Electron Emission Due to Exciton Breakup from Negative Electron Affinity Diamond

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We identify exciton breakup at the surface as the dominant source of photoelectron emission from negative electron affinity diamond (111):H for near band gap excitation up to 0.5 eV above threshold. Dependence of photoelectron emission characteristics upon excitation energy suggests the thermalization of carriers via a Fan phonon-cascade mechanism.

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Photoelectron emission is a well-understood process which has evolved into a powerful spectroscopy for the study of the electronic structure of solids and surfaces. In contrast to common understanding, we find that bound electron-hole pairs (Mott-Wannier excitons) are the dominant source for photoelectron emission from specially prepared diamond surfaces. In this Letter, we present the first identification of electron emission from exciton breakup at a semiconductor surface.

In a typical band scheme of a semiconductor surface (Fig. 1) the vacuum level lies above the conduction band minimum (CBM) creating an energy barrier (the electron affinity χ) which prevents low energy electrons from escaping into the vacuum. If the vacuum level lies below the CBM, then $\chi < 0$ and a negative electron affinity (NEA) surface is produced. NEA semiconductor surfaces are normally prepared by combining heavy p-type doping and monolayer cesium surface coatings [1]. Through band bending, this structure forces the bulk CBM to lie above the vacuum level and therefore produces an NEA surface. A direct empirical determination of the presence of NEA is to photoexcite valence electrons to the CBM and to observe whether electron emission occurs. Himpsel *et al.* first demonstrated [2] that the (111)-(1 × 1) diamond surface has negative electron affinity when hydrogen terminated [3]. In contrast, the hydrogen free (111)-(2 × 1) reconstructed diamond surface has positive electron affinity [4]. NEA activation of diamond (111) by hydrogen termination has been achieved by a variety of means including mechanical polishing in olive oil followed by solvent degreasing [3]. Other preparations have also produced diamond surfaces which exhibit NEA characteristics [5].

All data presented in this Letter are from the as-polished, (111)-(1 × 1):H diamond surface of a four carat, type IIb, diamond single crystal (our sample D5). The natural crystal was mechanically polished in olive oil, cleaned ultrasonically with organic solvents [3], and mounted on a liquid nitrogen cooled cryostat in an ultrahigh-vacuum (UHV) analysis chamber at 5×10^{-11} Torr base pressure. The diamond temperature was recorded using a chromel-alumel thermocouple in intimate contact with the back side. Total electron yield measurements were performed using a retarding field analyzer equipped with a position sensitive multichannel plate detector. Electron energy distribution measurements were taken with a hemispherical electron energy analyzer ($\Delta E = 0.1$ eV). The photon energy was selected from a Hg-Xe arc lamp by a 1 m normal incidence monochromator ($\Delta E \leq 50$ meV). Excitation spectra were normalized with respect to the photoyield of sodium salicylate which is known to be uniform [6]. Ultraviolet photoemission spectroscopy (UPS) measurements ($h\nu = 21.2$ eV and $h\nu = 40.8$ eV) indicate a diamond surface with NEA, and the absence of filled states in or near the gap, which are typical [2,3] properties of the (111)-(1 × 1):H diamond surface. Surface cleanliness characterization by Al $K\alpha$ x-ray photoelectron spectroscopy found 20% of a monolayer of oxygen.

The total photoelectron yield (Fig. 2) from the as-polished diamond (111)-(1 × 1):H surface at 295 (room temperature) and 130 K is found to exhibit an oscillatory structure [7] as a function of the excitation photon energy. The oscillations, which do not appear in the absorption coefficient [8], are evenly spaced with a 160 meV period. The oscillatory yield structure becomes more pronounced, and there is a striking increase in total electron yield as the temperature is lowered.

Spicer's three-step model [9] (absorption, transport, escape) may be used to estimate the functional form of the expected total electron yield. The electron yield as a function of the excitation photon energy $h\nu$, assuming

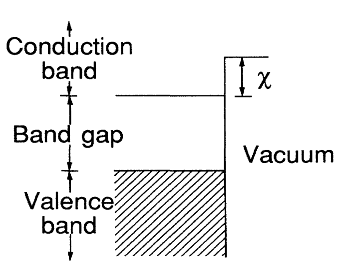

FIG. 1. Energy bands and vacuum level at a semiconductor surface. The electron affinity χ is defined as the energy difference of the vacuum level minus the conduction band minimum.

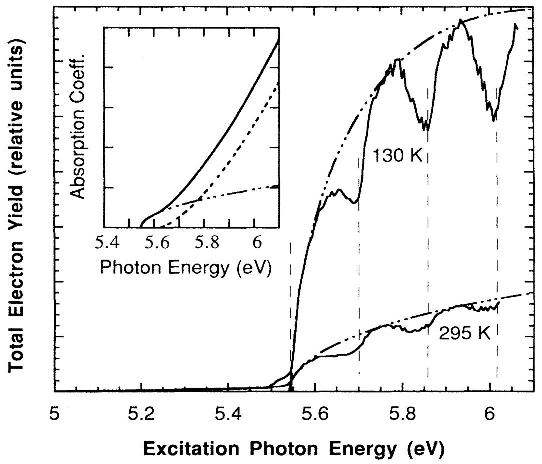

FIG. 2. Total electron yield vs excitation photon energy at 130 and 295 K from the as-polished (111)-(1 × 1):H NEA diamond surface (solid line).

transport via either a random walk or diffusion model, is given by [1,10]

$$Y(h\nu) = P(h\nu)\,\frac{L(h\nu)\beta(h\nu)}{1 + L(h\nu)\alpha(h\nu)}\,, \qquad (1)$$

where Y is the electron yield, P is the surface escape probability, L is the carrier escape length, α is the absorption coefficient, and β is the component of the absorption coefficient which creates the carriers that contribute to the emission.

Photoexcitation of an electron from the valence band maximum (VBM) to the CBM in diamond proceeds via an indirect transition which involves the simultaneous absorption of a photon ($h\nu$) with either phonon ($\hbar\omega$) emission ($h\nu - \hbar\omega = E_g$) or phonon absorption ($h\nu + \hbar\omega = E_g$). E_g denotes the band gap energy. Threshold photoexcitation into bound electron-hole pairs (excitons) similarly proceeds via an indirect transition ($h\nu \pm \hbar\omega = E_{gx}$), where E_{gx} denotes the indirect exciton energy gap. The exciton binding energy ($E_g - E_{gx}$) in diamond is 80 ± 5 meV [8,11]. Detailed analysis by Dean and co-workers [8,11] carefully identified the dominant indirect transitions which account for intrinsic photoabsorption in diamond. The inset in Fig. 2 shows the functional form of the total photoabsorption (solid curve) together with the first (dot-dashed curve) and second (dashed curve) principle components. Consistent with theory [12], Clark *et al.* [8] identified the first component ($\frac{1}{2}$ power law) to exciton producing indirect transitions, and the second ($\frac{3}{2}$ power law) to indirect transitions which create unbound electron-hole pairs (i.e., "free electrons" and "free holes"). Therefore, the absorption coefficient ($h\nu > 5.54$ eV) is given by $\alpha = A(h\nu - 5.54)^{0.5} + B(h\nu - 5.615)^{1.5}$. Using Eq. (1), the functional form of the total electron yield from the as-polished (111)-(1 × 1):H diamond surface (at both 295 and 130 K) can be reproduced from the absorption coefficient by assuming that the exciton producing component [$\beta(h\nu) = \alpha_{\mathrm{ex}}(h\nu) = A(h\nu - 5.54)^{0.5}$] dominates. This has been done (dot-dashed curve in Fig. 2) by assuming that P and L are independent of $h\nu$ and by taking the values of $\alpha(h\nu)$ and $\alpha_{\mathrm{ex}}(h\nu)$ from Clark *et al.* [8]. For a best fit, we choose values of L to be 1000 Å at 295 K and 5300 Å at 130 K while fixing P. The quality of the fit noticeably degrades if the escape lengths are changed by 20% or more. Except for periodic dips in the electron yield (discussed further below), there is striking agreement between the functional form of the total photoelectron yield and the exciton-derived emission model of Eq. (1). The total electron yield excitation spectra (Fig. 2) at excitation energies below $h\nu = 5.54$ eV can also be understood using the preceding analysis and a similar conclusion results [13]. The overall findings are that the total electron yield from threshold to $h\nu = 6.1$ eV is exciton derived.

The oscillatory dependence of the photoelectron emission on excitation energy appears similar to the oscillatory photoconductivity phenomena [14] which has been observed in a variety of semiconductors, and which can be understood within the framework of Fan's [15] phonon-cascade mechanism. In Fan's model, a short scattering lifetime for optical mode phonon scattering together with a much longer scattering lifetime for acoustic mode phonon scattering leads to a phonon-cascade thermalization of hot carriers which is dominated by optical phonon scattering. The photoexcited carrier energy increases with increasing photon energy. When the carrier energy is at or above the characteristic optical phonon energy, an optical phonon scattering event occurs which reduces the carrier energy. As discussed by Fan [15], this mechanism produces a mean carrier energy which oscillates as a function of the photoexcitation energy and with a period equal to the optical phonon mode energy.

In Fig. 3 we diagram the dispersion relationship of the exciton band for diamond, along with the unbound electron-hole states (continuum). In Fig. 2 with dashed lines we mark the excitation photon energies that result in hot excitons which can thermalize to the exciton band minimum via cascade emission of 160 meV phonons. Examination [13] of the phonon band structure of diamond [11,16] finds that TO phonon scattering is consistent with the observed 160 meV cascade. Because of the relatively flat optical phonon bands near the zone center, the energy of the small wave vector phonons involved in the cascade are quasimonochromatic. As the excitation photon energy increases above each threshold the mean kinetic energy of the excitons produced by the phonon-cascade mechanism also increases. When the kinetic energy of the exciton becomes comparable to its binding energy (80 meV), the probability of dissociation prior to reaching the surface becomes high. Therefore, beginning at 80 meV above

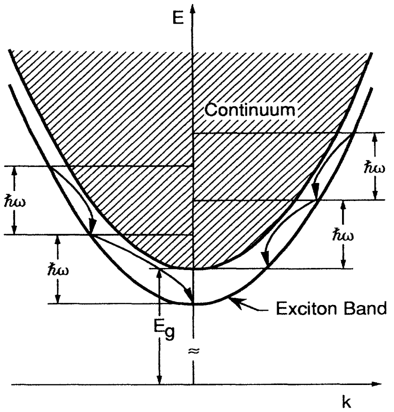

FIG. 3. Energy loss by phonon-cascade emission of photoexcited excitons for two different initial energies.

each cascade threshold and up to the next cascade threshold fewer excitons reach the surface. Consistent with the Fan model, the emission oscillations correspond to oscillations in the flux of excitons that reach the surface.

As shown in Fig. 3, a significant component of the total photoabsorption is the excitation of "free" conduction band (CB) electrons. However, as evidenced by the electron yield excitation spectra (Fig. 2), electrons derived from this absorption component are not seen in emission. Within the three-step model, one must consider both transport and escape mechanisms which affect electron emission from the CB of diamond (see below). Regardless of the mechanism responsible for the quenching of CB emission, the absence of this emission suggests that the exciton-derived emission must result from exciton dissociation at the diamond-vacuum interface.

Upwards band bending at the surface produces an electric field which repels CB electrons, yet has little effect on uncharged carriers such as excitons. In this way, upwards band bending can act to selectively "turn off" the transport of CB electrons to the surface without altering exciton transport. From UPS measurements we have determined that the VBM at the surface lies at an energy of 0.4 eV below the Fermi level. If the bulk VBM lies at an energy separation larger than 0.4 eV below the Fermi level then upwards band bending at the surface exists and could account for the absence of CB electron yield. A bulk VBM which lies greater than 0.4 eV below the Fermi level is consistent with doping levels which have been reported for natural type IIb diamond [17]. Consistent with these band-bending arguments, modification of the energy of the surface VBM (with respect to the Fermi level) to produce downwards band bending has resulted in an electron yield which is modeled by the total (CB and exciton) absorption coefficient [18].

The indirect band gap of diamond has implications for the escape probability of CB electrons from the (111) surface. A simple one-electron, transport-escape model of electron emission from a perfect surface requires conservation of the component of the electron wave vector ($k_{\parallel}$) in a direction parallel to the emission surface [19] in addition to conservation of energy. In order to emit CBM electrons from the (111) diamond surface, energy and $k_{\parallel}$ conservation arguments require that the magnitude of the negative electron affinity should satisfy the following condition (see Appendix C of Ref. [1]):

$$\chi \leq \frac{\hbar}{2m}\,\frac{2}{3}\left(\frac{2\pi k}{a}\right)^2 = -4.55\ \mathrm{eV}, \tag{2}$$

where a is the unit cell dimension ($a = 3.567$ Å) and $k = k_{\mathrm{CBM}}/k_X = 0.76$. From this analysis one concludes that if $\chi > -4.55$ eV, then CBM electrons are totally internally reflected at the vacuum-solid interface. Alternatively, if $\chi \leq -4.55$ eV, then both energy and $k_{\parallel}$ conservation are satisfied and electron emission could occur. In this case, the wave vector of the emitted electrons have a large $k_{\parallel}$ component which implies [due to (111) surface symmetry] a distinct threefold azimuthal angular distribution of emission, with little intensity directed along the surface normal. The observed emission [20] is directed along the surface normal with a broad (70° FWHM) angular width and cylindrical symmetry. The above considerations suggest that CB electrons are hindered from electron escape due to wave vector conservation. Higher order processes, such as phonon assisted emission, can overcome this restriction but do not qualitatively change the low escape probability for emission from the CB.

The emitted electron energy distribution at a variety of excitation energies (peaks and valleys of Fig. 2) is presented in Fig. 4. These energy distributions have been normalized to the same peak intensity for presentation purposes, and have been vertically shifted by an amount

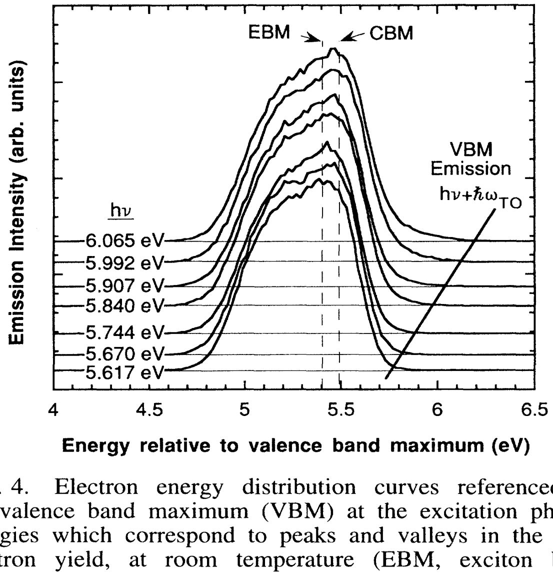

FIG. 4. Electron energy distribution curves referenced to the valence band maximum (VBM) at the excitation photon energies which correspond to peaks and valleys in the total electron yield, at room temperature (EBM, exciton band minimum).

proportional to the excitation photon energy. A solid line marking the emitted electrons with highest kinetic energy ($h\nu + \hbar\omega_{\text{TO}}$) corresponds to emission of CB electrons photoexcited from the VBM which have suffered no inelastic scattering during transport to or escape from the surface. The dominant emission is a broad energy distribution (0.6 eV FWHM) with emission energies which lie within the band gap of diamond. We attribute the emission at energies below the CBM as exciton derived, and emission at energies above the CBM as conduction band derived. Partial electron yield measurements [13] have found that the oscillatory photoyield is due to a uniform variation in the emission intensity of the broad emission below the CBM.

Another form of exciton-induced electron emission has been observed in certain alkali halides [21]. In the mechanism proposed by Apker and Taft [22], excitons which recombine at *F*-center sites transfer energy to the *F*-center electron and thereby produce hot CB electrons which are reflected in increased photoelectron yield. Apker and Taft found that electron energy distribution measurements directly demonstrate the existence of hot CB electrons with emitted energies equal to the sum of the excitation photon energy plus the energy of the defect center involved. This is in contrast to our observed electron energy distributions from diamond, which are dominated by emission at kinetic energies which correspond to the band gap region. The Apker-Taft model is also in conflict with our findings that emission from CB electrons (produced in photoabsorption or otherwise) is inhibited relative to exciton-derived emission. The exciton-induced emission of Apker and Taft is therefore distinct from the exciton-derived emission reported here.

Finally, we comment on the electron emission dynamics of exciton breakup at the NEA diamond (111) surface. Electron emission due to simple dissociation at the surface of the bound electron-hole pair is unlikely due to wave vector conservation arguments similar to those presented above for CB emission. However, because of the dipole nature of the surface-vacuum interface and the polar nature of the electron-hole pair, it is reasonable to expect strong exciton-lattice coupling which results in phonon emission during exciton breakup at the surface. Electron-emitting exciton breakup then becomes a many-body problem with emission of not only a free electron, but also multiple phonons and a hot hole. The qualitative effect of a many-body final state is (as in nuclear β decay) to produce a broad kinetic energy distribution of the emitted particle, due to the variety of accessible final states of the system. As discussed earlier, the exciton-derived emission is in the form of a broad electron energy distribution.

In conclusion, we have found that exciton-derived electron emission is the dominant emission mechanism for near band gap photoexcitation from the as-polished NEA (111)-(1 × 1):H diamond surface. Because of band bending and/or wave vector conservation there is an absence of electron emission derived from CB electrons created in the photoabsorption process. The exciton-derived emission must therefore result from exciton dissociation at the diamond-vacuum interface. The oscillatory yield structure is explained in terms of exciton transport (the Fan model) rather than a variation in the absorption coefficient. We suggest that the dominance of the exciton-derived emission and the broad kinetic energy distribution of emitted electrons is a direct result of the many-body dynamics of exciton breakup at the NEA surface.

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