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Beneficiary: Dr Aleksandar Milosavljevic, Institute of Physics Belgrade
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SCIENTIFIC REPORT

PURPOSE OF VISIT

The purpose of visit was the exchange of experiences and joint work related to the low-energy electron induced coupling of organic molecules (amine, alcohol) with inorganic material to form hybrid bioinorganic patterns. More precisely, the objective was to further investigate the involved mechanisms to improve the control of the electron induced surface chemistry and thereby the control of the tailored surface properties, which is of particular interest in the frame of the ECCL project. The investigation is also potentially important in several areas of technological interest, including biosensors, biomedical implants, and organic/biomolecular electronics.

DESCRIPTION OF THE WORK CARRIED OUT DURING THE VISIT

A method was developed in Orsay to functionalize semi-conductor substrates by low-energy electron irradiation of condensed molecular films and was successfully applied to the anchoring of CH_2CN chains on diamond [Lafosse et al. *Eur. Phys. J. D* **35** (2005)]. It consists in condensing a layer of organic molecules of interest at low temperature (< 30 K) on the passivated substrate, which will be irradiated by low-energy electrons (0.5-25 eV). One of the possible processes induced by this electron irradiation is a strong chemical modification of the substrate surface itself by chemisorption of key chemical functions onto the surface (functionalization). Therefore, it is of particular importance, as a first step, to perform a detailed investigation of the passivated substrate itself.

In the last decade, hydrogenated/deuterated diamond substrates have raised growing interest due to their remarkable electrical, chemical, thermal and mechanical properties and to their biocompatibility. Functionalization by small organic groups may serve as a route toward further complex chemical modifications of diamond substrates, such as immobilizilization of proteins or DNA molecules. The work during the visit has been focused on a detailed investigation, using temperature controlled desorption and High Resolution Electron Energy Loss Spectroscopy (HREELS), of a deuterated polycrystalline diamond substrate. The fully deuterated substrate was grown ex-situ on a *p*-type doped silicon substrate by a standard microwave chemical vapor deposition (mw-CVD) method using a CD_4 / D_2 gas mixture [A. Hoffman et al. *Phys. Rev. B* **63** 045401 (2001)]. The chemical (inertness) and electronic properties of the prepared substrate do strongly depend on the obtained deuterium coverage, associated with surface groups sp^m-CD_x (m = 1,2 and x = 1,3). The substrates were transferred in air to be implemented in our experimental setup. Before performing measurements they were annealed in the UHV to desorb all species possibly physisorbed on its surface like water or hydrocarbons. The obtained results extend the previous investigation of hydrogenated polycrystalline diamond films prepared using CH_4/H_2 gas mixture [Lafosse et al., *Phys. Rev. B* **73**, 195308 (2006)] to deuterated polycrystalline diamond.

The experiments were performed in the Orsay Laboratory (LCAM), on an ultra-high vacuum setup combining three complementary techniques: Electron Stimulated Desorption (ESD) of negative ions, Temperature Programmed Desorption (TPD) and HREELS. The HREEL spectrometer consists of a double monochromator and a single analyzer (model IB500 by OMICRON). It has been specially designed to record quasi-continually energy loss spectra as well as quasi-elastic (elastic reflectivity) and inelastic (vibrational) excitation functions in the energy range 2–30 eV. The measurements were performed at room temperature, in the specular geometry ($\theta = 55°$). The overall energy resolution was approximately 7 meV, measured as the full width at half maximum (FWHM) of the elastic peak.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

The measurement procedure consisted of repeated cycles of heating of the deuterated diamond substrate and electron scattering experiments, increasing the annealing maximum temperature step by step from about 200°C to 800°C. The modifications of the substrate surface composition and of the substrate electronic density-of-states (DOS) were followed by recording, complete sets of energy loss spectra up to 500 meV at different incident electron energies, elastic reflectivity functions and excitation functions at a number of fixed energy losses. This comprehensive data set allows us to investigate vibrational spectrum of deuterated diamond, dependence of the elastic reflectivity and vibrational losses on the incident electron energy and, finally, a temperature dependence of these processes.

An example of the obtained elastic reflectivity function for the deuterated polycrystalline diamond, after annealing to about 425°C is presented in figure 1. Similarly as for the hydrogenated diamond, it shows a marked structure around 8 eV, a small shoulder at about 10 eV and an intense peak at about 13 eV. The latter feature demonstrates that the substrate possesses a pronounced diamond-like character [Lafosse et al. *Surf. Sci.* **587** 134 (2005)] and is related to the second absolute band gap of bulk diamond.

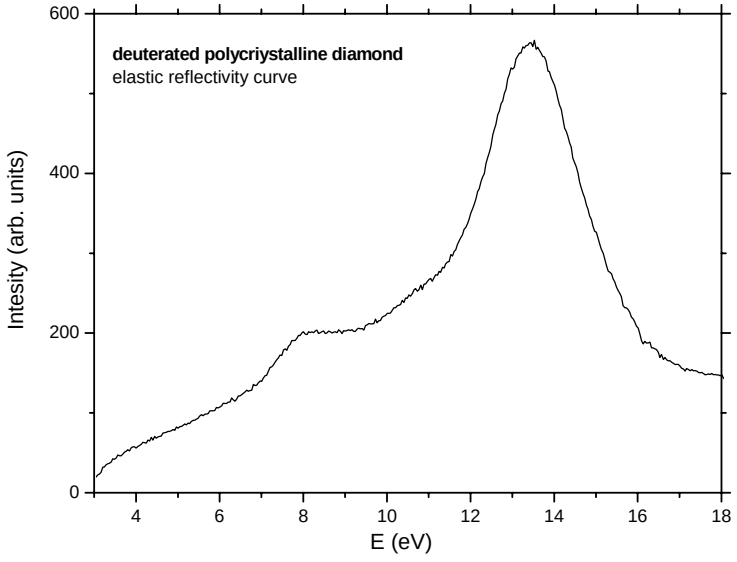

Figure 1. Specular electron elastic reflectivity curve for the deuterated polycrystalline diamond recorded over the incident energy range 3–18 eV with a step of 40 meV.

An example of the obtained vibrational excitation function for deuterated polycrystalline diamond film, for the energy loss of 272 meV corresponding to excitation of stretching C—D modes, is presented in figure 2. The broad intense peak at about 8 eV is attributed to resonant processes, also observed for the hydrogenated diamond and hydrocarbons in the gas phase, while intense peak at about 13 eV is attributed to the increased reflectivity due to DOS minimum which also affects the vibrational excitation function.

A set of excitation functions of vibrational losses attributed to mixed $\delta(CD_x)$ /ν(C—C) bending modes / lattice modes (phonons) was acquired. A detailed analysis will be undertaken to evaluate the contributions of (i) the deuterium terminations CD_x and (ii) one or several atomic layers to vibrational losses, characterizing the inertness and the diamond character of the prepared deuterated substrate.

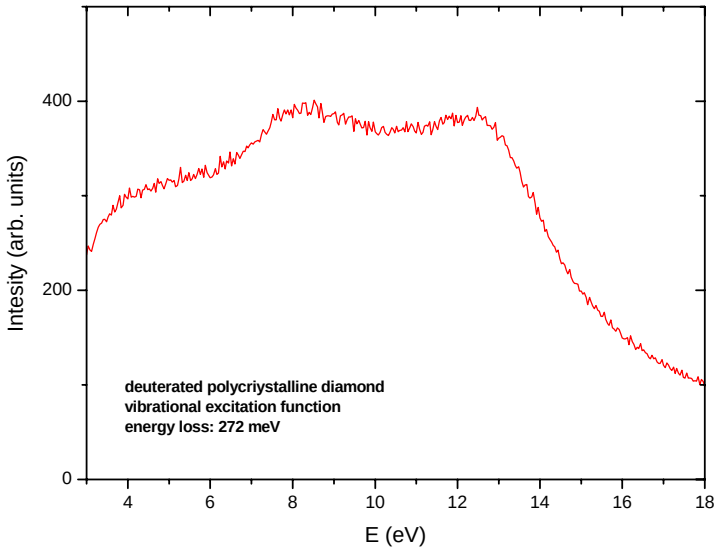

Figure 2. Specular excitation functions for the deuterated polycrystalline diamond, recorded for the energy loss of 272 meV.

FUTURE COLLABORATION WITH HOST INSTITUTIONS

The future collaboration with the host institution will involve further investigation of low-energy electron induced coupling of organic molecules (amine, alcohol) with synthetic diamond to form hybrid bioinorganic patterns. The main experimental investigation will be performed in Orsay, which has facilities for ESD, TPD and HREELS measurements, with molecular films deposited on a surface at low temperatures. The experimental set-up in Belgrade should be used for the gas phase investigation of the proposed molecules, including absolute differential cross section measurements for a specific electron scattering process, as well as measurements of energy and angular distributions of positive ions upon electron induced dissociation of a molecule.

PROJECTED PUBLICATIONS/ARTICLES RESULTING OR TO RESULT FROM THE STSM

We expect at least one publication in a leading international journal and several contributions to international conferences in a near future including results obtained during the visit, as well as further important results as a continuation of the started work.

Aleksandar Milosavljević
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Belgrade, July 22, 2008