Chemical effects in low-energy D^+ scattering from oxides

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The scattering of H^+ and D^+ ions from solid surfaces has been studied in a low-kinetic-energy region (50–500 eV), where the difference between these two projectiles can essentially be ascribed to their mass or velocity. It will be demonstrated that neutralization and inelastic scattering of D^+ are closely related to the bonding nature or the microscopic charge distribution of the solid surfaces. The neutralization of D^+ due to surface scattering from the ionic crystal (Sb_2O_3) is found to be small relative to that from the metal [Ta(111)] or the covalent materials [Si(111), SiO_2], indicating that the D 1*s* hole can readily diffuse into the ligands or the solid via the metallic or covalent orbital hybridizations while the isolated closed shell of the ionic crystal is not effective for hole diffusion. In D^+ scattering from the oxidized Ta(111) surface, the hole diffusion via the ionic O-Ta bond is suppressed while the metallic Ta-Ta bond retains high hole-diffusion efficiency. It is also concluded that oxygen chemisorption enhances reionization of neutral D^0 scattered after significant penetration into the solid, which contributes to the background in the D^+ energy spectra.

I. INTRODUCTION

The electronic transition between ions and solid surfaces is one of the most fundamental processes of particle-surface interaction, and is closely related to chemical reaction and heterogeneous catalytic processes. In practice, it is known that charge exchange between particles and surfaces is essential for understanding the dissociation of molecules on surfaces,[1-5] and the following chemisorptive bond formation with a specific electronic state of a surface.[6,7] This subject also provides the basis for various surface analysis techniques using ions. For example, noble-gas ions scattered by surface atoms are more likely to remain ionized than those emerging from the bulk, and form so-called surface peaks in their energy distributions. This peak has been widely used in ion scattering spectroscopy (ISS) to characterize the composition and structure of solid surfaces.[8-10] In terms of ion neutralization, it is believed that charge capture occurs via one-electron resonant (RN) and/or two-electron Auger (AN) processes where the solid surfaces have been treated as an isotropic continuum of electrons with specific band structures. This treatment would be valid for surfaces of elemental metals with extended conduction electrons, but more local electronic configuration must be taken into account for adsorbed O, semiconductors, or insulators. Indeed, anisotropic electronic distribution of compound surfaces or charge redistribution of elemental surfaces induced by heterogeneous adsorption is of essential interest with respect to neutralization of ions, which in this paper is referred to as "chemical effects."

In low-energy ion scattering, it would be a reasonable assumption that ion trajectories can be divided into three segments: incoming trajectory, collision, and outgoing trajectory.[11] Since ion trajectories are often uniquely determined when the incident and scattered beam energies and the scattering angle are known, the chemical state of the surface can be studied from the trajectory dependence of the charge-transfer probability.[12-16] More interestingly, the surface peak itself has recently been pointed out to offer chemical-state information about target atoms.[17,18] In the collisional regime, if energy-level crossing (ELC) occurs in the molecular state, the surface peak of scattered ions exhibits a drastic change in intensity, due to additional neutralization concomitant with inelastic scattering due to electron-hole pair excitation.

The chemical effects in H^+ scattering, on the other hand, have been discussed in some different respects.[19-21] The energy spectrum of H^+ with primary energy above several keV has been characterized by the absence of the surface peak at an elemental-metal surface and by the presence, instead, of an enhancement in "background intensity" due to oxygen chemisorption. Very recently, however, it has been claimed in low-energy (<200 eV) D^+ scattering that the surface peak clearly appears in the energy spectra from some ionic compounds such as alkali-metal halides and alkaline-earth halides,[7] and that the extended background caused by oxygen chemisorption comes from reionization of neutral D^0 scattered from the solid.[22] The difference between these two works stems only from the ion kinetic energy, and therefore results quite similar to those in D^+ scattering can be obtained in H^+ scattering.[23] These findings strongly suggest that the neutralization/reionization process in low-energy H^+ or D^+ scattering is closely related to chemical states of solid surfaces. In this paper, a demonstration will be made with use of D^+, because the surface peak corresponding to each target atom can be separated much better in the energy spectra of D^+ scattering than in those of H^+ scattering. It is found that the surface peaks are clearly seen in the D^+ spectra from Sb_2O_3 but are almost absent in those from Ta(111), Si(111), and SiO_2, indicating that the D 1*s* hole, although it tends to be localized at the deuterium site during collision with the ionic crystal, readily diffuses into the solid through the metallic and covalent bonds.

II. EXPERIMENT

The experimental setup has been described elsewhere.[17] The sample chamber, being evacuated down to an ultrahigh-vacuum (UVH) condition (1×10^{-8} Pa), was equipped with facilities for low-energy ion scattering, low-energy electron diffraction (LEED), ultraviolet photoelectron spectroscopy (UPS), and differentially pumped sample evaporation. The D^+ ions generated in a discharge-type ion source were collimated and were mass analyzed by a Wien filter. The D^+ dose was restricted below 5×10^{12} ions/cm^2 in each measurement, in order to minimize the surface decomposition. The Si(111) 7×7 surface was prepared by heating in UHV up to 1250 °C, while a thin film of vitreous SiO_2 was thermally grown on this surface following the procedure described in the literature.[24] Though the thickness or the precise composition of the film was not determined, the UPS spectrum exhibited a band structure characteristic of SiO_2.[25] A polycrystalline thin film of Sb_2O_3 was *in situ* evaporated in UHV on a substrate of graphite. The Ta(111) surface, prepared by heating up to 2500 °C in UHV, showed a clear 1×1 pattern in LEED and no detectable oxygen contamination in the preliminary ISS measurement using He^+ ions. The D^+ ions with a primary energy E_0 ranging from 50 to 500 eV were incident upon the surfaces with a glancing angle of $\alpha=80°$, and ions scattered with a laboratory scattering angle of $\theta=160°$ were detected by means of a hemispherical electrostatic energy analyzer operating with a constant energy resolution of 1 eV.

III. EXPERIMENTAL RESULTS

Figure 1 shows the energy spectra of D^+ scattered from Sb_2O_3; the measurements were made using a D^+ beam of (a) 50, (b) 100, (c) 200, and (d) 500 eV. The energy positions corresponding to the elastic binary collision (EBC) of D^+ on O and Sb are indicated by arrows on the abscissa. The spectra are characterized by clear surface peaks of D^+ scattered from each element, and a background shown by the broken line extending from zero energy to the maximum energy corresponding to the EBC of Sb. Each surface peak is basically composed of two peaks, *A* and *B*. As has already been reported for other ionic crystals,[7,22] peaks *A* and *B* are assigned to elastic scattering and inelastic scattering due to electron-hole pair excitation, respectively, and the background comes from reionization of neutralized D^0 scattered after significant penetration into the solid. It should be noted that the background tends to increase in intensity relative to the surface peaks with increasing kinetic energy, and hence the D^+ spectra are composed mainly of the background for large E_0 such as above 1 keV. This provides a main reason why the surface peak has not been clearly observed in the previous work on H^+ scattering with kinetic energy as large as several keV.[19-21]

Figure 2 shows the D^+ energy spectra from (a) the

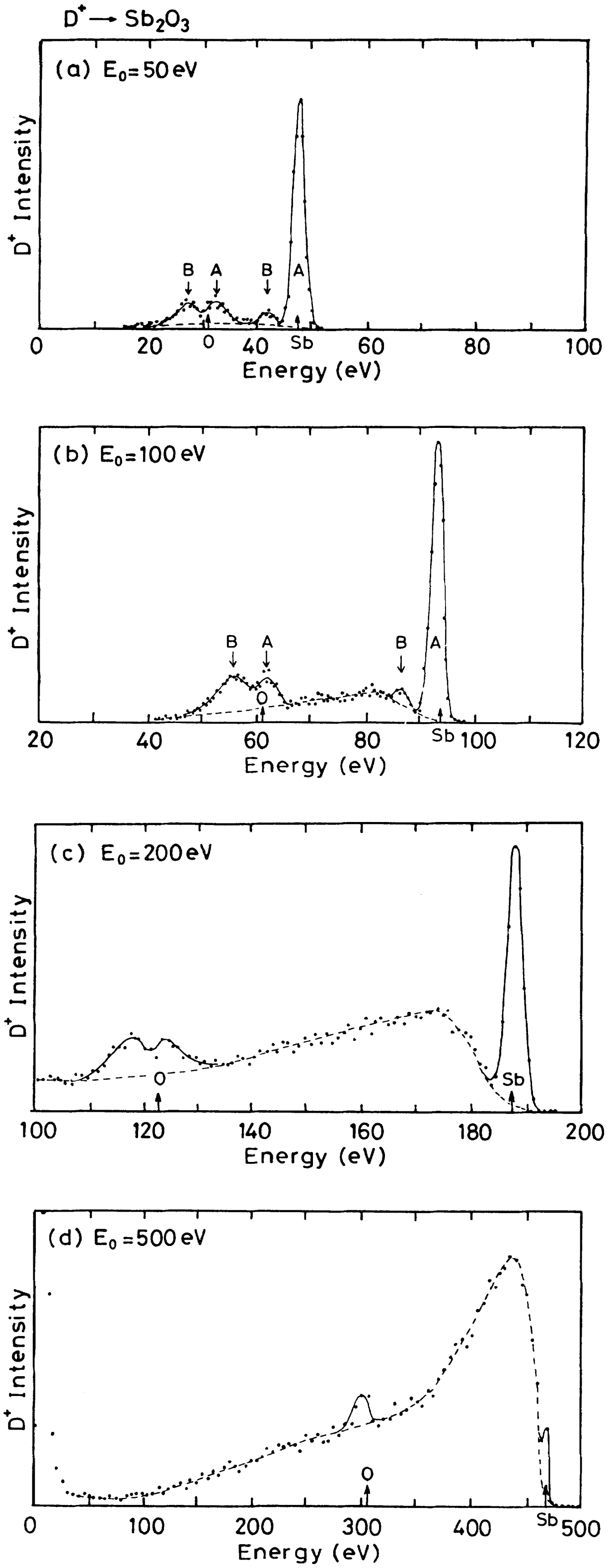

FIG. 1. Energy spectra of D^+ scattered from a thin film of Sb_2O_3 measured using a D^+ beam of (a) 50 eV, (b) 100 eV, (c) 200 eV, and (d) 500 eV under the scattering condition of $\alpha=80°$ and $\theta=160°$. The energies corresponding to the elastic binary collision are shown by arrows on the abscissa. The solid lines for the surface peaks and the broken lines for the backgrounds are drawn to guide the eye.

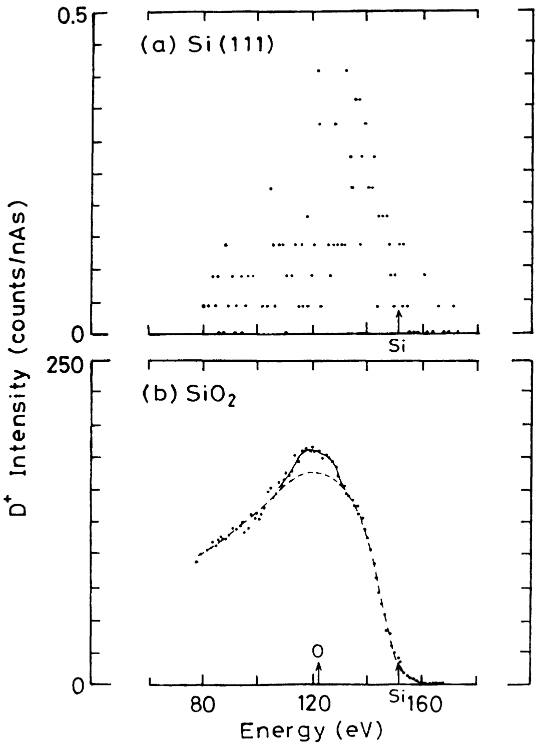

FIG. 2. Energy spectra of D^+, scattered from (a) the Si(111) surface and (b) the SiO_2 surface, measured with a D^+ beam of 200 eV. The intensities are normalized relative to each other through beam currents.

Si(111) surface and (b) the SiO_2 surface obtained using a D^+ beam of 200 eV; the spectra are normalized relative to each other through beam currents. The D^+ ions scattered from the clean Si(111) surface are neutralized almost completely so that no surface peak corresponding to Si appears. In the case of the SiO_2 surface, a small surface peak corresponding to O is superimposed on the large background while no clear surface peak corresponding to Si is observable relative to the background. Such behavior provides a striking contrast to the results of Sb_2O_3 shown in Fig. 1.

Figure 3 shows the energy spectra of D^+ scattered from (a) the Ta(111) surface exposed to a 10 L (1 L$=1.3\times10^{-4}$ Pa *s*) O_2 gas, and (b) the Ta(111) surface obtained by subsequent heating of this surface at about 2000 °C. The measurements were made using a D^+ beam of 100 eV and the data are normalized through beam currents. In Fig. 3(a), a clear surface peak corresponding to oxygen as well as a significant background is observed. The sample heating up to 2000 °C reduces the number of oxygen due to evaporation and/or diffusion into the solid and the D^+ spectrum shows a clear O surface peak being enhanced in intensity relative to the background. The complete removal of oxygen from the surface requires several flash heatings at about 2500 °C and the clean Ta(111) surface is characterized by the absence of both O and Ta surface peaks and a quite small background intensity in the D^+ spectrum. It should be emphasized that the surface peak corresponding to Ta is completely absent for all these surfaces though it appears clearly in the $E_0=100$ eV He^+ spectra with peak intensity of about 300 counts/nA sec at the clean surface.[18]

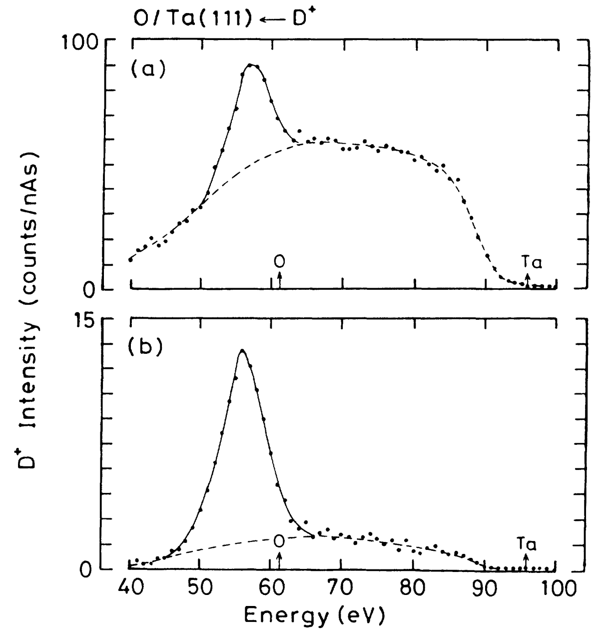

FIG. 3. Energy spectra of D^+ scattered from the O-chemisorbed Ta(111) surfaces. The measurements were made using a D^+ beam of 100 eV at (a) the Ta(111) surface exposed to a 10 L O_2 gas and (b) the Ta(111) surface obtained by the subsequent heating at about 2000 °C.

IV. DISCUSSION

In the preceding section, it is outlined how the chemical environment of the solid surfaces affects the energy spectra of D^+ scattering. The observed chemical effects can be summarized in (i) the appearance of the surface peak depending on the electronic state of the surface, and (ii) the increase in the background in the D^+ spectra due to the formation of the oxide or the existence of oxygen adsorbates. These results seem to be more marked for D^+ scattering rather than He^+ scattering,[7] relating to the fact that the D 1*s* level (-13.6 eV) is located so close to the valence band compared with the He 1*s* level (-24.6 eV) that the interaction with the band is more likely to occur (band effect). As regards the oxides, the critical difference between Sb_2O_3 and SiO_2 must be related to their bonding nature or electronic band structures. Figures 4(a) and 4(b) show schematic views of valence-band structures of Sb_2O_3 and SiO_2, respectively. Sb_2O_3 is an ionic crystal for which the valence band relevant to neutralization of D^+ is composed of the O 2*p* and Sb 5*s* states, while the valence band of SiO_2 stems from mixing of the sp^3 hybridization of silicon orbitals with 2*s*,2*p* orbitals of tetrahedrally arranged oxygen ligands.[25,26] The electronic transition to the D 1*s* level occurs via RN or ELC. The RN does not strictly require the resonance condition[27,28] because of the broadening or the shift of the D 1*s* level in the vicinity of the surface, so that all electronic states shown in Fig. 4 can make a contribution to neutralization of D^+. It might be possible that the partial occupancy of the band for elemental-metal sur-

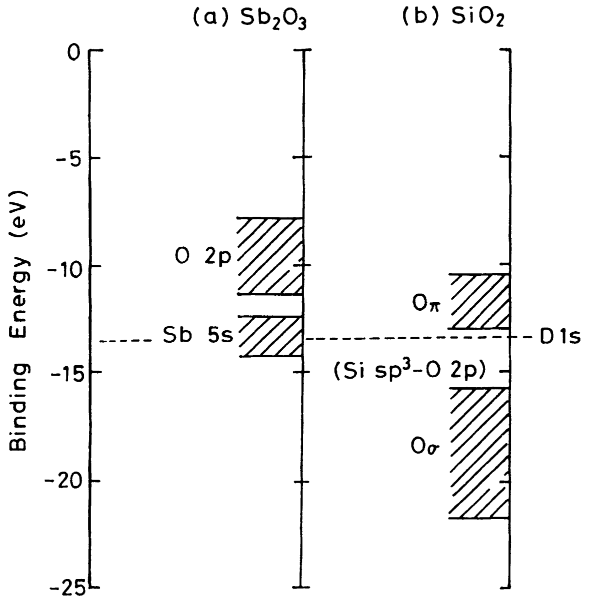

FIG. 4. Schematic views of the band structures of (a) Sb_2O_3 and (b) SiO_2, derived from the UPS spectra and the theoretical calculations (Refs. 25 and 26), respectively.

faces causes neutralization of D^+ via the Auger process, or the resonant process relevant to the excited states of D^+. In the case of Sb_2O_3 and SiO_2, however, these processes play only a minor role because they have a closed band with a large band gap.

It is a reasonable assumption in large-angle scattering discussed here that the backscattered D^+ ions contributing to the surface peak interact mainly with the electronic states of the target atom. Then, the following two steps are essential for determining the neutralization probability of D^+: (i) the transition of the D 1*s* hole to a specific target electronic state via RN and/or ELC, and (ii) the subsequent diffusion of the hole from the target atom into the solid. There are basically two ways to study hole diffusion, one being a band-theoretical approach and the other being a molecular-cluster approach. From the band-theoretical point of view,[29] the neutralization probability is determined by a lifetime τ of the hole in the band given by

$$\tau=\hbar/W\ , \tag{1}$$

where W indicates the bandwidth. The absence of the Si surface peak in the spectrum of SiO_2, therefore, seems to be reasonable because of the wider band of SiO_2 than Sb_2O_3. According to the local-cluster approach, on the other hand, the diffusion of the hole produced in the target is thought to occur via the orbital hybridization between the target atom and the ligand atoms. As will be discussed below, in fact, the neutralization probability of D^+ can be a measure of the covalent or metallic character in the bonding. It should also be noted that the hole transition between D 1*s* and the target electonic state (X) during collision is mediated by a temporary molecular state $(DX)^+$, with a smaller atomic separation than the ordinary molecule, which is referred to as a quasimolecule.

The assumption that these consecutive two processes are a prerequisite to neutralization of D^+ may be supported from the analogy of the quasiresonant neutralization of He^+ ions: It is known that if an inner-shell *d* level of a target atom is located close to the ground state He 1*s* level, the He^+ yield markedly oscillates as a function of the kinetic energy.[27,28] The oscillatory yield results from the fact that He^+ forms the quasimolecular state during collision with a target atom, and that the transition rate of the hole between the He 1*s* and the target *d* states is quite high, comparable to the inverse of the collision time ($\sim 10^{15}\ s^{-1}$). A further requirement for the appearance of the oscillatory yield is that the resultant target *d*-hole state must be a localized core level; otherwise, helium would be neutralized with a far higher probability due to diffusion of the hole. As regards D^+ scattering, the interaction of D 1*s* with the extended valence state is so favored that the target hole state produced by RN can readily diffuse into the solid especially for metals [e.g., Ta(111)] and covalent semiconductors [eg., Si(111)]. In the case of SiO_2, in fact, the covalency in the Si-O bonding is responsible for rapid hole diffusion resulting in the near absence of the Si surface peak as shown in Fig. 2(b). Similar to this, no remarkable cationic surface peak has been observed in the D^+ spectra from AgCl, $MnCl_2$, and $CoCl_2$.[30] The bonding of these compounds are characterized as ionic, but a significant contribution of covalency coexist in the bonds.[31] Hence, the D 1*s* hole can easily diffuse into the anion *p* band via the intermediate *d*-hole state, resulting in no surface peaks corresponding to the cations. Thus, the covalent bond, as well as the metallic bond, is found to offer an effective diffusion path of the D 1*s* hole.

In terms of the simple ionic compounds, hole diffusion is largely suppressed because of the band gap between the *p* shells of the nearest-neighbor anions and cations, so that the hole tends to be localized at the deuterium site during collision. Similarly, the ionicity in the Sb-O bond, in which the Sb 5*s* state may be isolated from the O 2*p* state as shown in Fig. 4, leads to the localization of the D 1*s* hole during collision, and hence the surface peaks appear in the D^+ spectra. In this respect, the D^+ spectra from $PbCl_2$ are also of interest: It has been reported that D^+ ions scattered from Pb^{2+} show no remarkable surface peak in contrast to those from Sb^{3+} shown here.[7] This is supposedly because the small binding energy of the Pb 6*s* state relative to the Sb 5*s* state results in a small overlap in energy with Cl 3*p* band, offering a diffusion path of the Pb 6*s* hole. It is thus suggested that the surface peak in D^+ scattering appears if the valence state of the target atom is separated from the ligand electronic state.

The concepts of ionic and covalent character in bonds are themselves crude, and do not give a full picture of the charge distribution in a bond, though this concept has a long tradition and has been successful in rationalizing a large amount of solid-state chemistry. Photoemission has been widely used for discussing the bonding nature of compounds or heterogeneous adsorbates on the basis of the chemical shift. The framework developed in this paper can also provide useful information on the chemisorptive bond. In terms of oxygen chemisorption, the charge state or the bond nature of oxygen is largely dependent on the electronic structure of the substrate.[7] Since alkali metals and alkaline-earth metals lose their *s* electrons easily in the presence of electrically negative species, the oxides of these elements are characterized by purely ionic bonds. Specifically, in fact, oxidation of metallic Ba surface results in BaO, as has been confirmed by the appearance of clear surface peaks corresponding to both Ba and O in the D^+ spectra.[7] In contrast to this, oxidation of the Ta(111) surface causes no clear surface peaks corresponding to Ta. The same is true for the oxidized Mo(111) surface.[7] This is probably because the surface oxides thus formed are not full-valency compounds such as Ta_2O_5 or MoO_3. The cationic surface peak has been observed for the early-transition-metal compounds such as LaF_3 and ZrO_2, in which only one or two *d* electrons are relevant.[30] This is concerned with the fact that the contribution of the *d* electrons to the ionic component of the bonding is relatively small due to their localized nature. Indeed, more than half-filled *d* shells of the late-transition-metal compounds tend to be localized as a cationic ion-core state, and take part only in the covalent bond with the anion *p* band rather than the ionic bond.[30,31]

The most remarkable features in the D^+ spectra from the oxidized Ta(111) surface is the clear appearance of the O surface peak despite the complete absence of the Ta surface peak. It is known that all the oxides of Ta, except for Ta_2O_5 are metallic. From the viewpoint of local bonding, this result suggests that oxygen is highly ionic due to the large amount of charge transfer in the Ta-O bond, though Ta retains a metallic bond with the Ta ligands. Moreover, if oxygen is negatively charged, the ionic interaction may also have significance for determining the neutralization probability of D^+: The D 1*s* hole is thought to diffuse via the intermediate D^+-O^{x-} $(x<2)$ ion-pair state into the Ta ligands. The ion-pair state is energetically preferable to the neutral state due to the electrostatic attractive energy, so that the hole-diffusion probability during collision can be suppressed. Supposedly, this is also responsible for the suppression of the diffusion of the D 1*s* hole into the anion *p* band of the purely ionic crystals. Thus, the appearance of the O surface peak might not be direct evidence of the O^{2-} state, but is a good measure of the ionicity or the charge transfer in the O-Ta bond. This is in fact the case for the O-Si bond in which ~ 1.4 electrons are calculated to be transferred from Si to each O atom.[26] The absence of the Si surface peak for SiO_2 shown in Fig. 2(b), however, does not necessarily require the Si-Si bond because the hole can diffuse from Si to O due to covalency in the bond.

It can be seen in Fig. 3 that the O surface peak is enhanced in intensity relative to the background by removing a part of chemisorbed oxygen. A similar result has been obtained in the spectra from the SiO_2 film and the O-chemisorbed Si(111) surface. This indicates that the background intensity is closely related to the thickness of the oxide layer. Comparing the O surface peak in Fig. 3 with that of Sb_2O_3 shown in Fig. 1(b), we find that the former, appearing at about 5 eV below the elastic binary collision energy for oxygen, coincides with loss peak *B* of the latter. The inelastic scattering comes from the *e-h* pair excitation in the O 2*p* state, and hence the loss energy corresponds approximately to the binding energy of the O 2*p* state at the O-chemisorbed Ta(111) surface or the band-gap energy of Sb_2O_3. The absence of the elastic peak in Fig. 3 implies that the band gap is not formed at the oxidized Ta(111) surface.

In terms of the background, we have revealed, using D^+ and D^0 beams of $E_0 = 1$ keV, that the D^+ energy spectra from the oxygen-chemisorbed Mo(111),[22] Ta(111), and Pt(111) surfaces, as well as the SiO_2 film grown on the Si(111) surface, obtained by D^+ incidence are essentially the same as those obtained by D^0 incidence, which indicates that the spectral background comes from reionization of D^0 scattered after penetration into the solid. These results seem to be in remarkable contrast to He^+ scattering, in which reionization contributes mainly to the surface peak, and the marked background appears relative to the surface peaks if the energy of emerging He^0 is as high as several keV,[19,20] or the outermost surface is composed of Si (Ref. 32) or Ta (Ref. 33) which have a relatively small threshold energy (~ 300 ev) for reionization.[17] These contrasts can essentially be ascribed to the fact that the threshold energy of reionization is much smaller for D^0 than for He^0, because of the smaller ionization energy of deuterium than that of helium by 11 eV. In other words, the minimum impact distance, or the cross section of reionization, is so large in D^0 scattering that reionization is not restricted only to the large-angle scattering leading to the surface peak. In this framework, the hole-diffusion probability is also essential for determining the final ionization rate of D^0. In fact, the absence of the background for the clean Ta and Si(111) surfaces implies that the hole-diffusion probability overcomes the ionization probability for the energies used here, while the contrary is true for the oxygen-chemisorbed surfaces.

V. SUMMARY

It is demonstrated that the chemical state of solid surfaces can be investigated on the basis of neutralization and inelastic scattering of the D^+ ions. The appearance of the surface peak of the D^+ ions depends on the bonding nature of the target atom. In the collisional regime, diffusion of the D 1*s* hole readily occurs via the extended metallic band or the covalent bond, so that no clear surface peak is observable in the spectra from Ta(111), Si(111), and SiO_2 while, on the other hand, a clear surface peak appears in the spectra from Sb_2O_3 in which the diffusion path of the hole may be broken due to isolation of the Sb 5*s* state from the O 2*p* state. The fact that the O surface peak appears clearly on the O-chemisorbed Ta(111) surface despite the absence of the Ta surface peak implies that the diffusion of the D 1*s* hole via the

O-Ta bond is suppressed due to the high ionicity of the bond, while Ta retains metallic bonds with the Ta ligands. This result suggests that D^+ scattering is promising for obtaining electronic and structural information around the target atom. The marked background increase by oxygen chemisorption of the elemental surfaces has been ascribed to reionization of D^0 scattered after significant penetration into the solid.

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