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Negative-electron-affinity effect on the surface of chemical-vapor-deposited diamond polycrystalline films

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Strong negative-electron-affinity effects have been observed on the surface of as-grown chemical-vapor-deposited diamond using secondary-electron emission. The samples were randomly oriented polycrystalline diamond films terminated with hydrogen. The effect appears as an intensive peak in the low-energy part of the spectrum of the electron energy distribution and may be described in the model of effective negative electron affinity.

One of the remarkable features of diamond is the negative electron affinity (NEA) that may be observed on its surface under specific conditions.[1–10] For NEA the vacuum energy level lies below the conduction-band minimum, which allows electrons to escape easily from the surface.[11] Semiconductors with NEA are widely used as photo- and cold-cathode emitters.

NEA from diamond has been shown to be correlated with the presence of hydrogen bonded to the surface.[1–5] Special surface treatment of single-crystal diamond and epitaxial films is, therefore, usually necessary to activate NEA. Recently, chemical-vapor-deposited (CVD) polycrystalline diamond films have received a great deal of attention because they are promising for novel electronic applications due to their advantages in comparison with diamond single crystals. Their fabrication is relatively easier and less expensive, they can be grown with high levels of impurity doping, and they can have correspondingly high conductivity.[12] CVD diamond has also been observed to display high secondary-electron emission (SEE) properties. Total secondary electron yield coefficients, $\sigma=12$–50, have been measured from such films terminated with hydrogen,[13–16] which is indirect evidence of a strong NEA effect in this material.

In this paper we present a direct proof of the NEA effect on the surface of as-grown CVD randomly oriented polycrystalline diamond films.

Since the pioneer work[1] a commonplace tool for determination of the presence of NEA in diamond has been the method of ultraviolet photoemission electron spectroscopy (UPS). The idea behind the measurement is very simple. Hot electrons photoexcited to the conduction band cool in the process of energy relaxation and accumulate in the conduction-band minimum. At a NEA surface these electrons can be emitted into the vacuum without any energy barrier and appear in the photoemission spectra as a sharp peak at low electron energies. Obviously, the existence of the same kind of peak should be expected at the low-energy edge of the SEE spectra under excitation of a NEA surface with a beam of primary electrons.

In this study, we use SEE spectroscopy to find a NEA phenomenon in CVD randomly oriented polycrystalline films. The samples were made by depositing 10–20-μm-thick continuous films on Mo substrates by microwave-plasma CVD. During the deposition process, the films were heavily doped with B up to a concentration of about 10^{20} cm^{-3}, which was estimated from the film conductivity measurements.[17] Raman spectroscopy of the grown CVD films has shown a very sharp peak at 1331 cm^{-1}, characteristic of the diamond sp^3 bond, and a negligible background of nondiamond carbon. After deposition the diamond films were exposed to air; however, analysis of their Auger spectra did not show any contamination by oxygen. Furthermore, the only element detected at the surface was carbon.

Experiments were conducted in an ultrahigh vacuum chamber with a base pressure of 2×10^{-10} Torr. Energy distributions of the secondary electrons were measured with a single pass (Perkin Elmer) CMA Auger analyzer with an energy resolution of 0.6% and collection angle of 42±6°. This resolution obviously cannot be sustained down to the very small energies; however, in other experiments with this analyzer we were able to observe features with full width at half maximum (FWHM) less than 0.1 eV at energies close to 0 eV. Consequently, we can conclude that the resolution of our analyzer was better than 0.1 eV.

All our samples were biased at $V_t=-1.5$ to -5 V, where V_t is the bias voltage of the target, during the measurements, to compensate for the work-function difference between the target and the analyzer and to make the measurements of the low-energy region of the spectrum more reliable. In this range of the applied bias the measured electron energy spectra shifted linearly with voltage. Hence, for convenience the experimental data are displayed as a function of energy $E=e(V_a-V_t)$ (where V_a is the analyzer sweep voltage).

Figure 1 shows the low-energy part of the secondary-electron spectra of an as-grown CVD diamond polycrystalline film. For this sample $\sigma=35$ was measured with a primary beam energy $E_p=3$ keV. It can be seen that most of the secondary electrons are collected in the form of a sharp low-energy peak with position of the maximum at $E_{\max}=(0.5$–$0.6)$ eV and with FWHM ranging from 0.6 to 0.7 eV. The sample bias had very little effect on the position of the maximum adjusted for the bias, the shape of the energy distribution curves, and their dependence on electron-beam energy, in the measured range. Therefore, we can conclude that there were no significant instrumental distortions of the true electron spectrum caused by changes in electron trajectories and collection angle in our experiments. Observation

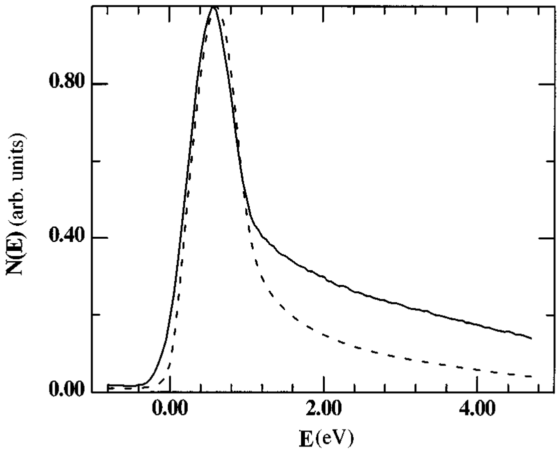

FIG. 1. Energy distributions of secondary electrons $N(E)$, for primary energies $E_p=200$ eV (solid curve), and $E_p=1500$ eV (dashed curve). Data are normalized to the low-energy peak maximum.

of the strong low-energy peak in the secondary-electron distribution is evidence of the NEA effect in CVD diamond films.

To investigate the role of hydrogen termination on the NEA effect, the influence of beam exposure on the spectrum was studied. Continuous electron-beam irradiation of these films is well known to result in desorption of hydrogen from the surface and, in turn, a decrease in the secondary-electron yield.[16] Figure 2 demonstrates the transformation of the secondary-electron spectrum after exposure to the electron beam for up to 6 h at a current density of 0.180 mA/cm^2 and $E_p=3$ keV. This treatment of the surface led not only to the significant reduction of the value of σ (from 32 to 5) but also to the decrease of the contribution of the low-energy peak to the energy distribution (dotted curve). Subsequent exposure of the sample to a molecular hydrogen environment at a pressure of 5×10^{-6} Torr for 1 h restored the primary distribution function of the secondary electrons (dashed curve). Therefore, we observed a direct correlation between hydrogen coverage and NEA effect of the diamond film surface. The change of the surface termination of the natural diamond crystal surfaces was earlier observed only under exposure to atomic hydrogen.[3,9] However, it was discovered[13–16] that exposure of the CVD diamond films to the molecular hydrogen environment can change the termination of the surface bonds for these films. In these experiments during the hydrogen exposure we did not have any hot tungsten filaments and did not make any other special efforts to create atomic hydrogen;[13–16] however, we cannot claim that absolutely no atomic hydrogen was present in the vicinity of the surface. It is also possible that there is a difference in the adsorption process at the single crystal and CVD diamond surfaces.

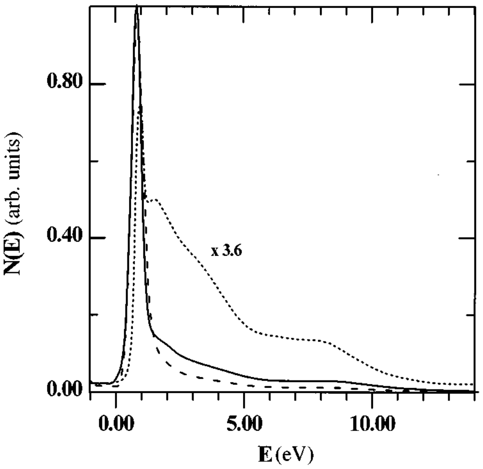

FIG. 2. Energy distributions of secondary electrons for as-grown diamond film, solid curve; after exposure of the film to the electron beam for up to 6 h at the current density of 0.18 mA/cm^2 and $E_p=3$ keV, dotted curve; and after subsequent exposure of the same film to a molecular hydrogen environment at the pressure of 5×10^{-6} Torr for 1 h, dashed curve. Data are normalized to the low-energy peak maximum of the solid line.

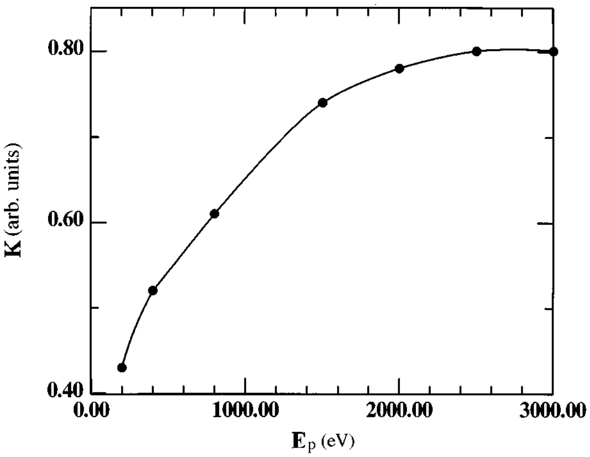

FIG. 3. The ratio K of the number of very-low-energy electrons in the peak of $N(E)$ to the total number of observed secondary electrons as a function of energy of the primary electron beam.

The total secondary-electron emission yield of the diamond films on Mo was previously observed to increase with an increase in the primary beam energy in the range of $E_p=1–1.5$ keV and to saturate at the larger beam energies.[13–15] In this study we investigated changes in the SEE spectra versus E_p and found that the yield increase was accompanied by the enhancement of the low-energy peak magnitude as compared with the rest of the energy distribution curve (see Fig. 1). The ratio K of the number of low-energy electrons in this peak (the area under the peak) to the total number of secondary electrons (the area under the distribution curve in the measured range up to $V_a=14$ eV) versus E_p is shown in Fig. 3.

There are two possible ways to describe the NEA phenomenon (Fig. 4).[6,9–11] It can be done in terms of either true or effective negative electron affinity. The effective NEA can be described as a consequence of the depletion band bending at the surface of the semiconductor. This band bending may result in the vacuum energy level occurring at an energy below the minimum of the conduction band.[11] The magnitude of the effective NEA can be defined as $\chi_{\mathrm{eff}}=\phi_{\mathrm{BB}}-\chi$, where ϕ_{BB} is band bending and χ is positive electron affinity [Fig. 4(b)]. Band bending occurs when electric charge is trapped by the surface states. Although it is known that a

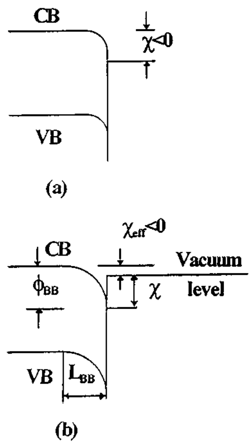

FIG. 4. Near the surface band diagram of a semiconductor for (a) true negative affinity and (b) effective negative affinity models.

hydrogen terminated surface of the single-crystal diamond does not exhibit surface states,[12] the case of the diamond film may be different. The surface of the CVD diamond film is quite jagged and the crystal structure might be distorted, which could result in the appearance of surface states. Surface states may be also induced by trapping residual oxygen at the surface at concentrations below the limit of detection by our Auger spectroscopy measurements.

Data obtained in this investigation agree with the effective NEA model for CVD diamond films rather than with the true NEA model, which was found to be valid for the surface of natural diamond crystals.[8,9] Indeed, the increase of the efficiency of the low-energy electron emission as the primary beam energy is increased (Fig. 3) may be easily understood in the model of the effective NEA. The thickness of the depletion layer can be evaluated from the expression[18] $L_{\mathrm{BB}}=(\phi_{\mathrm{BB}}\kappa/2\pi e N_A)^{1/2}\approx25$ Å for our samples,[19] taking for the estimation $\phi_{\mathrm{BB}}=1$ eV, dielectric constant $\kappa=5$, and $N_A\approx10^{20}$ cm^{-3}.[17] The mean free path of electrons with $E_p<1$ keV in solids does not exceed 20–30 Å and excitation of the secondary electrons occurs mostly in the surface depletion layer, from which the large number of low-energy electrons cannot escape due to the existence of a potential barrier. At $E_p>1.5$ keV the secondary electrons are excited below the depletion layer and the low-energy electrons can freely escape into the vacuum from the bulk conduction band (to be shown below). Therefore, the contribution of the very-low-energy electrons into the energy distribution spectrum increases sharply with the increase of the primary beam energy. In the case of true NEA it should be expected that the relative contribution of the very-low-energy electrons into the spectrum would not strongly depend on the energy of primary electrons, because the secondary electrons would not be trapped by the surface at any depth of their generation.

It can be seen from Figs. 1 and 2 that FWHM of the low-energy peak is much larger than kT. The same peak shape has been observed in all photoemission measurements independent of the crystal orientation of the surface and its preliminary treatment when samples were excited by photons with energy significantly exceeding the diamond band gap.[1–10] It might be, therefore, that the peak width is associated with the energy distribution of electrons inside the crystal rather than with surface potential fluctuations.[1] A strong nonequilibrium distribution of low-energy electrons in the conduction-band minimum is produced during the SEE process because their escape time τ_{esc} is smaller than the energy relaxation time, which is mainly determined by interaction with optical phonons. If the electron energy does not exceed the energy of a few optical phonons this relaxation time can be estimated as $\tau_\epsilon\approx10^{-12}$–$10^{-13}$ s.[20,21] At the depth of penetration of the primary electrons in the crystal $1\approx50$ Å, and velocity of the low-energy secondary electrons $v\approx10^{7}$ cm s^{-1}, $\tau_{\mathrm{esc}}=1/v<10^{-13}$ s. The condition $\tau_{\mathrm{esc}}<\tau_\epsilon$ is fulfilled for all electrons contributing to the peak, which has FWHM approximately equal to four times the energy of an optical phonon in diamond [$\hbar\omega_{\mathrm{opt}}=0.163$ eV (Ref. 12)]. The relaxation time of electrons with energies less than $\hbar\omega_{\mathrm{opt}}$ is much longer than 10^{-12} s. Therefore, we can anticipate that the maximum of the energy distribution of secondary electrons in the conduction band would be at least the energy of an optical phonon above its bottom. Consequently, assuming that the secondary electrons with zero kinetic energy are coming out of the solid at the vacuum level, we can estimate the value of χ_{eff} for the film under investigation as $|\chi_{\mathrm{eff}}|<(E_{\mathrm{max}}-E_0)-\hbar\omega_{\mathrm{opt}}$. Using data from Fig. 1 and the band diagram (Fig. 4) we obtained $|\chi_{\mathrm{eff}}|<0.4$ eV.

In conclusion, we have found a strong NEA effect on the surface of a randomly oriented CVD polycrystalline diamond film terminated with hydrogen using the SEE spectroscopy method. The effect appears as a strong peak at the low-energy part of the electron-energy distribution and may be described in the model of effective NEA.

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