Imaging electron emission from diamond and III–V nitride surfaces with photo-electron emission microscopy


Department of Physics, North Carolina State University, Raleigh, NC 27695-8202, USA
Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695-8202, USA

Abstract

Wide bandgap semiconductors such as diamond and the III–V nitrides (GaN, AlN, and AlGaN alloys) exhibit small or even negative electron affinities. Results have shown that different surface treatments will modify the electron affinity of diamond to cause a positive or negative electron affinity (NEA). This study describes the characterization of these surfaces with photo-electron emission microscopy (PEEM). The PEEM technique is unique in that it combines aspects of UV photoemission and field emission. In this study, PEEM images are obtained with either a traditional Hg lamp or with tunable UV excitation from a free electron laser. The UV-free electron laser at Duke University provides tunable emission from 3.5 to greater than 7 eV. PEEM images of boron or nitrogen (N)-doped diamond are similar to SEM of the same surface indicating relatively uniform emission. For the N-doped samples, PEEM images were obtained for different photon energies ranging from 5.0 to 6.0 eV. In these experiments, the hydrogen terminated surface showed more intense PEEM images at lower photon energy indicating a lower photothreshold than annealed surfaces which are presumed to be adsorbate free. For the nitrides, the emission properties of an array of GaN emitter structures is imaged. Emission is observed from the peaks, and relatively uniform emission is observed from the array. The field at the sample surface is approximately 10 V/μm which is sufficient to obtain an image without UV light. This process is termed field emission electron microscopy (FEEM). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Diamond; Photo-electron emission microscopy; Field emission electron microscopy

1. Introduction

Materials such as diamond, boron nitride, SiC, Al–Ga nitrides and their alloys are frequently considered in the group of diamond type materials because of their strong bonding. The wide bandgap, coupled with the hardness of these materials leads to high temperature stability and resistance to defect formation and dopant diffusion. In field emission applications, this robustness and the additional resistance to sputtering degradation makes these materials ideal for cold cathode applications.

Typically, the emitted electrons from a semiconductor field emitter can originate from either the...
valence band, the conduction band, defect states and/or surface states [1]. To optimally take advantage of a negative electron affinity surface and therefore realize low voltage electron emission, the Fermi level must be as high in the bandgap as possible. Unfortunately, conductive n-type diamond or AlN are not readily available. The success of doping Si with column V atoms is not transferable to diamond due to their insolubility or their occupation of too deep a level to be activated (nitrogen, for example has a deep donor level of 1.7 eV).

Wide bandgap semiconductors such as diamond and the III–V nitrides (GaN, AlN, and AlGaN alloys) exhibit small or even negative electron affinities. The discovery of a high quantum yield from the (111) surface of diamond indicated its potential as an electron emitting material [2]. Results have shown that different surface treatments will modify the electron affinity of diamond to cause a positive or negative electron affinity (NEA). It was found that if the diamond surface is terminated with hydrogen atoms, the surface will exhibit negative electron affinity properties [3]. A negative electron affinity places the vacuum level below the conduction band minimum. This allows electrons from the conduction band to be freely emitted from a surface into the vacuum without a barrier. For the III–V nitrides of GaN and AlN, results indicate a NEA for some surfaces of AlN and an electron affinity of 3.3 eV for GaN [4,5]. Alloys of AlGaN exhibit a composition dependent electron affinity which trends to a value of zero at about 70% AlN [5].

This study describes the characterization of diamond and nitride surfaces with photo-electron emission microscopy (PEEM). The PEEM technique is unique in that it combines aspects of UV photoemission and field emission [6]. The origin and properties of field emission from natural diamond as well as chemical vapor deposited diamond and nitride films needs to be understood. A number of possible mechanisms for the observed emission have been recently proposed and studied [7–11]. Proposed mechanisms of electron emission have included emission from mid-gap defect sub-bands, creation of electroformed conducting channels, back contact injection into the conduction band, and emission due to sharp asperities (created during dielectric breakdown) [12]. These mechanisms can be more easily studied with the aid of electron emission microscopy, both in photoemission and field emission modes.

The advantages of PEEM over other microscopies include the ability to image monolayer and submonolayer coverages on surfaces and the ability to study dynamic events such as the migration of reaction fronts [6]. The PEEM technique images the photoemitted electrons allowing a true relation of the emission to the surface morphology [13]. A promising application is the real-time observation of processes that alter the work function of a surface locally. For example, absorption/desorption processes are well-known to change the work function of a surface. In this study, PEEM images were excited using two different sources: (1) a 100 W Hg discharge lamp and (2) a UV-free electron laser. The Hg discharge lamp provides multi-line emission with a high energy cutoff at 5.1 eV, and the UV-free electron laser at Duke University provides tunable emission from 3.5 to greater than 7 eV.

The tunable UV light from the free electron laser is employed to examine electron emission from light excitation near the photothreshold. For a traditional semiconductor with a positive electron affinity, the photothreshold is the minimum energy to excite an electron from the valence band to the vacuum energy, i.e., the bandgap plus the electron affinity. For a semiconductor with a negative electron affinity, the photothreshold is simply the bandgap.

2. Experimental

The samples employed in this study included diamond films deposited by microwave plasma chemical vapor deposition (MPCVD). A p-type sample was prepared with boron doping. While n-type character is not typically available, nitrogen doping has been shown to exhibit a deep donor at ~1.7 eV from the conduction band [14]. A nitrogen (N)-doped film was also studied in the PEEM. Prior to the PEEM measurements, the diamond surfaces were exposed to a remotely excited hydrogen plasma which was operated with the following conditions: 20 W RF power, a hydrogen pressure of 20 mTorr, a substrate temperature of 450°C, and an exposure
time of 5 min. An array of GaN pyramid structures was prepared by selective MOCVD growth processes. The growth properties have been described elsewhere [15].

The PEEM images were obtained using a high resolution microscope. The PEEM which was obtained from Elmitech has a demonstrated ultimate lateral resolution of 12 nm. Shown in Fig. 1 is a schematic view of the photoemission electron microscope including the trajectory of electrons from the photoemitting surface. The specimen holder supports the sample and the top surface is imaged. A pierced anode (diameter 2 mm) is situated facing the sample at a distance of approximately 2 mm. The anode is grounded while the specimen is connected to a high voltage supply (variable to $-20\,\text{kV}$). The photoemitted electrons are excited with a UV light source. In the experiments described here, measurements were obtained with either a 100 W Hg discharge lamp or tunable UV light from a free electron laser. The UV light is focused onto the sample using quartz optics.

The relatively slow photo-electrons emitted by the sample are accelerated towards the anode in a static field of up to 10 V/μm. The electrons are injected through an axial aperture in the anode into a five stage electron microscope with magnetic lenses. The optical system consists of a magnetic objective, a transfer lens, a field lens, an intermediate lens and a double-gap projector, as well as stigmators. Contrast apertures of 50, 70 and 100 μm in size can be inserted in the back focal plane of the objective. By using the five stage imaging process, direct electron optical magnification between $2 \times 10^2$ to $1 \times 10^5$ can be achieved. The magnified electron image is projected onto a microchannel plate to increase the brightness and then onto a phosphor screen. The image on the phosphor screen is recorded with a low light CCD camera. This signal is then sent to an integrator to increase the signal/noise ratio of the image. The images can then be either recorded via a frame grabber installed in a PC or video taped for analysis of real-time surface processes.

The Duke OK-4 FEL is a device situated in one of the long straight sections of the Duke 1 GeV storage ring. The OK-4 has been described in detail elsewhere [16,17], but a summary of the most salient features are provided here. An electromagnetic undulator is capable of providing spontaneous emission in the 3–10 eV range for its fundamental. The large energy range can be tuned by adjusting both the magnetic field strength of the undulator and/or the energy of the stored electron beam. In spontaneous emission mode, each electron in the storage ring radiates with a random phase relative to the other electrons, i.e., incoherently. The bandwidth is about 5% of the photon energy, which corresponds to an energy width of about 250 meV. Lasing is achieved by setting up a cavity with multilayer coated mirrors at either end of the straight section. In the experiments described here, the FEL was operated in the spontaneous emission mode (i.e., not lasing). The images were obtained with the free electron laser.

![Fig. 1. A schematic view of the photoemission electron microscope including the trajectory of electrons from the photoemitting surface.](image-url)
operating at currents between 0.50–0.65 mA at an electron energy of 500 MeV.

3. Results

In Figs. 2 and 3, respectively, the PEEM images of boron or N-doped diamond films are compared with SEM images of the same films. The PEEM and SEM images have been scaled to reflect a similar field of view. Both samples had been exposed to a hydrogen plasma prior to loading into the PEEM system. Prior UV photoemission measurements have established that hydrogen termination of (100), (111) and (110) surfaces causes a negative electron affinity [18,19], and it is anticipated that the surfaces of the film are hydrogen terminated and that they exhibit a negative electron affinity.

Note that the PEEM image of the p-type sample was obtained with the 5.1 eV Hg discharge lamp. For the N-doped sample, images obtained with the Hg lamp were significantly less intense. It is interesting to note that the 5.1 eV Hg lamp excitation is significantly below the 5.45 eV bandgap of single crystal diamond. To characterize the atomic bonding in the films, Raman spectra were obtained from both samples. The spectra showed the presence of the 1332 cm⁻¹ line indicative of diamond crystal structure. Both films also exhibited features attributed to sp² bonded carbon. In fact, the spectra of the N-doped sample exhibited a significantly larger relative sp² bonded fraction. Prior studies have suggested that the sp² bonded carbon contributes states in the diamond bandgap. We suggest that these states are responsible for the PEEM images obtained using the sub bandgap Hg lamp excitation. The fact that only faint images could be obtained with the N-doped films is an apparent contradiction since these films seem to exhibit increased sp² bonding.

Several possibilities may explain this effect: (1) the electron affinities of the two surfaces are different, (2) different band bending effects may play a role, (3) the nitrogen or the doping affects the in-gap defect states. In considering the electron affinity due to surface termination, it is usually considered that this affect is due to the atomic bonding within the first few atomic layers of the surface. While the electron affinity of the N-doped samples has not been established, it is certainly anticipated that the surface dipole effects will be similar and independent of doping. With regards to band bending, prior results have indicated downward band bending for the hydrogen terminated p-type, B-doped diamond surfaces. While the band bending of the N-doped samples has not been established, it is certainly anticipated that the surfaces exhibit upward band bending. However, the band bending may not play a significant role in the PEEM images of the two samples. The applied field in the PEEM is $\sim 10$
V/µm, and this should result in downward band bending for the N-doped sample. Moreover, since the absorption of the UV light occurs near the surface, band bending may not play such a significant role. We are then left with the last possibility. Here it is possible that the nitrogen somehow affects the sp²
bonded defects. To our knowledge, there has been no detailed calculation to establish this affect, but it is well-known that some nitrogen incorporation increases the resistivity of diamond films.

It is interesting to note that the PEEM images are similar to the SEM micrographs of the same surfaces. This suggests that the electrons are emitted relatively uniformly from the film surface, but the strongest emission is evidently from the edges protruding from the surface. We attribute this to the high field at the sample surface and field enhancement from the protrusions. We note that there is no evidence of preferential emission from regions of the sample that might contain higher defect densities.

To further explore the effect of the surface termination, FEL-PEEM images were obtained from the N-doped films before and after annealing. The N-doped films were more appropriate for this study since the photothreshold appeared to correspond to the bandgap of the diamond, which would be expected for a negative electron affinity surface. A series of images were obtained at different photon energies ranging from 5 to 6 eV. The sample was heated to 400, 600, 800 and 1000°C for 10 min and imaged each time after returning to room temperature.

We note again that the initial surface had been exposed to a hydrogen plasma prior to loading into the PEEM system, and it is anticipated to exhibit a negative electron affinity. Recent studies have established that hydrogen desorbs from the (110) and (111) surfaces at temperatures less than 1000°C, and that these surfaces then exhibit a positive electron affinity [20]. In Fig. 4, the PEEM images obtained before and after annealing are compared. Images obtained with 5.4 and 6.0 eV UV excitation are displayed. These energies reflect images obtained with light near the photothreshold and well above the photothreshold of the diamond.

It is evident that before annealing, an image is observable with both the 5.4 eV and 6.0 eV light. Note also that the images are essentially similar except that the electron emission from the lower energy light is reduced in intensity. However, after annealing to 1000°C, the image obtained at 5.4 eV is significantly reduced in intensity while the image at 6.0 eV is essentially unchanged. We suggest that this change is a reflection of the increase of the electron affinity that occurs after hydrogen desorption. Prior results indicate that the adsorbate free surface exhibits a positive electron affinity of ~0.5 eV. Thus, the annealing would be expected to result in an increase in the photothreshold by 0.5 eV, and this is consistent with our observations.

To explore the effect of surface morphology with PEEM, we have examined a structure based on n-type (Si-doped) GaN. An array of GaN pyramid structures has been prepared by selective growth processes. An SEM of the array is shown in Fig. 5(a). Also, as indicated in Fig. 5(b), these GaN pyramids exhibit a small radius of curvature which will lead to substantial field enhancement. While GaN exhibits a moderate electron affinity of 3.4 eV (according to UV photoemission measurements), these pyramid arrays exhibit emission at a very low average field. Recent measurements indicate detectable, stable field emission at a field of 7 V/μm.

![Image](image_url)

Fig. 5. (a) SEM of an array of GaN pyramid structures prepared by selective MOCVD growth, and (b) high magnification image of a single pyramid showing the apex.
Fig. 6. (a) PEEM image of the pyramid structures of the Si-doped GaN, and (b) FEEM image of the same surface. In these images, the dark regions represent the areas of more intense electron emission. The PEEM image was excited with a 100 W Hg lamp and there was no photoexcitation in the FEEM.

Images of the same sample have been obtained in the PEEM system and are displayed in Fig. 6. In this set of measurements, images were obtained with the UV light excitation, Fig. 6(a), and also without the UV light excitation, Fig. 6(b). In the case of no UV light, the electron emission is stimulated by the applied field (of \( \sim 10 \text{ V/\(\mu\)m} \)) in the microscope. Imaging in this mode is termed field emission electron microscopy (FEEM). The PEEM and FEEM images of the GaN pyramid array both show preferential emission apparently from the points of the array. The fact that a FEEM image is detected is consistent with our field emission measurements from this sample. It is also interesting to note that the PEEM image indicates relatively uniform emission from all of the pyramid structures.

4. Discussion

While the goal for most cold cathode materials applications is to obtain emission with a low applied field and no light, the results presented here allow examination of the emission properties of a surface with both light and field present.

Several studies have indicated that defects or \( \text{sp}^2 \) structures play an important role in obtaining electron emission at low applied field from carbon films [21]. Examination of these carbon films has also shown that the emission is strong from widely separated spots on the sample. In contrast, the measurements presented here do not identify any correlation of electron emission from defect or \( \text{sp}^2 \) bonded structures, and in fact, the emission is relatively uniform over the surface. These results amplify a critical issue in field emission. That is that the photoemission does not exhibit the same non-uniform emission as the field emission. We presume that the UV light essentially populates electrons in the conduction band uniformly over the surface. Apparently, these photoexcited electrons see a relatively uniform low barrier to emission.

Unfortunately, the diamond films employed in this study did not exhibit measurable emission at the 10 V/\(\mu\)m average field available in the PEEM microscope. A future goal of the research will then be to examine carbon films with increased defects so that the photoexcited and direct field emitted electrons can be measured from the same sample. This will involve PEEM and FEEM measurements of carbon films with both diamond and \( \text{sp}^2 \) bonding. Moreover, it is also critical to examine the role of surface termination of hydrogen or oxygen on these samples.

5. Concluding remarks

The PEEM images of both the B-doped and N-doped samples exhibit images which are similar to the SEM from the same samples. Elevated sharp edges exhibit the strongest emission, and this is attributed to field enhancement from these protrusions.
sions. There was no evidence of enhanced emission from regions of high defects. PEEM images of the N-doped samples were obtained at different UV excitation energies using UV light from the free electron laser at Duke University. For UV excitation near the diamond band gap the results indicate a reduction in the image intensity when the hydrogen terminated surfaces are annealed to 1000°C. The image changes are consistent with a threshold shift of >0.2 eV for the case where the sample is annealed. We suggest the desorption of the hydrogen results in an increase in the photothreshold, and this corresponds to previous measurements which indicate a negative electron affinity for the hydrogen terminated surface and a 0.5 eV positive electron affinity for the adsorbate free surface.

PEEM of an array of GaN emitters displays relatively uniform emission. In fact, emission was detected both with the UV light on (PEEM mode) and with the light off (FEEM mode). The emission in both modes displayed the same emission pattern.

The results presented here demonstrate the value of PEEM for characterizing the electron emission properties of wide bandgap semiconductors.

Acknowledgements

We gratefully acknowledge the Duke University FEL Laboratory for access to the OK-4 UV FEL. This project was supported through the Office of Naval Research.

References