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Role of electronic band structure and resonances on electron reflectivity and vibrational excitation functions: The case of hydrogenated diamond

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We report on an high resolution electron energy loss study of electron surface reflectivity and excitation of the C–H stretch mode of hydrogenated polycrystalline diamond films at low energy. Their specular energy dependences demonstrate that (i) the reflectivity is dominated by the conduction band structure. In particular the second absolute band gap of bulk diamond results in a strong increase of the elastic backscattered intensity around 13.5 eV. (ii) The vibrational excitation is dominated by a negative ion resonance process around 8 eV and a band gap induced scattering enhancement around 13 eV.

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Low energy electron scattering by means of high resolution electron energy loss spectroscopy (HREELS) technique is widely used for the study of adsorbate chemisorbed on metals[1] or semiconductors surfaces.[2] This technique is a highly surface sensitive method capable in particular of determining adsorbate vibrations, and thereby basic adsorption geometries and bonding to the substrate. Scattering mechanisms are usually derived from vibrational cross sections measured as a function of the scattering angle and/or as a function of the incident electron energy.[3] In number of studies vibrational excitation functions (intensity variation of vibrational energy losses as a function of the incident electron energy) are normalized to the elastic peak or to the background intensities and any observed enhancement in these curves is associated with resonant processes.[1,2,4] However this normalization procedure may complicate or make impossible the understanding of the electron scattering mechanisms, as the elastic or background intensities are modulated by the conduction band density of states (CB DOS) above the vacuum level of the substrate-adsorbate complex.

In order to clarify this point we investigate experimentally in this work the role of CB DOS on electron scattering, i.e., surface reflectivity (cross section of quasielastically backscattered electrons) and vibrational excitation, from bare and hydrogenated (CVD and in-situ) diamond. These systems have been chosen because they have been extensively studied in view of their many possible applications[5] and are thus particularly well known. More specifically (i) possible bonding configurations of hydrogen on diamond have been experimentally determined by vibrational spectroscopy.[6,7] (ii) The electronic band structure of diamond above vacuum level has been calculated.[8] (iii) It has been established from near-edge x-ray absorption fine structure (NEXAFS) measurements[9,10] that adsorption of atomic hydrogen preserves the bulk electronic band structure up to the surface. As expected the major features of the reflectivity curves obtained are related to the characteristics of the CB DOS, in particular the strong enhancement of the backscattered intensity observed around 13 eV is associated to the existence of the second absolute band gap of diamond. Concerning the vibrational excitation functions of the C–H stretching bond, they present peaks around 8 and 13 eV. We associate the latter to the second absolute band gap: the backscattered electrons in this energy range cannot penetrate the substrate and the most probable exit channel for these electrons is the vacuum, which explains the observed enhancement. The peak at 8 eV is attributed to the negative ion resonance (NIR) responsible for H^- desorption.[11] This work demonstrates that the understanding of any scattering mechanisms requires the knowledge of *both* the energy dependence of the quasielastically and of inelastically backscattered electrons.

The experiments were performed in a UHV system (base pressure below 5×10^{-11} Torr) with a HREEL spectrometer (IB500 by OMICRON), which has been specially designed to record energy loss spectra as well as quasielastic (reflectivity) and inelastic (vibrational) excitation functions in the energy 2–20 eV.[12] All the spectra presented were obtained in the specular geometry with an incident direction of 55 degrees from the surface normal and an overall resolution of ~ 5 meV, measured as the full width at half maximum (FWHM) of the elastic peak.

The samples, polycrystalline diamond films, were deposited on *p*-type doped silicon substrates by a standard microwave chemical vapor deposition (CVD) using conditions described elsewhere.[11] The thickness of the as grown films were 5–10 μm with crystallite size of 1–2 μm. These CVD conditions result in fully hydrogen terminated surfaces. The surface composition and phase purity of the films were examined ex-situ by various spectroscopic methods and photodesorption. Before performing the measurements these ex-situ hydrogenated samples were annealed to 400 °C in the UHV to desorb all species possibly physisorbed on its surface like water or hydrocarbons.

Bare diamond films surfaces were prepared in-situ by several annealing cycles to 1000 °C. In-situ hydrogenated/deuterated diamond surfaces were prepared by exposure of the bare surface to activated hydrogen/deuterium during of 1–1.5 h. This was achieved by molecular gas flow over a hot

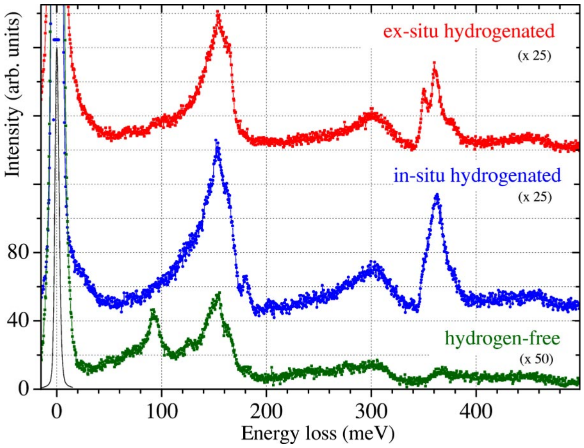

FIG. 1. (Color online) HREEL spectra of the hydrogen-free diamond ($E_0 = 9$ eV), in-situ hydrogenated ($E_0 = 8$ eV), and ex-situ hydrogenated ($E_0 = 8$ eV) surfaces. The elastic peak intensity is arbitrarily normalized to 200.

(1850 °C) tungsten filament positioned 3 cm away from the sample surface. The surface temperature during this process was only few tens degrees above room temperature, and the pressure of hydrogen was kept at 1×10^{-5} Torr by leaking hydrogen into the system and continuously pumping with a turbomolecular pump to maintain high-purity conditions.

Figure 1 shows HREEL spectra of the bare diamond surface at incident electron energy of 9 eV and of CVD and in-situ hydrogenated surfaces obtained at incident electron energy of 8 eV. These spectra are in general agreement with those obtained in previous studies and are quite well understood.[7] Only the striking features are described in this paper and we refer to previous publications for exhaustive discussion of the HREEL spectra.[7,13] The spectrum of the bare surface is mainly characterized by a strong C–C vibration peak around 154 meV and its overtones around 300 and 450 meV, and a peak at 92 meV which corresponds to the π^* bonded carbon dimers (C═C) upon closing the surface dangling bonds (surface reconstruction). The HREEL spectra of the hydrogenated surfaces present remarkable changes as compared with the bare surface one. The C═C bond peak is completely absent, while the peak associated with the C–H stretching modes and centered at 361 meV is now strong, indicating that the diamond surface is fully hydrogen terminated. This last feature[14] results from the contribution of losses attributed to the excitation of symmetric and asymmetric stretching vibrations in different types of C–H bonds (mono-, di-, and tri-hydrides) present on the polycrystalline diamond surface.[4,6,7]

The specular elastically backscattered electron curves (reflectivity curves) measured for incident electron energies, E_0, in the 3–17 eV range for the three types of sample are shown in Fig. 2. These curves of hydrogenated and of hydrogen-free diamond surfaces present completely different features. For the hydrogenated surfaces the reflectivities are very similar and are essentially dominated by an intense peak at 13.5 eV and smaller peaks at 10.5 and 8 eV. In the case of hydrogen-free surface, peaks at 11.5 and 8.5 eV are observed.

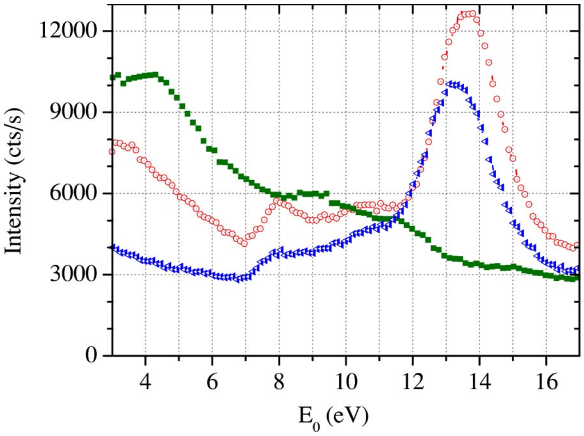

FIG. 2. (Color online) Specular electron reflectivity curves for the hydrogen-free (full squares), in-situ hydrogenated (triangles), and ex-situ hydrogenated (hollow circles) diamond surfaces.

As expected the reflectivity curve for in-situ deuterated surface (not shown here) is identical to the in-situ hydrogenated one, since the electron reflectivity depends *essentially on the electronic structure* of the substrate upper atomic layers. Given that for the hydrogenated diamond surface, bulk band structure is maintained up to the surface as determined in NEXAFS experiments due to carbon dangling bonds saturation by hydrogen atoms,[9] we associate in this case the features in the reflectivity to the details of diamond band structure above vacuum level, and thereby to the features of the density of states.[8] In particular we associate the 13.5 eV feature with the second absolute band gap of diamond, since an electron having an energy in this range cannot propagate into bulk diamond. The fact that this band gap shows up in our experiment despite the polycrystalline nature of our substrate comes from its absolute character.

For hydrogen-free surface the reflectivity curve must be associated to the electronic structure of the reconstructed surface. As we observed from the NEXAFS spectrum of these surfaces, the electronic structure is modified upon reconstruction. In particular new states are created, located in the second diamond band gap, thus resulting in the absence of a maximum in the reflectivity curve around 13.5 eV.

The lower intensity peaks measured at 10.5 and 8 eV observed in the case of hydrogenated surface can also be associated with minima in the calculated conduction band density of states that also showed up in the NEXAFS spectrum. These features will be discussed in details together with those of hydrogen-free surface in a forthcoming paper.

Figure 3(a) presents the intensity of the C–H stretching mode excitation (energy loss 362 meV) scanned as function of the incident electron energy for in-situ and ex-situ hydrogenated surfaces. These curves related to the hydrogen terminations are as expected also similar to the energy dependences (not shown) for all the losses in the 350–380 meV range and for the C–D stretching mode, in the case of in-situ deuterated diamond substrate. The two main peaks around 8.5 and 13 eV are superimposed on a decreasing background. These different features have to be discussed in terms of electron scattering mechanisms: dipole, impact, and reso-

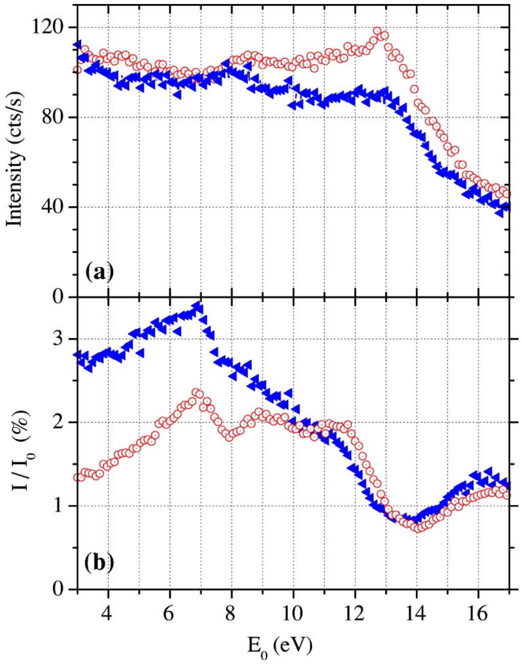

FIG. 3. (Color online) C–H stretching mode excitation functions for the in-situ (triangles) and ex-situ (hollow circles) hydrogenated diamond surfaces (a) as measured and (b) after normalization to the elastic peak intensity.

nance scattering. We associate the decreasing background to the contribution of the dipole scattering mechanism.

Resonant scattering for chemisorbed systems involves the temporary capture of the incident electron, either into an empty orbital of the adsorbate forming a negative ion resonance[15] or by the crystal surface giving surface state or surface resonance (SR). In the latter case, the resonant mechanism is connected with the electronic properties of the adsorbate-surface complex and two cases can be distinguished: one is related with beam emergence thresholds in LEED experiments[16,17] and the other to the coupling between the incident electron and a localized surface state.[18,19] Surface resonances associated to diffraction effects are not expected in this case considering the polycrystalline character of the present substrate, and furthermore considering the threshold for emergence of a new diffracted beam, estimated from the electron beam angle of incidence and the size of the reciprocal lattice of a diamond surface taken as monocrystal. We associate the 8.5 eV peak of Fig. 3 to an excitation process via NIR, which has been observed in around 9 eV in H^- electron stimulated desorption (ESD) experiments.[11] This assignment is also in agreement with the existence of a NIR in saturated hydrocarbons, contributing to vibrational excitation in the same 8–10 eV energy range.[20] In the NIR mechanism the incident electron may be captured into an empty orbital of the adsorbate and the increased interaction time between the incoming electrons and the system results in an increased efficiency in electron-molecule energy transfer. The competing decay channels of the NIR state are (i) electron autodetachment leaving the adsorbate-substrate complex in a vibrational excited state (as observed here) and (ii) dissociative electron attachment (DEA)[15] leading to the emission negative ion.

The enhanced excitation observed around 13 eV has to be related, most probably, to the presence of the diamond second absolute band gap. Since the probability for the electrons to enter the substrate is strongly reduced, the probability to be re-emitted is greatly enhanced. The number of electrons backscattered into the vacuum strongly increases, whatever the scattering process has been elastic or inelastic, i.e., in this particular case the excitation of the C–H stretching vibration. We prefer this tentative interpretation to the alternative ones, involving an increased probability of adsorbate-substrate complex vibrational excitation by resonant mechanisms, as no NIR are known in this energy range in saturated hydrocarbon molecules[20] and as SR have already been excluded for the studied system.

Figure 3(b) represents the excitation functions normalized to the intensity of the elastically backscattered electrons. The features of the divided curves can hardly be understood when considering the different scattering mechanisms, in particular the wide deep around 13 eV. These results show that such a normalization procedure is not suitable when working with a substrate presenting a band gap above the vacuum level.

Thoms and Butler have investigated hydrogen terminated C(100) single crystal diamond.[4] From angular measurements and integrated intensities of C–H related vibrational losses (155, 303, and 362 meV), deduced from HREELS spectra recorded over the reduced energy range 7–14 eV and normalized to the background, these authors concluded that impact scattering is the main involved electron mechanism. According to the presented elastic and inelastic excitation functions continuously recorded over the energy range 3–17 eV, dipole and resonant scattering are involved in addition to energy band structure effects.

In conclusion our work demonstrates that the understanding of electron scattering mechanisms from surfaces requires the knowledge of both the energy dependence of the quasielastically and of inelastically backscattered electrons. Electron surface reflectivity of hydrogenated polycrystalline diamond films is dominated by the conduction band electronic structure of diamond, in particular the second absolute band gap of bulk diamond results in a strong increase of the elastic backscattered intensity around 13.5 eV. The excitation processes of the C–H stretch mode at low energy is dominated by NIR around 8 eV and a band gap induced scattering enhancement around 13 eV.

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