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Electron affinity of undoped and boron-doped polycrystalline diamond films

O. Romanyuk[a,*], I. Bartoš[a], I. Gordeev[a], A. Artemenko[a], M. Varga[a], T. Ižák[a], M. Marton[b], P. Jiříček[a], A. Kromka[a]

[a] Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 00 Prague 6, Czech Republic
[b] Institute of Electronics and Photonics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 841 04 Bratislava, Slovakia

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ABSTRACT

The electron affinity of polycrystalline undoped and boron-doped diamond films was investigated by means of X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy. It was demonstrated that both as-grown and hydrogenated polycrystalline diamond films exhibited true negative electron affinity (NEA). Positive electron affinity (PEA) was observed after diamond surface oxidation in plasma. NEA reduction was observed after hydrogenation of the polycrystalline film surface in plasma. This effect was related to depolarization of the surface dipoles, an increase in the density of surface defects, and an increase in contaminations on the surface. Boron doping of the diamond film had a negligible effect on electron affinity. Downward surface band bending was found for all the samples that were studied, and there was larger band bending for polycrystalline diamond surfaces modified in plasma than for as-grown polycrystalline diamond surfaces.

1. Introduction

The electron affinity in semiconductors is defined as the energy distance from the conduction band minimum (CBM) to the vacuum level. When the vacuum level is above CBM, the electron affinity is positive (PEA). When the vacuum level moves below CBM, the electron affinity changes to negative (NEA). Taking into account the electron band bending at the surface of a semiconductor, the NEA is often further classified as true or effective, depending on the position of the vacuum level with respect to CBM in the bulk or at the surface [1, 2]. Semiconductor surfaces with true NEA are desirable in many electronic applications, since the total electron emission from surface can be significantly greater than for PEA.

Monocrystalline diamonds, polycrystalline diamond thin films and even nanoparticles [2–8] with NEA are promising materials for cold photocathode devices [9, 10], field emission [11] and thermoemission [12] devices, and flat panel displays [13]. The NEA of monocrystalline diamonds was observed for a certain surface termination. In particular, diamond surface hydrogenation gives rise to a polarization charge on the atomic scale: the surface dipole is formed due to the different electronegativities of the carbon and hydrogen atoms. For example, from electron affinity measurements of a hydrogen passivated C(111) surface, the surface dipole has been determined as 0.08 eÅ, which gives rise to NEA of −1.3 eV [14, 15]. By contrast, monocrystalline diamond surface oxidation turns NEA to PEA [14, 16, 17].

Theoretical ab initio density functional theory (DFT) studies of the electron affinity of monocrystalline diamond and diamond nanoparticles were carried out recently [18]. NEA was predicted even on hydrogenated diamond nanoparticles. Calculations revealed unoccupied ‘surface-bound states’, which should be localized just outside the nanoparticle surface. These states, and also the positive surface dipole, are responsible for the NEA of diamonds.

Several approaches have been utilized in studies of the electron affinity of diamonds, e.g. total photo-yield spectroscopy (TPYS), secondary electron emission, and photoelectron spectroscopy. In TPYS, the quantum efficiency of the photoelectron emission is measured as a function of photon energy, and NEA has been determined from the strong rise in the photoelectron emission in the band gap energy range. The threshold of photon energy was used for determining the electron affinity [1, 6, 14, 19].

In secondary electron emission, the intensive peak in the low-energy part of the spectrum has been used as an indicator of NEA [20]. It has been demonstrated, however, that the electron affinity has sometimes appeared to be positive [21], in spite of the presence of a sharp onset feature at the low electron energies associated with NEA.

A sharp peak in the low kinetic energy region of the ultraviolet photoelectron spectroscopy (UPS) spectra close to the cutoff of the UPS spectra [3, 22–24] appeared as the most striking feature of NEA. The low kinetic energy electrons, which are excited during UPS measurements to various conduction band energy levels, thermalize through

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[*] Corresponding author.
E-mail address: romanyuk@fzu.cz (O. Romanyuk).

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inelastic collision processes and accumulate partly at CBM. The accumulated electrons are then easily emitted to the vacuum, and those electrons thermalizing to even lower unoccupied energy levels below CBM give rise to a sharp peak at energy close to or at the vacuum level (spectrum cutoff). The sharp peak close to cutoff (in the case of NEA only) could also be accompanied by a peak at energy close to CBM [7]. In the case of PEA, the vacuum level lies above CBM and the sharp peak close to the UPS spectrum cutoff is absent. In this case, the spectrum cutoff determines the position of the vacuum level.

The intensity of the sharp peak close to the cutoff due to NEA (or the NEA peak) is reduced when there is a potential barrier on the surface that suppresses the electron emission to the vacuum. This typically happens when the surface electron band bending is directed upwards. Contrasting behaviour between upward-directed band bending and downward-directed band bending has been observed for terminated boron-doped diamond monocrystals (downwards bending) and for nitrogen-doped (upward bending) diamond monocrystals [23]. In addition, the width of the NEA peak is enhanced in highly-doped monocrystals, where the surface band bending is sharp and the photoemission signal originates from the whole bent space charge region in which the CBM energy changes in parallel to the band bending [24].

Electron band bending plays an important role in electron affinity measurements by surface-sensitive techniques. It has to be taken into account in the interpretation of experimental data, and also in distinguishing between the true NEA and the effective NEA [1]. X-ray photoelectron spectroscopy (XPS) from atomic core levels enables surface electron band bending to be determined [25, 26] and, in combination with UPS [23], it provides all necessary data for electron affinity measurements.

NEA has been reported not only for H-terminated monocrystalline diamond, but also for H-terminated polycrystalline diamond films [8, 27] and nanoparticles [28]. TPYS measurements from H-terminated polycrystalline films indicated NEA regardless of the crystal structure and/or the grain size of the sample. The quantum efficiency of photoelectron emission was found to be even greater from polycrystalline films than from diamond monocrystals [27]. The enhanced photoemission was attributed to the enlargement of the surface area of the polycrystalline diamond films [27].

Optical measurements of polycrystalline diamond films revealed electronic states localized in the band gap of diamond [29, 30]. It has been suggested that these states originate from the disordered (non-diamond) phase of carbon. The localization of electronic states in the band gap was also confirmed experimentally by electron energy loss spectroscopy and by dielectric function calculations for various allotropic forms of carbon [31, 32].

Here, a combination of two photoemission techniques is utilized to investigate the effect on electron affinity of doping and surface termination of polycrystalline diamond films. We reveal the true NEA for as-grown and hydrogenated polycrystalline diamond films, regardless of doping. Surface treatment of diamond with oxygen plasma turns NEA to PEA, irrespective of the magnitude of the band bending.

2. Material and methods

2.1. Growth of diamond films

A polycrystalline undoped diamond thin film was grown on 10 × 10 mm^2 p-type Si(100) substrates. The Si substrate was seeded by applying ultrasonic agitation in a nanodiamond colloid (a NanoAmando aqueous dispersion of nanodiamond particles; concentration of the stock solution 5.0 w/v%; median nanodiamond size 4.8 ± 0.6 nm (98.8 wt%); dilution by deionized water 1:40 v:v). Diamond growth was performed by focused microwave plasma chemical vapour deposition (MWCVD), using an ellipsoidal cavity resonator, from a hydrogen and methane gas mixture (5% of CH_4 in an H_2 atmosphere) at a total gas pressure of 6 kPa, microwave power of 3 kW and deposition time of 25 min. The substrate temperature was about 700 °C during the growth. The thickness of the diamond film was determined by evaluating the interference fringes in the reflectance spectra measured in the visible and near-infra red region. The spectra were evaluated by the FilmWizard commercial optical thin film modelling software. The polycrystalline undoped diamond film was about 70 nm in thickness.

The B-doped diamond thin film was grown on 10 × 10 mm^2 n-type Si(100) substrates. Before deposition, the substrates were ultrasonically seeded for 45 min with diamond nanoparticles (CAS No. 7782-40-3, Sigma Aldrich) diluted in deionized water. Deposition was carried out using the bias-enhanced hot filament chemical vapour deposition (HFCVD) method [33] in a gas mixture of CH_4, H_2 and trimethylboron (2.5% of CH_4 in H_2 atmosphere), i.e. the boron to carbon ratio was 10,000 ppm. The deposition pressure was 3 kPa and the substrate temperature was kept at 650 °C during 4-hour growth. The B-doped diamond film was about 2 μm in thickness.

2.2. Surface modification of diamond films

Undoped and B-doped film surfaces were hydrogenated in a modified linear antenna microwave plasma system (AK 400, Roth&Rau) [32]. The process conditions were as follows: gas pressure of 10 Pa, radio frequency power of 100 W, process duration 30 min. Oxidation of the diamond films was carried out in the Diener (FEMTO) radio frequency plasma reactor for 4 min at radio frequency power of 100 W, at a working pressure of 110 Pa and O_2 gas flow of 30 sccm.

2.3. Characterization of the materials

The surface morphology of the diamond films was analysed using a field-emission scanning electron microscopy gun operating in secondary electron mode (FE-SEM Tescan MAIA3). Raman spectra were measured using a Renishaw In Via Reflex Raman spectrometer with an excitation wavelength of 442 nm (He-Cd laser). The exposure time was set to 60 s and the output power of the laser was set to ~1 mW to minimize the heating effect of the laser beam. All spectra were measured in the back-scattering setup with a 100× objective in confocal mode with a grating of 2400 lines/mm and with a corresponding spectral resolution of 1.2 cm^{-1}. The laser spot was approximately 5 μm in diameter.

The survey XPS spectra and the high-resolution C 1s, O 1s, and B 1s core level spectra were measured from the entire sample surface using monochromatized AlKα radiation (1486.6 eV) in the ADES-400 photoelectron spectrometer. The photoelectrons were collected in constant energy mode with a pass energy of 100 eV resulting in overall energy resolution of 2.2 eV (determined on the Au $4f_{7/2}$ photoelectron line). The X-ray incidence angle was set at 70° and the photoelectron emission angle was set at 0° with respect to the surface normal. The core-level binding energy position with respect to the spectrometer Fermi level and the corresponding band bendings were verified in the Kratos AXIS Supra photoelectron spectrometer with higher energy resolution of 0.45 eV (measured on the Ag $3d_{5/2}$ photoelectron line). The chemical composition of the film was determined from the corresponding high-resolution XPS peak areas after standard Shirley inelastic background subtraction and using the relative sensitivity factor method.

The UPS spectra were measured in the ADES-400 photoelectron spectrometer by an He I discharge lamp with excitation energy of 21.2 eV, and by an He II discharge lamp with excitation energy of 40.8 eV. The He I energy was used for spectrum cutoff measurements (low kinetic energy), while the He II lamp was used for valence electron emission measurements close to the valence band maxima (VBM). The energy resolution of the UPS measurements was 0.15 eV (He I), determined at the Fermi level of the Au reference sample.

The Fermi level of the sample is aligned to the Fermi level of the spectrometer. The Fermi level of the spectrometers was determined by