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Negative-electron-affinity effects on the diamond (100) surface

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A negative electron affinity (NEA) was found both experimentally by photoemission spectroscopy and theoretically by *ab initio* calculations for the 2×1 reconstructed diamond (100) surface. This surface is the dominant growth surface for thin diamond films and can be obtained by chemical-vapor deposition. Various surface-preparation methods which result in a NEA are described. Theoretical results indicate that the observed NEA is associated with a monohydride-terminated surface, while the hydrogen-free surface exhibits a positive electron affinity.

Negative-electron-affinity (NEA) surfaces are semiconductor surfaces that have a work function such that the vacuum level lies below the conduction-band edge. Electrons that are present in the conduction band can therefore readily escape the surface. The NEA surfaces are utilized in a number of important applications, such as photocathodes, secondary electron emitters, and cold-cathode emitters. In general, wide-band-gap semiconductors are particularly suitable candidates for NEA emitters, since the conduction-band minimum is likely to be close to the vacuum level. Diamond, with a 5.5-eV band gap can be grown as high-quality films, both homoepitaxially on (100) substrates and highly oriented textured films on (100) silicon surfaces.[1] We have investigated the possibility of inducing a NEA on the diamond (100) surface and have found several surface preparation methods which led to this effect. *Ab initio* calculations were used to compute the electron affinity of different surface structures, and to identify the structure of the NEA surface and the origin of the NEA effect.

Photoemission is a highly sensitive tool to determine the presence of a NEA. Electrons that are excited in the photoemission process from the valence band into various conduction-band energy levels lose energy through inelastic collision processes and accumulate in levels at the conduction-band minimum. At a NEA surface, the vacuum level lies below the conduction band and the electrons accumulated at the conduction-band minimum can be emitted into the vacuum. These electrons appear in the photoemission spectra as a sharp peak at low electron energies. The position of the peak can be correlated with other features in the photoemission spectra to verify that the emission originates from the conduction-band minimum.

A NEA has been demonstrated for the diamond (111) surface[2] and has been associated with the presence of hydrogen bonded to the surface.[3,4] The bulk-terminated diamond (100) surface has two unsatisfied bonds which would in principle allow the formation of a dihydride-terminated surface. The existence of the dihydride-terminated surface has been subject to some debate.[5–9] Recent large-scale *ab initio* calculations indicate that this surface is locally stable, but it is preferred only at very high values of hydrogen chemical potential.[10] It is, therefore, uncertain whether a stable dihydride-terminated surface can be achieved. Thin diamond films, grown at 700–1000 °C in a hydrogen-rich environment, typically exhibit a 2×1 reconstruction. This surface is found to be stable in air,[11] and is presumed to be a monohydride-terminated surface.[7] A 2×1 reconstructed surface can also be obtained by annealing the diamond surface to ~1000 °C. Temperature-programmed-desorption (TPD) studies show that at these temperatures hydrogen evolves from the surface.[7,12,13] Hamza, Kubiak, and Stulen[13] suggest that the surface is monohydride terminated with higher annealing temperatures required to obtain a H-free surface. Based on steric hindrance arguments that suggest that a dihydride-terminated diamond (100) surface cannot exist, Yang *et al.*[7] suggest that the hydrogen evolves from a monohydride-terminated surface. They therefore conclude that the surface is free of hydrogen after annealing to ~1000 °C.[7] However, the high temperatures required make TPD studies difficult. Furthermore, the H bonding may also depend on other aspects such as surface preparation and the presence of in-diffused H into the bulk.

In this study natural diamond wafers with a (100) surface orientation were polished with diamond grit, etched in chromic acid and aqua regia, and introduced into the vacuum system. The wafers measured $3\times3\times0.5$ mm^3, and were type IIb (p-type semiconducting) with resistivities of 10^3–10^4 Ω cm. Photoemitted electrons were analyzed with a 50-mm hemispherical analyzer operated at a 15-eV pass energy, which resulted in a 0.15-eV energy resolution. The analyzer has a 2° angular resolution. A ~1-V bias was applied to the sample to assure that low-energy electrons have enough energy to overcome the work function of the analyzer. Photoemission was excited with 21.21-eV light from a helium discharge lamp. The UHV system used in this study consisted of multiple chambers with a UHV sample transfer system. The capabilities used for this study included the angle-resolved ultraviolet photoemission spectroscopy (UPS) system, low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES).

The photoemission spectra, shown in Fig. 1, were obtained after the diamond surface had been annealed to temperatures ranging from 545 °C to 1070 °C. The spectra exhibited small, random shifts on the order of 0.2 eV with respect to each other. This is attributed to charging effects. The spectra were therefore aligned according to a bulk fea-

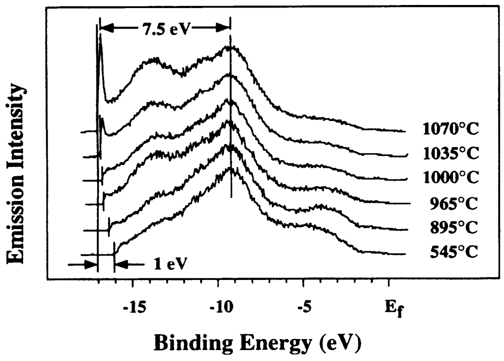

FIG. 1. Photoemission spectra showing the effects of annealing on the diamond (100) surface. The shift in the back edge is indicative of a lowering of the work function and the presence of the sharp peak indicates a NEA. The spectra have been aligned according to the peak at ~9 eV below the Fermi level.

ture indicated by the line in Fig. 1 to allow comparison between them. As can be seen in the figure, the low-energy onset of the spectra shifts by as much as 1 eV towards lower energies as the annealing temperature is increased. This is indicative of a lowering of the work function of the surface since electrons with lower energies are able to escape from the surface. After a 1035 °C anneal the spectrum exhibits a peak at low energies which becomes more pronounced after a 1070 °C anneal. As mentioned above, the appearance of this peak indicates that the vacuum level lies below the conduction-band edge and that the surface has a NEA. The peak is positioned at ~7.5 eV below the bulk feature indicated by the solid line in Fig. 1. An identical peak at ~7.5 eV below this bulk feature can be observed in the spectra of NEA diamond (111) surfaces.[14–16] The appearance of the peak on the (100) surface coincided with the appearance of a 2×1 surface reconstruction.

Auger electron spectra, shown in Fig. 2, indicate that oxygen was present on the as-loaded surface. No oxygen or any other contaminants could be detected at the surface after the diamond had been annealed to 1050 °C. The surface was observed to transform from a 1×1 structure to a 2×1 structure, coincident with the removal of oxygen. However, the presence of hydrogen on the surface both before and after the anneals cannot be ruled out on the basis of these measurements, since AES is not sensitive to hydrogen.

To further explore the issue of whether the surface is H terminated, a sample was exposed to a remotely excited H plasma. The H plasma produces a flux of atomic hydrogen and the remote excitation results in a much lower density of ions and electrons at the sample surface. Prior to transfer into the plasma chamber the sample was annealed to 1050 °C in UHV, and a 2×1 surface was obtained with the NEA as described above. This sample was then exposed to a pure hydrogen plasma at a pressure of 50 mTorr while heated to 350 °C. The high flux of atomic H will assure that the surface is H terminated. A weaker 2×1 LEED diffraction was observed after the plasma exposure. The reduced intensity of the LEED could be attributed to either disorder in the dimer structures or the presence of some dihydride structure on the surface. The photoemission spectrum from the surface is also shown in Fig. 4 below. The spectrum displays the feature indicative of a NEA, and supports the conclusion that the growth surface exhibits a NEA that is related to hydrogen termination. We note that the low-energy features attributed largely to secondaries vary significantly from sample to sample. This may be partially due to the different surface preparation and/or due to alignment which can more strongly affect the low-energy electrons.

We have carried out *ab initio* calculations for both the bare and the hydrogen-terminated 2×1 reconstructed diamond surfaces, in order to resolve whether the observed 2×1 reconstructed surface is a hydrogen-free or a monohydride-terminated surface. The calculations were based on the local-density approximation and the Car-Parrinello formalism.[17] The hydrogen-free (100) surface was modeled by a supercell consisting of a slab of ten layers of diamond with twelve carbon atoms on each layer. The slabs were separated by 10 Å of vacuum. One hydrogen atom was attached to every surface carbon atom to model the monohydride surface. Due to the size of the supercell, only Γ-point sampling was used. Starting from an approximate structure, the ground-state geometry was obtained by steepest descents and/or fast relaxation methods.[18] The vacuum level of the surface was determined from the plane-averaged, self-consistent potential in the vacuum region. Since calculations based on the local-density approximation do not reproduce well the experimentally measured band gap,[19] the position of the conduction-band minimum is determined by adding the experimental value for the band gap (5.47 eV) to the position of the valence-band maximum. The position of the valence-band maximum was found by adding the energy difference between the average self-consistent potential in the bulk and the highest occupied energy level in bulk calculations to the average self-consistent potential inside the slab.

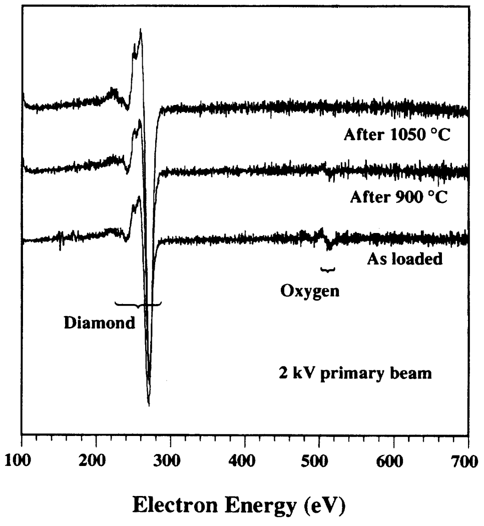

FIG. 2. Auger spectra, obtained from the diamond (100) surface, as a function of annealing temperature. Oxygen, which is present on the surface after sample preparation, is observed to evolve at ~900 °C, and removed after a 1050 °C anneal. The removal of oxygen coincides with the transformation of the surface from a 1×1 to a 2×1 reconstructed surface.

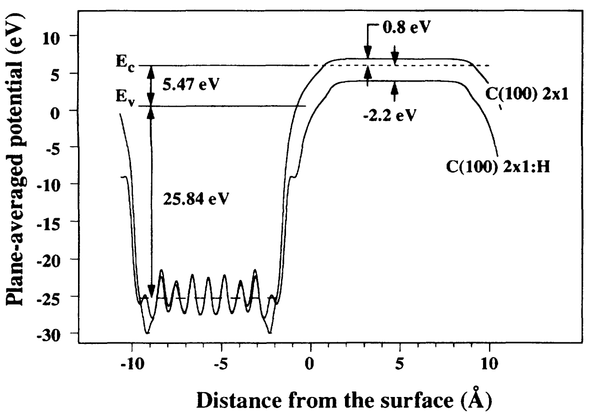

FIG. 3. Calculated plane-averaged, self-consistent potentials of a hydrogen-free and monohydride-terminated 2×1 reconstructed diamond (100) surface.

The calculations indicated that the monohydride-terminated surface relaxes to a 2×1 reconstructed surface. The plane-averaged, self-consistent potential for this surface is shown as a function of the distance to the surface in Fig. 3. As can be seen in the figure, the effective potential has flattened out in the vacuum region, which indicates that the slab separation used in the calculations is sufficiently large to avoid interactions between the slabs. The flat region is representative of the vacuum level. The conduction-band minimum is found at ~2.2 eV above the vacuum level, resulting in a ~2.2-eV NEA for C(100)-2×1:H surface.

The bare C(100) surface also relaxes to a 2×1 reconstruction, with a geometry similar to that obtained by other authors.[9,20] Substantial displacements from the ideal bulk positions were found in the surface layers. The plane-averaged self-consistent potential for this surface is also shown in Fig. 3. A ~0.8-eV positive electron affinity was found for this surface. We also find that occupied surface states exist inside the band gap near the valence-band maximum, in agreement with photoemission studies.[13] The calculations indicate that these states are related to dangling-bond orbitals on the dimer atoms. The electronic charge in these dangling orbitals results in a stronger dipole layer of the bare surface when compared to the hydrogenated surface. The differences in work function and electron affinities between these two surfaces are due to this dipole layer.

The chemical-vapor-deposition (CVD) -grown diamond (100) surface is known to exhibit a 2×1 reconstruction, which has been shown to be stable in air.[11] This 2×1 reconstruction has been attributed to the presence of a monohydride structure.[5–7] Based on the results described above it is expected that the CVD growth surface would exhibit a NEA. To further explore the structure of the growth surface, diamond was deposited on a (100) oriented, type-IIb diamond wafer, resulting in a homoepitaxial film. After transport in air a faint pattern associated with the 2×1 reconstruction could be discerned. The film was etched with chromic acid to remove a dark discoloration that was attributed to the presence of sp^2 bonded carbon. After the etch, the 2×1 reconstruction could not be discerned but the 1×1 bulk pattern remained. The dark discoloration largely remained, indicating that the sp^2 bonded carbon likely resided near the film-substrate interface. Photoemission spectra, shown in Fig. 4, exhibited a clear peak at 7.3 eV below the bulk feature indicating the presence of a NEA. From this experiment it appears that the 2×1 growth surface either exhibits a NEA during or after growth, or that a NEA can be easily induced on the growth surface (i.e., without a high-temperature anneal).

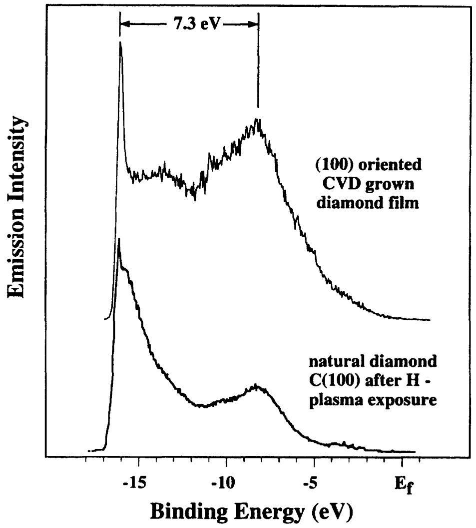

FIG. 4. Photoemission spectra obtained from CVD-grown, homoepitaxial (100)-oriented diamond film, and a H-plasma exposed (100) diamond surface at 350 °C.

In summary, a NEA was obtained on the diamond (100) surface by annealing a polished and chemically cleaned surface to ~1000 °C. This resulted in the desorption of oxygen and the appearance of a 2×1 reconstruction. After exposure to an H plasma at 350 °C, a 2×1 LEED pattern remained and the UPS indicated a NEA. Theoretical calculations indicate that the NEA is associated with a hydrogen-terminated surface. It was found to be possible to prepare a NEA on a CVD-grown diamond (100) surface without a high-temperature anneal, and it was suggested that the surface may exhibit a NEA during or immediately after growth. Many more NEA emitters are likely to be found as the methods for growth of wide-band-gap semiconductors are improved. Local-density-based calculations, when corrected for the band-gap effect, appear to predict correctly the occurrence of the NEA effect. These calculations can thus be used to identify other promising passivant-semiconductor combinations for NEA emitters, and to establish trends in dipole strength and sign. Photoemission experiments provide unambiguous evidence of the existence of NEA, and can be used both to calibrate the theoretical findings and to verify the actual occurrence of NEA.

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