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Scattering of small molecules from a diamond surface

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Abstract

The scattering of molecules from clean and hydrogen terminated (1 1 1) diamond surfaces is studied in the energy range from 400 to 3000 eV. The primary molecules are N_2 and O_2. At grazing incidence we observe scattering of intact molecules and dissociation processes. Most of the scattered particles are neutrals. Negative molecular ions are observed in the case of O_2. There are also negative atomic ions in the case of primary atomic O, and some positive atomic ions in all cases. The yield of O^- reaches the 10% range. The O_2^- yield is much lower, i.e. in the 1% range. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The formation of negative ions by scattering from surfaces has been subject of research for applications in fusion experiments [1]. More recently this kind of negative ion production was proposed as a technique for the detection of low energetic neutral particles in the Earth's magnetosphere [2,3]. In the mass spectrograph proposed for the IMAGE satellite mission, the neutral particles will scatter from Cs/W(1 1 0) [4] or Ba/W(1 1 0) [5] surfaces. At these low work function surfaces the affinity levels of atoms or molecules can be filled by resonant capture processes [6,7]. The disadvantage of the Cs/W and Ba/W 'converter' surfaces is the lack of long term stability making them not an optimal tool for satellite missions. Recently the diamond C(1 1 1)-surface has been investigated to serve as a converter [8]. Molecules and atoms scattered from C(1 1 1) reach negative ion yields of interest for the proposed applications. In the present paper we will report detailed results on the scattering, dissociation and negative ion formation of light molecules scattered from C(1 1 1) and for comparison from Pd(1 1 0).

2. Experiment

The experimental setup is a UHV system described previously [9]. We use a plasma ion source and a sector field magnet to make mass analysed monoenergetic beams of atoms and molecules. After the ion source and upstream from the magnet the ion beam is pulsed to afford time-of-flight (TOF) measurements. After the magnet, a gas cell is used to neutralise the ion beam if neutral incident particles are used. The target is mounted on a

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three axis manipulator equipped with electron beam heating. For the temperature control we use a thermocouple. For our experiments with C(1 1 1) we apply an old ‘trick’, i.e. mounting two targets in parallel on the same target holder [10]. The targets are aligned with respect to the *z*-direction of our experiment, or the vertical movement of the manipulator. That way all beam adjustments could be made using a metal target, here Pd(1 1 0), without causing possible damage of the diamond or having problems with charging. During the experiments we learnt that charging is no problem, the possible reasons being the small size of the diamond ($4\times4\times0.25$ mm^3), sufficient surface conductivity and/or the low primary beam current usual for TOF experiments. Since we use a natural, type IIa diamond, there is some conductivity. Downstream from the target, the TOF detector is mounted under a fixed scattering angle of 10° which means, we use a fixed angle of incidence of 5° measured against the surface. At such a small angle, the perpendicular momentum of the incident particles is small enough for surface channeling. After the target a postacceleration voltage can be applied to separate ions and neutrals. The Pd target is prepared by the usual cycles of sputtering and annealing. The C(1 1 1) target was sputtered at grazing angles of incidence only. The target cleanliness was probed by the TOF technique looking for recoil ions. Since the diamond surface is H-terminated, we tried scattering from sputter cleaned and H covered surfaces.

3. Results

From previous experiments we know N_2 dissociates when scattered off metal surfaces including Pd(1 1 0) by vibrational and rotational excitation only, i.e., there is no charge exchange process involved in the dissociation process [11,12]. The experimental evidence in the case of diamond shows very similar behaviour as for Pd(1 1 0) (Fig. 1). The molecular survival yield $N_2/(N_2+\frac{1}{2}N)$ has for both targets essentially the same energy dependence. The dissociation is slightly enhanced for diamond probably due to the better mass match of N and C compared to N and Pd. Therefore more energy can be transferred to the N_2 molecules in a collision.

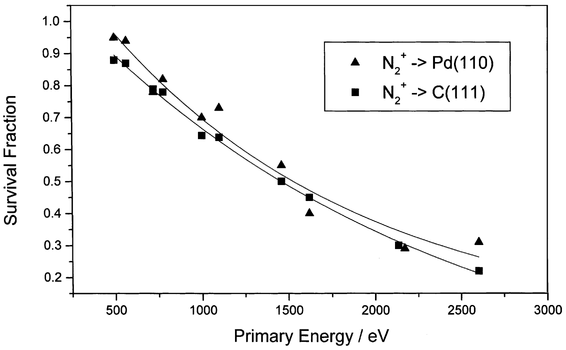

Fig. 1. Molecular survival fraction of N_2 scattered off Pd(1 1 0) and hydrogen terminated diamond C(1 1 1) at a grazing angle of incidence of 5° and a scattering angle of 10° as a function of the primary energy. Lines are drawn to guide the eye. The experimental error bars are ±10%.

In Figs. 2a and 2b we compare energy spectra of O_2 scattered off C and Pd. The large lower energy peak is the sum of the atoms produced by dissociation and of the surviving neutral molecules. The molecules form the narrow peak on top of the broad distribution of the dissociated atoms. This distribution exceeds partly the primary energy because of the energy gain of the atoms in the dissociation process. This gain is ‘multiplied’ when converting from the center of mass system, where the dissociation actually happens, to the laboratory system, where the process is observed, according to:

$$E = \frac{1}{2}E_0 + \frac{1}{2}E_D \pm \sqrt{E_0 E_D}\cos\alpha$$

where E_0 is the primary energy, E_D the dissociation energy and α is the angle between the molecular axis and the primary beam direction. The width of the dissociated atomic spectra from diamond shows no marked difference from the corresponding spectra from clean Pd. There are some differences in detail, i.e., the position of the ‘hat’ of the surviving molecules is shifted with respect to the distribution of dissociated atoms. This shift can be explained by the larger electronic energy loss and straggling of the atoms scattered off Pd

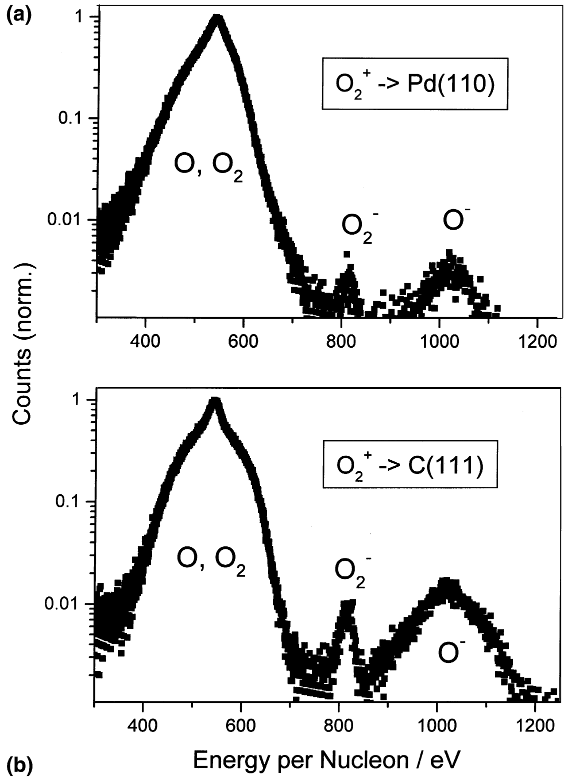

Fig. 2. (a) Energy spectra of O_1, O_2, O^- and O_2^- for O_2^+ incident on Pd(1 1 0) at an angle of incidence of 5° and a scattering angle of 10°. The primary energy is 1142 eV. The left part of the spectra shows the neutrals, where the small peaks are the neutral O_2 and the broad distribution exceeding the primary energy are the O. The negative ions O_2^- (narrow peak) and the O^- (broad peak) appear at higher energies due to the postacceleration. (b) Same as (a) for the hydrogen terminated diamond C(1 1 1) target.

compared to the scattering off diamond. Additional peaks appear at higher energies when a postacceleration voltage is applied. In the Pd(1 1 0) spectra these negative ion peaks are lower in intensity. The peaks are negative ions because they are postaccelerated with a positive voltage in order to separate them from the neutral peaks. The positive ion yield (negative postacceleration) is always lower than the negative yield. The narrow peak are obviously the O_2^- molecules and the broad peak the O^- atoms. For atomic primary particles (Figs. 3a and 3b) there is also a marked difference in the O^- yield for C(1 1 1) and Pd(1 1 0), respectively, quite obvious from the raw data.

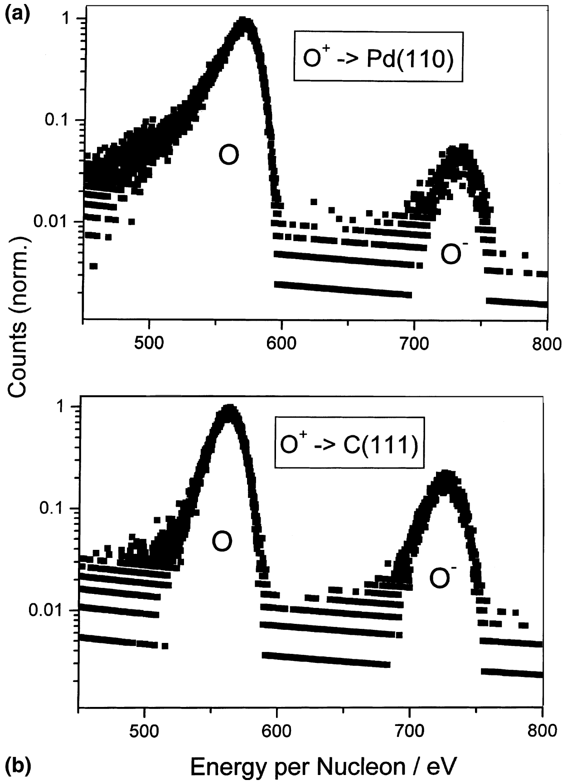

Fig. 3. (a) O^+ scattering off Pd(1 1 0), primary energy 1188 eV, angle of incidence 5°, scattering angle 10°. The left peak are neutralized O atoms, the right peak are O^- ions (postaccelerated). (b) Same as (a) for the hydrogen terminated diamond C(1 1 1) target.

Qualitatively, the neutral O-peak off Pd shows more straggling (low energy tailing) than O off diamond indicating larger electronic energy losses at the metal surface. With H covered surfaces the yield of negative ions is slightly increased. The O^- yield is above 1% at the particular energy of 1188 eV (Fig. 3a). The energy dependence of the negative ion yield is not very strong, i.e., smoothly dependent on the parallel velocity and/or the vertical component of the velocity as shown before [8]. There is no signature of a 'kinetic resonance'.

Fig. 4 shows the molecular survival of O_2 as a function of the primary beam energy for the clean diamond C(1 1 1) and the Pd(1 1 0)-surface. Note that the molecular survival probability of O_2 is approximately a factor two lower than the N_2 survival on diamond and Pd(1 1 0) (Fig. 1). At the

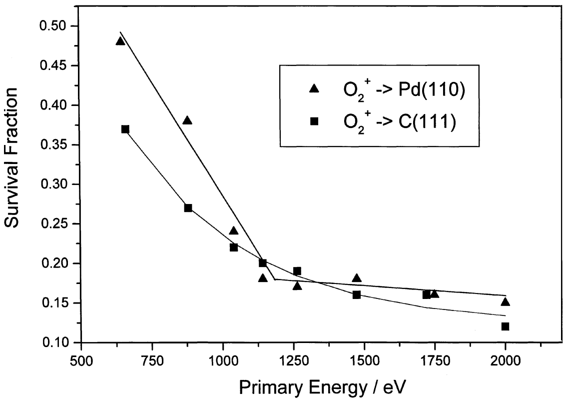

Fig. 4. Molecular survival fraction of O_2 scattered off Pd(1 1 0) and hydrogen terminated diamond C(1 1 1) at experimental conditions as in Fig. 1. Note the different scale of the ordinate. Lines are drawn to guide the eye. The experimental error bars are ±10%.

lower energies diamond causes more dissociation of O_2 than Pd. This is a clear evidence for strong electronic effects causing the high dissociation of O_2 on diamond. In this respect the diamond surface is behaving like a low work function metal surface.

4. Discussion

The results show clear differences in the dissociation of O_2 at the two surfaces, Pd(1 1 0) and diamond C(1 1 1). Since there is approximately no difference in the molecular survival probability for N_2 scattering from the two surfaces, we can ascribe the differences for O_2 to electronic effects. This interpretation is supported by the observation of higher yields of negative atomic and molecular ions in case of diamond. The scattering of N_2 off Pd has been studied in great detail [10,11]. It is understood that the dissociation is caused mainly by vibrational and rotational excitation. Depending on the crystallographic orientation of the surface the one or the other mechanism is more important, i.e., for scattering along low index surface directions, e.g. ⟨1 1 0⟩, there is more rotational excitation than for scattering along high index directions. From the close resemblance of the molecular yield of C(1 1 1) and Pd(1 1 0) (Fig. 1) we may safely conclude that the vibrational excitation mechanism is dominating the dissociation in case of C(1 1 1) too. Interestingly, there is also no remarkable difference in the N-ion yields for the two surfaces in question, indicating equal electron capture probabilities into th N_2 ground state. For O_2 scattering off Pd(1 1 0) the molecular yield is approximately a factor of two lower through the whole energy range, for C(1 1 1) the yield is even lower below 1000 eV. So we conclude that over the whole energy range, 500–2000 eV, an additional dissociation mechanism has to be considered.

One mechanism is the capture of electrons into the dissociative triplet states of O_2, which is possible in the case of Pd but not in the case of diamond owing to its band structure. The other possible mechanism has been identified for the dissociation of O_2 on Ag(1 1 1) [13,14], O_2 on Ni(1 1 0) and Ni(1 1 1) [15,16] as the 'electron harpooning'. This is in short the formation of negative molecular ions by a resonant electron capture from the conduction band of the metal into the affinity level of the molecule. This is facilitated due to the image potential induced lowering of the affinity level when the molecule approaches the surface [14,17]. The negative molecular states have a multitude of dissociative channels. Similarly, the dissociation of CO_2 can be understood [18]. Supportive evidence comes from experiments in which the work function of the surface is lowered which causes both the negative ion yield of atoms and molecules and dissociation of molecules to increase [14,16–18]. Hence for incident O_2^+ on a metal surface we have two paths for dissociation: (i) direct capture of an electron into a triplet state and (ii) the consecutive capture of two electrons into first, a neutral bonding molecular state followed by a capture into the affinity level. Additional evidence for the triplet state mechanism is obtained when neutral primary molecules are used, dissociation occurs then via the negative states only [16,18].

We are now faced with the problem of the electron capture from diamond. Diamond has an electronic structure of an insulator, with a bandwidth of the valence band of 21 eV, a gap of 5.47 eV and an electron affinity of −0.7 eV. This electron affinity level exists for the hydrogen terminated surface only. The bottom of the conduction band is above the vacuum level at approximately 0.7 eV. The affinity levels of O and O_2 are at -1.46 and -0.45 eV, respectively, i.e., below the vacuum level. The valence band is formed by the sp^3 hybridised C electrons, the bonds are absolutely covalent. The band is filled and there is no electron mobility. All models using the conventional idea of resonant electron capture from the conduction bands of metals, e.g. the 'Hagstrum model', can be excluded here from the further discussion. The 'dangling bonds' at the surface are saturated by H as it is the case with Si. Since we run experiments with sputter cleaned C(1 1 1) and hydrogen exposed C(1 1 1) and found no large effects in either the ion yields or the dissociation, we may exclude the surface dangling bonds and the adsorbed H from consideration. A problem in this context is experimental proof for the H depletion. The H recoil yield is low for the H covered surface, so, the lack of H-recoils of the 'clean' surface is not a very strong evidence.

For ionic crystals, e.g. LiF or MgO, charge exchange proceeds via capture of electrons from the anionic sites, e.g. F or O, of the surface [17,19–21]. At grazing collisions, high negative ion yields are found. This has two reasons: (i) electrons can be captured from the anion in a binary ion atom interaction, and (ii) once the negative ion is formed, it cannot be destroyed by resonant transitions as in the case of metals due to the gap of the ionic crystal. The latter conclusion applies to diamond as well, but there is no such charge localisation which would facilitate a binary collision type capture. It could be possible that the diamond affinity level allows the capture of electrons from a negative ion.

The binary collision model has been refined more recently [22]. The theoretical base is the Newns–Anderson Hamiltonian obtained from LCAO calculations. The theory allows the calculation of the occupation of the atomic levels of a projectile passing on a classical trajectory along a surface. Actual examples calculated were the H^- formation at moderate velocities scattering from Al, Si and LiF. With respect to our results it is of interest, that the estimated capture linewidths of H off Al and Si are about equal at velocities $v = 0.4\ v_0$. The velocities in our experiment are of the same order of magnitude, so we may transfer the theoretical observation to our case, even though we observe O^- and O_2^-. It is also worth noting that the surface states of Si play no major role in the charge capture process due to their low spectral weight. We may conclude therefore that also on diamond the actual state of the surface, e.g. hydrogen terminated or not, is not of major importance as found experimentally. The authors [22] argue with respect to the similarity of the results for Al and Si, that the atomic matrix elements describing the electron hopping, which is not a resonant metal–ion charge transfer, are not very different for Al and Si. We may extend this argument for diamond being very similar to Si, but not directly to Pd not being a jellium type metal. The comparison of diamond with Si is supported by earlier results from scattering O_2 off Si(1 0 0) where qualitatively comparable results were found with respect to the negative ion yields [23,24]. The second argument is that the parallel velocity of the projectile causes a smoothening of the surface density of states, SDOS, of Si to make it look like Al for the moving ion. This argument may safely be applied to diamond as well. In this theoretical approach the capture of electrons from a covalent semiconductor or insulator is a fascinating combination of a local charge transfer and many body effects.

Acknowledgements

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