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Photoemission spectroscopy was used to compare the effects of a hydrogen or argon plasma on natural-type 2B diamond (111) surfaces, while the diamond was heated to 350 °C. After the hydrogen plasma the surface exhibits a negative electron affinity, indicative of a hydrogen-terminated surface. In contrast, the argon plasma was found to result in a surface with a positive electron affinity of 1.0 eV, indicating the removal of hydrogen from the surface. Features characteristic of graphite were not observed. After reexposing the surface to a hydrogen plasma, the spectrum was identical to the spectrum obtained after the initial hydrogen plasma.

The wide band gap of diamond (5.47 eV), its high carrier mobilities ($\mu_n = 2200$ cm^2/V s, $\mu_p = 1600$ cm^2/V s) and high breakdown fields (10^7 V/cm), make diamond an excellent semiconductor material to be used for high speed, high temperature, or high power transistors. In addition, the diamond (111) surface is known to exhibit a negative electron affinity, so that electrons in the conduction band have enough energy to cross the surface, and be emitted into vacuum. This effect could allow the use of diamond in applications such as cold cathode emitters, and ultraviolet detectors.

With the development of chemical vapor deposition growth of diamond, diamond has the possibility to become an economically viable electronic material. In current silicon device technologies, surface preparation is an important aspect of device fabrication, and it will certainly become an issue in the fabrication of diamond devices. Currently there are many different *ex situ* cleaning methods in use for preparing diamond surfaces. These are generally a combination of polishing the diamond, followed by a solvent rinse or an acid etch. Exposure to various plasmas is currently under investigation as a cleaning technique for silicon wafer processing.[1]

In the experiments presented here, angle resolved ultraviolet photoemission spectroscopy was used to compare the effects of hydrogen or argon plasmas on the diamond (111) surface. It was found that the diamond (111) surface after exposure to a hydrogen plasma, exhibited a negative electron affinity effect. This is indicative of a hydrogen-terminated surface. After exposure to an argon plasma the surface was found to exhibit a 1 eV positive electron affinity, suggesting the removal of the hydrogen.

The diamond substrates used in this study were $3 \times 3 \times 0.5$ mm^3 2B (*p*-type) natural diamond with a (111) surface orientation and a typical resistivity of 10^4 Ω cm. The substrates were polished with 0.1 μm diamond grit and chemically cleaned before loading. The chemical clean consisted of 10 min in fuming sulfuric acid, 30 min in fuming chromic acid, a deionized water rinse, and a 10 min aqua regia etch. The diamond was fastened to 1.6-mm-thick molybdenum disk with tantalum wire.

After loading, the diamond was exposed to a remote hydrogen or argon plasma. The gas flow was kept at 9 sccm while the pressure was held at 14 mTorr, using a turbo-pump-backed throttle valve. The gas was introduced through a 25-mm-diam quartz tube. A 12 turn coil around the tube was used to couple 20 W of radio frequency radiation into the plasma. Using Langmuir probes the plasma potential was found to be approximately 50 V positive, with respect to the chamber walls and the sample. The sample faced the plasma region, and was located at about 40 cm from the end of the tube. While exposed to either plasma, the sample was heated by a tungsten filament in close proximity to the back of the molybdenum disk. The temperature was measured at the back of the molybdenum disk. The samples were exposed for a duration of 10 min. During the exposure the sample was kept at a temperature of 350 °C. This is comparable to the lowest temperature at which Muranaka *et al.* report the growth of diamond.[2] After each plasma exposure the sample was transferred *in vacuo* to the angle resolved photoemission chamber for analysis.

For comparison a $2 \times 1/2 \times 2$ reconstruction was obtained by annealing a diamond (111) wafer for 10 min at 950 °C. The emission was excited with 21.21 eV He I radiation. The photoemission data presented here were obtained with a 50 mm hemispherical analyzer with an angular resolution of 2°, and the analyzer was operated with an energy resolution of 0.15 eV. All photoemission spectra presented in this letter are from emission normal to the surface.

Photoemission spectra of a diamond (111) surface, obtained after sequential exposure to hydrogen and argon plasma, are shown in Fig. 1. The spectrum obtained after hydrogen plasma exposure shows a sharp peak, labeled (A), at the low energy end of the spectrum. This peak is located 15.7 eV below the onset of emission, labeled (E_v) in Fig. 1. After the diamond had been exposed to the argon plasma, the spectrum was shifted ~ 0.3 eV toward lower energies. The low energy cutoff of the spectrum was moved by 0.7 eV toward higher energies, and the large peak (A) had totally disappeared. Low energy electron diffraction (LEED) measurements, performed on a similarly prepared surface, showed a sharp 1×1, unreconstructed sur-
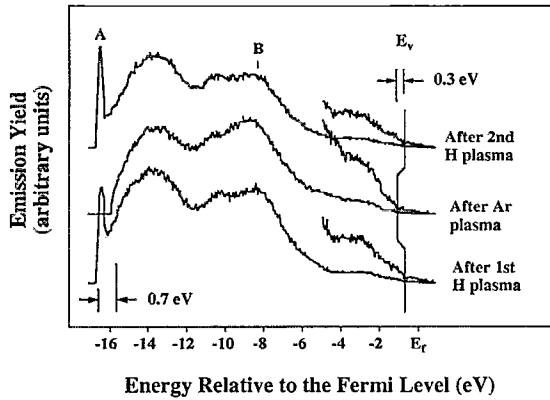
FIG. 1. Photoemission spectra of diamond (111) after exposure to: from bottom to top, a hydrogen plasma, an argon plasma, and a second hydrogen plasma.

face. The difference spectrum between the hydrogen plasma exposed surface, and the argon plasma exposed surface, is shown in Fig. 2. The difference spectrum was found by scaling and aligning the spectra with respect to peak (B), prior to subtraction. The difference spectrum shows a peak at 1.4 eV below the valence band maximum. For comparison purposes the difference spectrum between a reconstructed surface and the hydrogen exposed surface is also shown. The peak in this spectrum is centered around 1.2 eV below the valence band maximum. The spectrum, obtained after a subsequent exposure to a hydrogen plasma, reverted back to the spectrum obtained after the first hydrogen plasma exposure.

The hydrogen-terminated diamond (111) surface is known to exhibit a negative electron affinity. The work function of a negative electron affinity surface, is such that the energy position of the vacuum level lies below the conduction band minimum. Secondary electrons that are collected at the conduction band minimum, are therefore able to escape the surface. These electrons appear in the photoemission spectra as a sharp peak. The positions of this negative electron affinity peak and the valence band edge
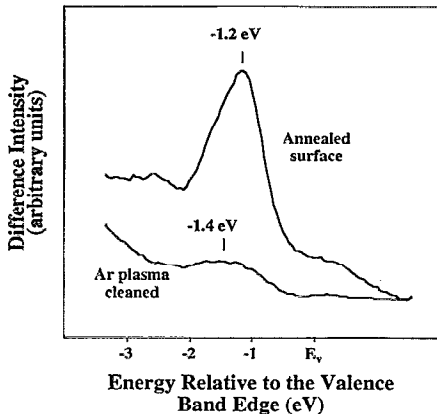

FIG. 2. The lower curve shows the difference spectrum of the argon plasma exposed surface, and a hydrogen plasma exposed surface. The upper curve shows the difference spectrum of the reconstructed surface, and the hydrogen exposed surface.
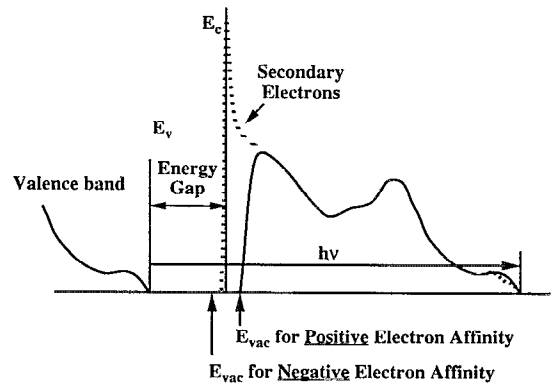

FIG. 3. Schematic representation of the spectra of the hydrogen plasma exposed surface (dotted line) and the argon plasma exposed surface (solid line). The hydrogen plasma exposed surface exhibited a negative electron affinity, and the low energy cutoff of that spectrum is determined by the conduction band minimum, while for the argon plasma exposed surface the cutoff is determined by the vacuum level.

are related. As is shown in Fig. 3, emission, originating from the valence band maximum (E_v) has an energy of $E_v + hv$. The energy of the secondary electrons, emitted from the conduction band minimum have an energy of $E_v + E_g$, where E_g is the band gap energy. The valence band emission, observed in the spectra, occur therefore at an energy of $hv - E_g$, above the conduction band minimum. Since the indirect band gap of diamond is 5.47 eV at room temperature,[3] and the energy of the exciting He I radiation is 21.21 eV, the emission from the valence band maximum occurs at $\sim$15.7 eV above the negative electron affinity peak.

It has been shown by Pate et al.[4-7] that thermal desorption of hydrogen from the diamond (111) surface, will remove the negative electron affinity. The chemisorbed hydrogen can be desorbed from the surface by annealing at temperatures above 950 °C. Photoemission spectra of these annealed surfaces are typically shifted with respect to the spectra of the hydrogen terminated surface by 0.5±0.2 eV toward lower energies,[8] while the low energy feature, attributed to the negative electron affinity, disappears. Subsequent exposure of the surface to atomic hydrogen, causes the surface to revert back to its original state.[6,7] These effects are similar to those we observed after exposing the surface to argon and hydrogen plasmas. This suggests that the argon plasma has removed the hydrogen that was chemisorbed on the surface after the hydrogen plasma.

The thermally cleaned surface, however, is reported to show a 2×1/2×2 reconstruction.[5,8] Associated with this reconstruction is a surface state, which, for surface normal emission, appears at 1.1 eV below the valence band edge. In contrast to the thermally cleaned (111) surface, the argon plasma exposed surface, showed a sharp, unreconstructed 1×1 LEED pattern, with no evidence of the 2×1/2×2 reconstruction. Indication of bonding characteristic of the reconstruction could, however, be found in the difference spectra between the argon and hydrogen exposed surfaces, as shown in Fig. 2. Based upon the relative intensity of the peak in the difference spectrum after argon plasma exposure, compared with the peak in the difference

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spectrum of the reconstructed surface, we estimate that less than 15% of the surface has a bonding characteristic of the reconstructed surface. The fact that no reconstruction was observed in the LEED can be explained if the domain size of the reconstruction is too small to form an interference pattern. A similar situation has been described by Hamza et al.[9] Using electron-stimulated desorption time-of-flight measurements, they observed that hydrogen can be desorbed from the diamond (111) surface, without the appearance of a $2 \times 1/2 \times 2$ reconstructed LEED pattern.

We suggest that the mechanism by which the argon plasma removes the hydrogen is physical bombardment by argon ions accelerated by the potential difference between the plasma and the sample. The plasma typically has a positive potential with respect to the walls and the sample of about 50 V, under the conditions of our experiments. The sharp cutoff at the back edge of the spectrum after argon plasma exposure indicates that the surface has uniformly changed.

The possibility was considered that the argon plasma might result in a graphitized surface. Cong et al. report that about a monolayer of graphite is formed, after bombarding a diamond film with 50 eV argon ions for 10 min.[10] The photoemission spectrum of graphite exhibits a strong peak in the secondary electrons at ~ 13.5 eV below the Fermi level. Also, in studies done on an intentionally graphitized diamond surface, the work function was found to be ~ 4.0 eV.[11] This would result in emission features at energies lower than the back edge of the spectra. We did not, however, observe any features in the spectrum of the argon plasma exposed surface that indicated the presence of graphite.

The creation of vacant sites, by removal of hydrogen from the surface, is an important step in the diamond growth processes. Growth occurs when a radical hydrocarbon molecule attaches to the vacant site. In typical growth situations these vacant sites are created by mono-atomic hydrogen which reacts with the hydrogen on the surface. This reaction is made possible by keeping the surface at high temperatures (> 700 °C). The results presented in this letter suggest that the presence of argon may enhance the removal of hydrogen from the surface, especially at lower temperatures. This would lead to increased growth rates, and growth at lower temperatures. Increased growth rates and lower growth temperatures have indeed been reported for argon containing gas mixtures.[2]

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