwalled carbon nanotubes (MWCNTs). They have a high thermal stability and surface area. To improve their activity, we followed two different pathways.

For the oxidative dehydrogenation, the quinones are known as active centres. Thus, we oxidized the CNTs with different oxidizing agents to achieve different ratios and amounts of the oxygen containing groups. We have found that a treatment with ozone in air generates the most quinones.

Furthermore, we treated the CNTs with KOH at high temperatures. This results in an increase of the surface area up to 500%. Thereby carbon atoms and fragments were etched from the tube structure. The KOH treatment had a very high impact on the thermal stability and on the ratio of different oxygen containing groups.

Studies on the catalytic properties showed that the samples with the highest amount of the oxygen containing groups showed the best performance at high and low temperatures. During the reaction, a significant transformation of the type of oxygen groups takes place. Especially the KOH treated CNTs showed a deactivation due to the decomposition of quinones and generation of more acid groups.

Keywords: Catalysis, Oxidation, Activation, Modification

[O9B.3]

Graphene-based TiO2 nanocomposites for enhanced degradation of organic dye in the visible light

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Graphene oxide–TiO_2 (GO–TiO_2) composites prepared by a simple solution mixing method are evaluated for methylene blue (MB) photodegradation under visible light irradiation. Screening test using four commercial TiO_2 materials showed that particle size and pore structure of TiO_2 material played an important role in the photocatalytic performance of commercial TiO_2 for degradation of MB dye. Such factors define the accessible active surface area for photocatalytic reaction. Two commercial TiO_2, Kronoclean 7000 and Aeroxide P25, were then selected for synthesis of a series of GO-TiO_2 composites, which showed greatly improved MB photodegradation performance in comparison with pristine TiO_2 materials. The performance improvement can be explained by two aspects. Firstly, GO can serve as photosensitizer through to the strong Ti-O-C bonds formed between TiO_2 and GO as confirmed from the obvious redshift of the absorption edge to higher wavelength region along with strong absorption in the visible light range in the FTIR spectra. Secondly, GO addition can significantly increase the dye adsorption capability which can not only be attributed to the increased specific surface area of the composites, but also the non-covalent interactions between graphene layer and methylene blue dye. The synergies between the improved photodegradation activity and the enhanced dye adsorption capability simultaneously lead to the excellent photocatalytic performance for GO-TiO_2 nanocomposite materials. This finding is of considerable importance as it suggests that even the simple synthesis process still provide remarkable improvement in the photocatalytic activity. This simple chemical process can be easily scaled up and hence promotes the potential of GO-TiO_2 composites towards wider practical applications.

Keywords: Environment, Graphene oxide, Titanium dioxide, Visible-light activated photocatalyst

[O9B.4]

Enhanced photoelectrochemical water splitting with tailored TiO2/SrTiO3@g-C3N4 heterostructure nanorod in glycerol-based photo fuel cell

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Solar hydrogen production through water photosplitting by photo fuel cell (PFC) is one of the most desirable, cost-effective and environmentally friendly processes but still suffering from a low efficiency. Graphitic carbon nitride (g-C_3N_4) coated on a novel tailored TiO_2/$SrTiO_3$ heterostructure nanorod to investigate photocatalytic hydrogen production under visible light conditions in a photo fuel cell (PFC) in the presence of glycerol. A series of TiO_2, $SrTiO_3$, TiO_2/$SrTiO_3$ nanorod arrays were grown onto a FTO substrate by a hydrothermal method. Then g-C_3N_4 was coated on all prepared nanorod arrays by immersing the prepared nanorod arrays into a solution of urea and then calcined at 550°C.

In this procedure, the amount of g-C_3N_4 on the nanorod arrays can be controlled by tuning the concentration of the urea solution. These materials were fully characterized with different characterization techniques, including x-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), x-ray photoelectron spectroscopy (XPS), diffuse reflectance UV-Vis spectroscopy (DR-UV-Vis), Electrochemical impedance spectra (EIS), Mott-Schottky (M-S), and photocurrent densities versus measured potential (I−V) to explore physicochemical and photoelectrochemical properties of prepared photocatalysts.

The prepared TiO_2/$SrTiO_3$@g-C_3N_4 served as an efficient and stable photoanode for PEC water splitting compared to others. The Mot-Schottky analysis revealed that the presence of $SrTiO_3$ strongly control the photocatalytic hydrogen production and shifted the flat band potential to more negative potentials which is desirable for hydrogen production. Furthermore, DR-UV-Vis analysis demonstrated that the absorbance of prepared photocatalyst extended to the visible region. Photocurrent density in TiO_2/$SrTiO_3$@g-C_3N_4 reached up 2.5 mA/cm^2 under 500 W halogen lamp with intensity of 100 mW/Cm^2. These results approved that the presence of g-C_3N_4 decreased the charge transfer resistance and charge carrier recombination rate in the surface of photocatalysts. This study indicates the co-existence of $SrTiO_3$ and g-C_3N_4 in TiO_2 structure can enhance environmentally friendly photocatalytic hydrogen production.

Keywords: Heterostructure, Graphitic carbon nitride, TiO2/SrTiO3, Photo fuel cell