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Interface and interlayer barrier effects on photo-induced electron emission from low work function diamond films

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ABSTRACT

Nitrogen-doped diamond has been under investigation for its low effective work function, which is due to the negative electron affinity (NEA) produced after surface hydrogen termination. Diamond films grown by chemical vapor deposition (CVD) have been reported to exhibit visible light induced electron emission and low temperature thermionic emission. The physical mechanism and material-related properties that enable this combination of electron emission are the focus of this research. In this work the electron emission spectra of nitrogen-doped, hydrogen-terminated diamond films are measured, at elevated temperatures, with wavelength selected illumination from 340 nm to 450 nm. Through analysis of the spectroscopy results, we argue that for nitrogen-doped diamond films on metallic substrates, photo-induced electron generation at visible wavelengths involves both the ultra-nanocrystalline diamond and the interface between the diamond film and metal substrate. Moreover, the results suggest that the quality of the metal–diamond interface can substantially impact the threshold of the sub-bandgap photo-induced emission.

1. Introduction

Diamond is unusual for its property of obtaining a negative electron affinity (NEA) surface after hydrogen passivation [1–3]. With an NEA and *n*-type doping, a low effective work function can be achieved, which enables thermionic electron emission from the diamond surface at relatively low temperatures (<500 °C). Current state-of-the-art techniques for preparing nitrogen-doped diamond thermionic electron emitters involve introducing sufficient sp^2 bonds at the grain boundaries to reduce the upward band bending, and an effective work function of 1.3 eV has been reported [4]. Low energy photons have also produced electron emission from N-doped diamond films. This visible light photo-induced emission from N-doped diamond was found to share the same low threshold energy as the thermionic emission [5]. Combining these emission mechanisms may enable applications in thermionic energy conversion [6,7], and use as a photocathode [8].

A recent study suggested that photon-enhanced thermionic emission (PETE) [9] could be an advantage for combining photo-induced and thermionic emission processes in a novel device structure. Application in a concentrated solar cell was suggested. The proposed cell is composed of two parallel plates serving as the electron emitter and collector, and a vacuum gap that separates the two plates. Solar light illuminates the emitter to induce PETE. According to Ref. [9], in this structure the electron affinity of the semiconductor emitter provides a significant contribution to its PETE efficiency. Based on this effect we proposed that, by coating a semiconductor with a low work function diamond film, high efficiency solar energy conversion could be achieved due to the reduced emission threshold [5]. Efficient transport of electrons through the interface between the substrate and the diamond film thus becomes a key objective in engineering the related materials. Understanding the effect of film structure on the photo-induced emission from the diamond emitters will be crucial in the further development of such multilayer structures. In this work we report a spectroscopic study of photo-induced and thermionic electron emission from N-doped diamond films on metal substrates with different interface and interlayer conditions.

2. Experiment

In this research, microwave plasma enhanced chemical vapor deposition (MPCVD) was employed to prepare nitrogen-doped diamond emitters on 25 mm diameter molybdenum substrates. Four variations were prepared for comparison of different interface structures. They include: 1) a combination of mirror polished Mo substrate/nitrogen-incorporated ultra nanocrystalline diamond ((N)UNCD) inter-layer/N-doped polycrystalline diamond (N-diamond) surface layer; 2) bead-blasted Mo substrate/(N)UNCD/N-diamond; 3) bead-blasted Mo substrate/(N)UNCD; and 4) polished Mo substrate/nanodiamond/N-diamond. The four

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variations are designated by "D1", "D2", "D3" and "D4". Details of the deposition process are described elsewhere [4]. Films of the same structure as D1 were used previously in photo-induced emission studies of N-doped diamond electron emitters [5,10]. Bead-blasted Mo substrates have a significantly higher surface roughness, and have been typically employed in prior thermionic emission measurements of N-doped diamond [11]. The nanodiamond layer was deposited under the same parameters as the (N)UNCD, except argon gas was not introduced during the growth process. The (N)UNCD layer has a typical grain size of 2–5 nm, while the nanodiamond layer has a nanocrystalline structure with a grain size between 10 and 50 nm [12]. The top N-doped diamond layer was deposited under growth conditions for polycrystalline diamond with predominantly sp^3 bonding. Therefore, comparison between D1 and D2 represents a similar diamond film structure on differently treated Mo substrates, while D1 and D4 share the same Mo substrate properties but with different diamond interlayers. After growth, the samples were exposed to a hydrogen plasma. This process provides hydrogen termination that leads to an NEA surface, and consequently a low effective work function of the film.

To study the optical absorption in the diamond layers, a set of samples were prepared for UV–vis spectroscopy measurements. This included a sample with (N)UNCD + N-diamond layers and a sample with only the (N)UNCD layer. Both were grown on polished fused silica substrates, following the same growth conditions as sample D1. Due to the transparency of the substrates, it was difficult to measure the layer thickness using *in situ* laser reflection interferometry (LRI). The thickness of the (N)UNCD layer was empirically estimated to be ~500 nm, and that of the N-doped diamond layer was between 300 and 400 nm. The absorbance data was obtained using a Perkin-Elmer Lambda 18 UV–vis spectrometer.

For spectroscopic electron emission measurements, the diamond samples were transferred into a UHV chamber for measurements of the photo-induced and thermionic electron emission characteristics. A toroidal tungsten coil beneath the sample holder was used for heating the sample, and the sample temperature was measured with a thermocouple positioned at the center behind the substrate holder. The thermocouple temperature was calibrated with a Mikron M90Q infrared pyrometer. Two photon sources were employed in the experiments. A He discharge lamp was optimized for generation of He I (21.2 eV) photons, which were delivered to the sample surface through a ~1.5 mm diameter quartz capillary. An Oriel 100 W ozone-free Xe arc lamp, fitted with band pass filters ranging from 340 to 450 nm, provided photon illumination at an angle of ~35° to the normal direction. The filters had an FWHM of ~10 nm. A VSW-HA50 hemispherical electron analyzer positioned normal to the surface was employed to acquire the photo-induced and thermionic emission spectra. The analyzer was operated at resolutions of ~0.15 or 0.25 eV to achieve appropriate signal intensity. A negative 15 V bias was applied to the sample surface to maximize the collection of the low energy electrons. Prior to spectroscopic emission measurements, the samples were heated to 450 °C for 15 min and then cooled in vacuum. Previous results indicate that water and hydrocarbon contamination is removed from the sample during the degassing process [13]. After this process the samples were heated to and maintained at the specific temperatures so that the thermionic emission intensity was either negligible, or comparable to the photo-induced emission intensity, and the photo-induced and thermionic emission spectra were then collected. Spectra obtained at elevated temperatures include contributions from photo-induced emission and thermionic emission. The thermionic emission data was subtracted from the combined spectrum in order to obtain the photo-induced emission component. This step has been previously described in more detail [5].

Photoelectron emission and thermionic emission electron microscopy (PEEM/ThEEM) measurements were performed with a prototype Elmitec LEEM III instrument. Samples were loaded onto a holder with integral heating and then inserted into the ultra-high vacuum microscope through a dry-pumped airlock. The sample temperature was controlled in a range from ambient to ~500 °C. During the heating experiments the pressure in the main chamber was maintained below 5×10^{-9} Torr. The voltage between the sample surface and anode was kept at a level of 10 kV, and the sample–anode distance was about 2 mm throughout the measurements. An Energetiq Laser Driven Light Source (LDLS), combined with selected optical band pass filters, was used for photo-excitation. The spectrum of the lamp is that of a xenon discharge source, with a nearly constant output from 170 nm to 800 nm. Due to field emission from high points on the sample, PEEM/ThEEM imaging of the N-doped diamond emitters was only possible from the samples on polished substrates [10]. The images were recorded with the UV "light-on" (total emission) and "light-off" (thermionic emission). To obtain an image of the photo-induced emission from a heated sample, the thermionic component was subtracted from the total emission using the image acquisition and processing program (Actos WinView).

3. Results

In order to compare the effects of different layers, optical absorbance measurements were taken from an efficient emitter diamond sample and one without the top N-diamond layer, both on similarly polished fused silica substrates. Data are shown in Fig. 1, which span from 200 to 900 nm. Comparison between the two curves suggests that a significant portion of the light was absorbed in the (N)UNCD layer, and the absorption was stronger in the UV regime. When the wavelength was below 300 nm, the optical absorbance increased significantly to the point that the signal intensity was below the detection limit of the instrument. Restricted by this detection limit, we suggest that this increase is possibly due to absorption from grain boundaries, defects, and diamond band gap transitions.

Fig. 2 shows the photoelectron spectra from sample D2 and D3 under He I (21.2 eV) photon illumination. Effective respective work functions of ~1.8 eV and 2.7 eV were deduced from the energy difference of the Fermi level (at 21.2 eV binding energy) and the back cut-off of the UPS spectrum. For semiconductors, the front and back cut-offs of a UPS scan follow the relationship:

$$\chi = E_V + \Phi_W - E_G, \tag{1}$$

where E_V is the front cut-off (the valence band maximum), Φ_W is the back cut-off (the work function), E_G is the bandgap of the material, and χ is the electron affinity (which is 0 for NEA materials). Because of the weak emission from the valence band maximum states, we have used this expression to determine the VBM assuming an NEA and then comparing the value with the extrapolation of the states

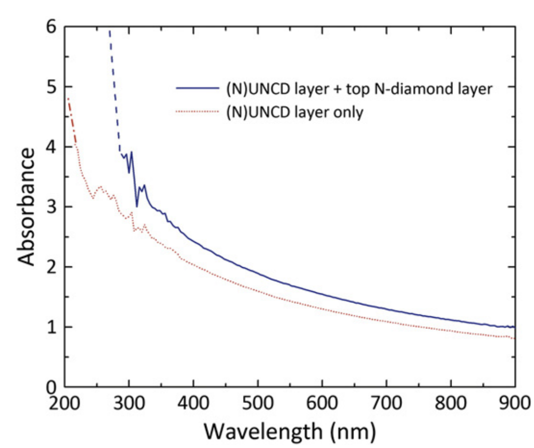

Fig. 1. Optical absorbance of the diamond structures, obtained through UV–vis spectroscopy measurements. The samples are diamond films deposited on polished transparent fused silica substrates, one with only the (N)UNCD layer and the other has a top N-diamond layer in addition. The dashed parts in the curves are extrapolated beyond the detection limit.