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Spatial correlation of photo-induced and thermionic electron emission from low work function diamond films

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ABSTRACT

Hydrogen terminated, nitrogen doped diamond thin films have been the focus of recent research for application in thermionic energy conversion devices and possibly in solar cells. Nitrogen doped diamond films can attain negative electron affinity (NEA) through treatment with hydrogen plasma, which also produces a very low work function surface. Photoemission and thermionic emission spectroscopy measurements confirm a work function of approximately 2 eV for such films. The research presented here includes results from imaging these thin films with photo-electron emission microscopy (PEEM) and thermionic electron emission microscopy (ThEEM), in addition to spectroscopic studies using ultraviolet photoelectron spectroscopy (UPS). From the images it can be concluded that the photo- and thermionic emission are spatially uniform and do not originate from different isolated emission sites. This observation holds true up to the highest resolution and for all temperatures investigated (300–800 K). While relatively uniform, the emission is found to be influenced by the surface morphology and film microstructure. The spatial intensity distributions of the PEEM and ThEEM images are very similar, as reflected by the structure present in both of these images. This observation indicates that both emission processes are enabled by the low work function of the film.

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1. Introduction

Thermionic electron emission from semiconductor materials (e.g. diamond films) has been under investigation for its application in energy conversion devices [1–3]. Among the outstanding attributes of diamond films are their high electric and thermal conductivity, stability, and the ability to attain a negative electron affinity (NEA) surface through hydrogen termination [4]. As low-temperature thermionic electron emission from doped diamond films has been achieved in recent years [5–7], these films are now of interest for thermionic energy conversion applications.

Photo-electron emission microscopy (PEEM), thermionic electron emission microscopy (ThEEM), and field electron emission microscopy (FEEM) have been employed broadly for imaging the spatial distribution of electron emission from diamond materials [8–14]. The n-type doping and NEA are critical for diamond materials to achieve a low work function. However, for nitrogen-doping of single crystal samples this condition has been difficult to attain due to significant upward band bending [15,16], which shifts the relative position of the Fermi level in the band gap. Consequently the surfaces may exhibit an effective work function greater than 4.5 eV, and PEEM imaging typically requires a photon energy above the band gap of diamond (5.5 eV) for excitation.

* Corresponding author. E-mail address: robert.nemanich@asu.edu (R.J. Nemanich). Recently low-work-function n-type doped diamond films have been grown by incorporating sp² bonded grain boundaries, which can apparently provide sufficient electrons to compensate the empty surface states. Work functions of 1.3 eV with nitrogen doping [3] and 0.9 eV with phosphorus doping [17] have been measured. Such work functions make imaging diamond films with long wavelength UV or visible light not only possible but also crucial for understanding the emission mechanism. This report is focused on the relative properties of photo-induced emission and thermionic emission from these low work function, nitrogen-doped diamond NEA films. In this paper results of PEEM/ ThEEM imaging and low energy electron spectroscopy are presented in an effort to determine if the same low work function applies for both thermionic emission and photoemission, by investigating the spatial correlation of the two types of emission.

2. Experimental

The samples used for this study were produced by growing nitrogen doped diamond films on polished metal (molybdenum) substrates using plasma enhanced chemical vapor deposition (PECVD) at Arizona State University. Prior to growth the surface was sonicated in a nanodiamond slurry for 40 min, then rinsed with acetone and dried with nitrogen gas. This nucleation step was followed by the deposition of a nitrogen-incorporated ultra-nano crystalline diamond ((N)UNCD) layer and then N-doped diamond. The UNCD layer was deposited using

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10 sccm argon, 100 sccm nitrogen and 20 sccm methane. The N-doped diamond layer deposition employed hydrogen at 400 sccm, methane at 2 sccm, and nitrogen at 40 sccm. An NEA surface was produced by cooling the sample in a hydrogen plasma. After producing multiple samples with different growth parameters, we were able to prepare a set of samples under similar conditions which met the requirements for both emission microscopy and photoemission spectroscopy. The thicknesses of the films were in the range of 440 \pm 25 nm. The main challenge was to reduce the surface roughness in order to avoid field emission in the electron microscope while maintaining a low effective work function similar to those achieved in previous studies [3].

PEEM and ThEEM images were acquired with an Elmitec LEEM III instrument [18]. During heating of the sample the temperature was monitored with a thermocouple, while the pressure did not exceed 10^{-9} Torr. In the experiment a strong field is applied to the sample to accelerate the emitted electrons into the imaging column of the instrument. At the standard acceleration voltage of 20 kV, considerable field emission was observed from our samples. Therefore, the microscope was operated at 10 kV for the experiments discussed here. The standard sample to anode distance was about 2.5 mm, corresponding to an electric field $\sim 4 \times 10^6$ V/m. The specific local field varies due to the morphology of the sample surface. At this reduced voltage the field emission intensity was kept below the random noise level. Prior to observation the samples were heated to 400 °C for 15 min inside the microscope vacuum chamber to remove surface contamination. A mercury arc lamp equipped with band pass filters was employed as the light source for photo-excitation. A microchannel plate electron multiplier coupled to a phosphor screen and a CCD-camera served as the detection system. The emission images with and without photo-excitation were recorded from ambient temperature up to 530 °C.

In order to investigate the surface structure of the diamond samples at higher resolution than was available from the PEEM, complementary scanning electron microscopy (SEM; done with a FEI Nova 200 NanoLab instrument) and atomic force microscopy (AFM; using an Autoprobe CP from Park Scientific Instruments) measurements were conducted at the University of Bremen.

Ultraviolet photoelectron spectroscopy (UPS) has been broadly applied to determine the effective work function of diamond [4,6,13]. In the present spectroscopy study, photo- and thermionic emission spectra of the diamond sample were recorded with a VSW HA50 hemispherical spectrometer with 0.15 eV resolution, operating in a 10^{-9} Torr vacuum. During the experiment, radiation heating was provided by a tungsten coil beneath the sample. The temperature was monitored with a thermocouple also located behind the center of the sample, which had been calibrated with a pyrometer. The UV sources included 21.2 eV light from a He I discharge and a focused Xe arc lamp used with bandpass filters to provide 2 to 4 eV photons. The photoemission spectra are referenced to the Fermi level (E_F) of the metallic sample

holders, which is calibrated with a standard gold sample by extrapolating the kinetic energy cut-off to the baseline intensity.

3. Results and discussion

The SEM images of the diamond surface shown in Fig. 1 display parallel lines of varying size and contrast, possibly reflecting the morphology of the mechanically polished substrate. These parallel lines are apparently composed of small bumps. At higher magnification, as shown in the inset, the surface morphology is further resolved to consist of shard-like structures which reside on top of the larger structures. Due to the limited resolution of the AFM used here, these shard-like structures are not resolved in the image shown on the right-hand side of Fig. 1. However, this AFM image reveals that the line-and-bump contrast observed with SEM indeed corresponds to the surface morphology. The bumps have been observed in a previous study [19] and are typical of polycrystalline CVD diamond films [20] due to local variations in diamond nucleation. The anisotropy represented by the line structure can be attributed neither to the crystal structure nor to the CVD growth process. Most likely, it is due to scratches in the metal substrate generated by mechanical polishing, as presented on the image of a bare substrate.

The primary motivation of this study is based on a previous publication from our group, which reported visible light photoemission from diamond emitters of the same structure as studied here [21]. Based on these prior results, the conclusion was drawn that photo-excitation originates at or near the diamond-metal interface as a result of the transparency of the diamond film, while thermionic emission is induced near the sample surface due to thermal ionization of the donors. To characterize the emission properties of the samples used in this study, the photoemission and thermionic spectra were measured and are shown in Fig. 2. Photoemission was excited with 400 nm light at a sample temperature of 382 °C. The spectra were recorded with the light on (total emission) and light off (thermionic emission). Subtracting the second spectrum from the first gives the photo-induced emission at this temperature. The thermionic and photo-induced emission are of similar intensity in these experimental results, displayed in Fig. 2(a). Focusing on the photo-induced component, Fig. 2(b) shows photoemission spectra collected with different photon energies (2.7 to 21.2 eV) at ambient temperature (25 °C).

All of these spectra (thermionic emission, 400 nm high-temperature photoemission, and UV/visible and 21.2 eV photoemission) share the same low energy cut-off at about 2 eV above the Fermi level, which represents the effective work function, Φ_{eff} , of the sample. Since we presume that the visible light photoemission from these diamond films takes place at the diamond–metal interface, the UPS results imply that neither this interface nor the diamond layers produce an additional barrier higher than Φ_{eff} , so that both photoemission and thermionic emission are limited by the surface energy barrier Φ_{eff} .



Fig. 1. SEM images of the polished molybdenum substrate (left) and the N-doped diamond film surface (middle), and AFM (right) image of the diamond film. All images display similar line structures which are attributed to polishing induced scratches of the substrate.



Fig. 2. (a) Combined photoemission and thermionic emission spectra at 382 °C and 400 nm illumination. Subtracting the thermionic emission spectrum from the total emission provides the photoemission component. (b) Emission spectra from different illuminating photon energies, measured at ambient temperature. The inset displays the variable excitation energy results near the emission threshold on an expanded energy scale.

A series of PEEM and ThEEM images were recorded between room temperature and 530 °C in order to investigate and compare the spatial intensity distribution and average intensity of both emission types at varying temperatures. To acquire comparable data in each type of image, the sample was first heated to the desired temperature point and then both images were recorded immediately: one after another at the same magnification. This ensured that both images were made under the same conditions, e.g. the same temperature and at the same spot on the sample. At sufficiently elevated temperatures, the PEEM image includes both photo-induced emission and thermionic emission. The average intensity was obtained for each image by subtracting the background and taking a digital average over the largest square area that would fit within the field of view. This value was then normalized to intensity levels per second by dividing by the dwell time of the image. Since the digital levels produced by the CCD camera are actually representing voltages measured from the charge accumulation capacitors on the chip, we cannot speak of counts per second as we would in a pulse counting system. The detector chain (microchannel plate electron multiplier, phosphor screen and CCD camera) behaved linearly during the relevant time frames. The pure photoemission intensity at each temperature was obtained by subtracting the average of the ThEEM image from the average of the PEEM image.

In Fig. 3 the average intensity for both photoemission (under 336 nm illumination) and thermionic emission is plotted on a logarithmic scale versus temperature. The photoemission intensity is essentially



Fig. 3. Photoemission and thermionic emission average image intensity versus temperature, collected for 50 μ m FOV images. A 336 nm filter was employed for photoemission. Specimen bias voltage was 10 kV (rather than the typical 20 kV) to avoid field emission. The thermionic emission intensity was fit to the Richardson–Dushman equation using a work function of 2.0 eV (solid curve). The photoemission intensity was fit to the Fowler–DuBridge model at a constant work function of 2.0 eV (dashed curve).

constant and does not show any temperature dependence within the temperature range investigated here. However, the thermionic emission was observed to increase exponentially and follow the temperature dependence described by the Richardson–Dushman equation. The thermionic data was fit by this equation using a work function of 2.0 eV, as suggested by the UPS results, and varying the amplitude for lowest residual. This varied amplitude is the product of the Richardson constant of the sample and the collection efficiency of the PEEM system (detector gain per ampere). The photoemission intensity was fit using the Fowler–DuBridge equation, again with a work function of 2.0 eV, and the amplitude was varied to fit the data. Here the amplitude is a function of the Richardson constant, the photoelectric absorption factor and the collection efficiency [2].

Fig. 4 presents PEEM and ThEEM images of two magnifications at two different temperatures, which were collected from the same spot on one diamond film sample. At these temperatures the PEEM image intensity without band pass filters is much greater than that in the ThEEM image, and therefore subtracting the thermal emission component from the photoemission image does not change the spatial intensity distribution of the latter significantly. The intensity scales on each image provide the evidence used to draw this conclusion. From these scales we can see that the highest intensity in the PEEM image is a factor of 26 and 6 larger at 450 °C and 530 °C respectively. However, the spatial distribution of intensity in the images from both emission modes shares significant similarities. For instance, the same bright lines are found to be the dominant features in both PEEM and ThEEM, which are likely the same structures observed by SEM and AFM. Thus we conclude that the surface morphology has a significant influence on the spatial distribution of both photoemission and thermionic emission intensities. Nevertheless, apart from this line contrast, the images for both emission processes show uniform intensity within an order of magnitude over the whole surface, as opposed to being limited to a few bright regions as seen in typical field emission images of nanostructured diamond films [10].

As mentioned above, prior spectroscopic studies of photo-induced and thermionic emission from these multi-layer diamond films indicated sources for the two emission processes that are clearly separated in depth. However, the obvious similarities of the spatial intensity distributions in the PEEM and ThEEM micrographs indicate that the emission yields for both processes are determined by the same surface physical properties, i.e. surface roughness, film microstructure and surface work function. While field emission from the samples is insignificant under the experimental settings in this work, the effect of different



Fig. 4. Comparison of PEEM and ThEEM images from the same regions. The white to dark intensity scale is shown in each image. The PEEM images were obtained with direct Xe lamp illumination without filters. Note that these PEEM images have significantly greater intensity than the ThEEM images at the same temperature. The same characteristic features such as bright lines and spots can be found in both PEEM and ThEEM images. (The constant dark spots are damaged areas on the detector, which contribute little intensity to the average.)

acceleration fields on the thermionic emission is not studied, which calls for future efforts. Also, the spatial distribution of the surface work function still needs to be examined through spectro-microscopic methods.

4. Conclusions

The diamond films studied here display a temperature onset for measureable thermionic emission of about 250 °C and show a nearly exponential increase of emission intensity with temperature. Strong photoemission by excitation with visible light was also observed by both PEEM and photoelectron spectroscopy. Furthermore, relatively uniform electron emission from both photon and thermal excitation mechanisms is observed with electron emission microscopy. A comparison of PEEM and ThEEM images suggests that the same effective work function determines the photoemission and thermionic emission properties of these composite films. This work function was measured to be about 2 eV by electron spectroscopy. We conclude that the surface of the N-doped diamond layer determines the effective work function. Surface morphology and film microstructure are also evident in the PEEM and ThEEM images. In order to provide homogeneous emission over the whole surface, which would be desirable for applications in energy conversion devices, our results indicate that it is important to control not only the electronic properties but also the surface roughness and microstructure of the diamond films.

Prime novelty statement

Hydrogen terminated, nitrogen doped diamond films exhibit a low work function. This research employs electron emission microscopy (PEEM and ThEEM) to establish that both thermionic electron emission and photoemission exhibit a relatively uniform spatial distribution that is limited by the surface work function.

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