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Interactions of SrF_2 and PrF_3 with TiC(111) and Si(111) surfaces studied by low-energy D^+ scattering spectroscopy

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On the basis of neutralization of scattered low-energy D^+ ions, the nature of the bonding of ionic molecules adsorbed on metal and semiconductor surfaces has been investigated. It is found that SrF_2 reacts with the active dangling-bond states of the TiC(111) surface and the ionic bonding between Sr^{2+} and F^- ions is strongly weakened. However, the ionicity of the adsorbates recovers after oxygenation or hydrogenation of the TiC(111) surface since H or O passivates the dangling-bond states at the interface. On the other hand, the dangling bond of Si(111) has relatively little effect on the ionic Sr-F bond formation and rather dissociation of SrF_2 is promoted at an elevated temperature due to preferential reaction of F with Si. In terms of PrF_3, ionicity is strongly reduced on both Si(111) and TiC(111) surfaces and oxygenation of the surface has very little effect, suggesting that PrF_3 is dissociatively adsorbed and Pr forms covalent or metallic bonds with the substrate. [S0163-1829(98)03739-4]

I. INTRODUCTION

The interaction of insulating ionic compounds with metal and semiconductor surfaces has attracted considerable attention. In terms of practical applications, interface properties are of crucial importance for manufacturing electronic devices in semiconductor-on-insulator (SOI) technology.[1–6] It is a common recognition that the growth mode in heteroepitaxy is governed by the surface free energy and the lattice mismatch. Since free energy or wetting of two different materials is related to atomic bonding at interfaces, knowledge of the atomic and electronic structure of the first monolayer in epitaxial processes is of crucial importance for better understanding of the mechanism of thin-film growth. Moreover, the study of dissociative adsorption or bond weakening of adsorbates due to interactions with the substrate electronic state should give insight into surface chemistry, such as heterogeneous catalysis and corrosion, etc.

We have investigated the nature of the bonding of alkali halides adsorbed on metal and semiconductor surfaces on the basis of neutralization and inelastic scattering of low-energy D^+ ions.[7] Low-energy ion scattering (LEIS) has been developed as a tool for surface structural and compositional analyses[8–10] and its simplicity is mainly based on classical mechanics. However, if the internal electronic states of ions are considered, the processes involved in low-energy ion scattering are governed by the laws of quantum-mechanical dynamics. Indeed, scattered ions experience transient adsorption at a surface for an ultrashort time scale in the femtosecond range and, hence, charge states of scattered ions should give insight into elemental chemical processes at a surface. These processes are typical for scattering of reactive ions with an open shell electronic structure such as H^+ or D^+, since capture of valence electrons occurs via a transient chemisorptive bond during scattering.[11,12] The neutralization probability should therefore be strongly dependent on the electronic band structure or ionicity (reactivity) of the surface. Specifically, the D^+ ion can survive neutralization during a single collision with a topmost-layer atom provided that that atom is highly ionic in nature.[11,12] This is because the duration of a binary collision (a few femtoseconds) is longer than the lifetime of a hole in the band of typical metallic and covalent materials but shorter than that of highly ionic compounds, thus leading to marked differences in the neutralization probabilities (the band effect).[13] Charge exchange in D^+ scattering is actually even more local in nature than expected from the averaged band picture or the electron continuum model because the D 1s orbital is spatially localized. In LEIS, the collision events with specific target atoms can be distinguished via the energy of the scattered ions. This ability and the lifetime difference enable us to investigate the ionicity of specific target atoms.[11,12]

Here, we report on the experimental results of D^+ scattering from SrF_2 and PrF_3 deposited on the Si(111) and TiC(111) surfaces as an extension of our previous work.[7] The experiments were aimed for determining the electronic structure at the ionic/covalent or ionic/metallic interface in the submonolayer coverage regime. In connection with the SOI technology, alkaline-earth fluorides and the rare-earth trifluorides are important to grow an insulating layer epitaxially on the Si(111) surface.[1–6] Moreover, the dangling bond of Si is known to play an important role in surface chemistry and thin-film growth, etc.[14] The TiC(111) surface is chosen as a metal substrate with a hexagonal lattice so that the stable $SrF_2(111)$ and $PrF_3(0001)$ faces can be grown. TiC is a refractory compound with a NaCl-type structure and its (111) surface is known to be terminated by Ti atoms. It is believed that dangling-bond states with a mostly 3d character exist at the fcc threefold hollow site,[15,16] which is also inferred from the fact that covalent molecules such as H_2 and O_2 are dissociatively chemisorbed on this particular site.[17,18] In this paper, emphasis is placed on the effects of such active dangling-bond states on the formation of ionic bonds between Sr^{2+} (Pr^{3+}) and F^- ions in the first-deposited monolayer.

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II. EXPERIMENT

The experiments were made in an ultrahigh-vacuum (UHV) chamber (base pressure of 2×10^{-10} mbar) equipped with facilities for standard-surface characterization. The ion beams were extracted from discharge in a mixed gas of He and D_2 and were mass analyzed using a Wien filter. The D^+ ions with kinetic energy of 50 or 100 eV were incident upon a surface at an angle of 80° measured from the surface and the ions backscattered through 160° relative to the incidence beam direction were detected by means of an electrostatic energy analyzer operating at a constant-energy resolution of 2 eV.[11] The Si(111) (*p* type, 20–50 Ω cm) surface was cleaned by resistive heating in UHV up to 1500 K. The surface showed a sharp 7×7 pattern in low-energy electron diffraction (LEED). A single-crystal rod of TiC was grown by the floating-zone method.[19] A specimen was cut from the rod within an accuracy of 0.5° parallel to the (111) face by spark erosion, and one face of the specimen was polished mechanically to a mirror finish. The surface was cleaned by several flash heatings up to 1900 K in UHV. The surface thus prepared showed a sharp, well-ordered 1×1 pattern in LEED and no visible contamination in He^+ ion scattering. The SrF_2 and PrF_3 were deposited onto the clean surfaces as well as onto oxygenated/hydrogenated surfaces by thermal evaporation. The amount of the adsorbate was estimated *in situ* by using low-energy He^+ scattering ($E_0=1$ keV) since the scattered He^+ intensities were much less affected by the bond nature of the surface. One monolayer (ML) was defined as the occurrence of complete absence of the surface peaks of the substrate atoms due to shadowing or neutralization induced by the adsorbates. A Si(111) and a TiC(111) sample could be mounted together on a tandem sample holder so that the scattered ion intensities under the same experimental conditions could be compared to each other.

III. RESULTS AND DISCUSSIONS

The energy spectra taken for thick layers of SrF_2 and PrF_3 deposited on graphite are shown in Fig. 1. The measurements were made using $E_0=100$ eV D^+ ions. The arrows on the abscissa indicate the energy positions for ideal binary collisions. The energy spectra consist of surface peaks of the constituent elements, which are superposed on an extended background. As described above, the intensity of a surface peak due to survival from neutralization can be used as an experimental measure of the ionicity of specific atoms. Thus, the presence of both cationic and anionic surface peaks in Fig. 1 evidences the ionicity of the SrF_2 and PrF_3 bonds. Another characteristic of the surface peak is the existence of an energy-loss peak due to electron-hole pair excitation across the band gap, which also indicates that a highly ionic film with a well-defined band gap is deposited on the substrate. The ions backscattered from deeper layers are neutralized completely by multiple scattering events. In reality, however, there exists usually a broad background in the energy spectra on which the surface peaks are superposed. The background is ascribed to reionization of neutralized D during collisions with the surface atoms just before D leaves the surface. It provides no information about the ionicity of specific target atoms. With increasing ion energy, the contribution of the surface peak is reduced relative to the background due to the decrease of the scattering cross sections and the increase of the reionization probabilities. Therefore, lower-energy ($E_0<100$ eV) D^+ scattering is preferable for the analysis of the nature of the bonds.

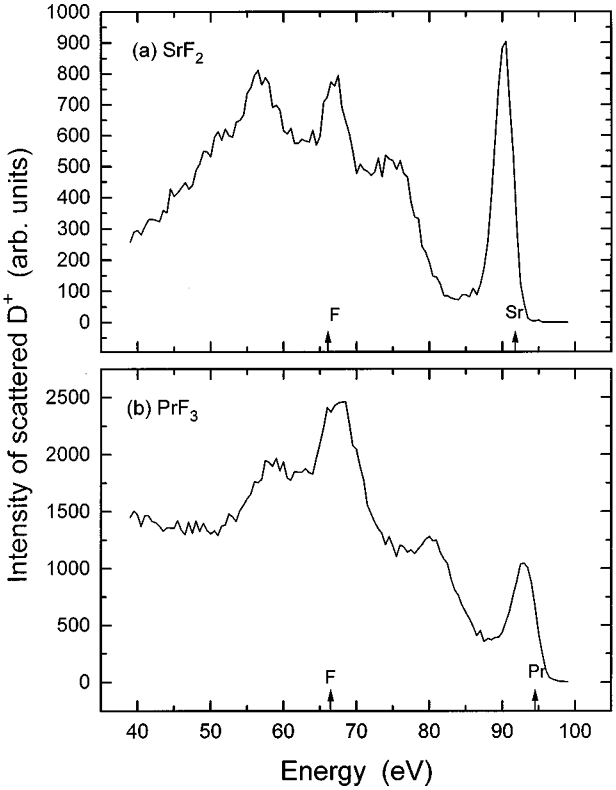

FIG. 1. Energy spectra of $E_0=100$ eV D^+ ions scattered from SrF_2 (a) and PrF_3 (b) deposited on graphite. The arrows on the abscissa indicate the energy positions in case of ideal binary collisions. The measurements were made at an incidence angle of 80° measured from the surface and a laboratory scattering angle of 160°.

The energy spectra of $E_0=50$ eV D^+ ions scattered from SrF_2 deposited on the Si(111) surface are shown in Fig. 2. A quarter of a monolayer of SrF_2 was deposited onto the surface at a temperature of 300 K (a) or 1050 K (b). The measurements of the energy spectra were made at room temperature. The D^+ ions scattered from a clean Si(111) surface are almost completely neutralized and, hence, all of the scattered ions should be related to the presence of the adsorbate. The spectral change due to subsequent oxygenation (10 L; $1\ \mathrm{L}=1.0\times10^{-6}$ mbar s) is indicated by the dotted line. The energy spectra in Fig. 2(a) consist of surface peaks of Sr and F, together with a broad structure for $E<32$ eV. The latter is caused by multiple scattering from the Si substrate and by reionization during collisions with the adsorbate. The effect of oxygenation is not so remarkable when the deposition is made at room temperature. On the other hand, the intensity of the energy spectrum for SrF_2 deposited at 1050 K is rather low and no surface peak is observable. Oxygenation increases the Sr surface-peak intensity but no F peak emerges. The F peak is not observable in He^+ scattering either. These facts show that SrF_2 is decomposed and F is missing completely from the surface.

The presence of the surface peaks in Fig. 2(a) indicates that ionically bonded SrF_2 can be deposited on the Si(111) surface. However, it is likely that the ionicity of the bonds

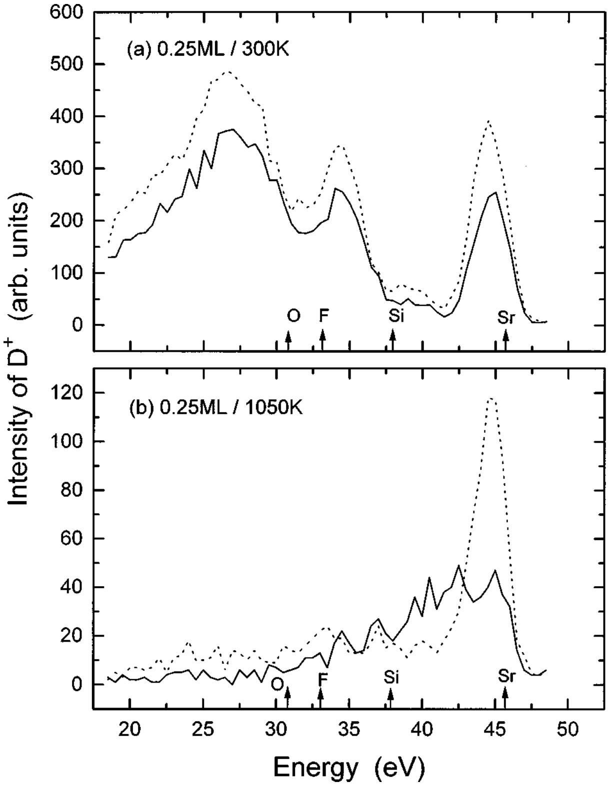

FIG. 2. Energy spectra of $E_0 = 50$ eV D^+ ions scattered from SrF_2 deposited on the Si(111) 7×7 surface. One quarter of a ML SrF_2 was deposited on the surface at (a) room temperature and (b) 1050 K. The spectrum after adsorption of 10 L O_2 gas is shown by the dotted line.

can be weakened with respect to bulk SrF_2 due to the interaction with the substrate. Oxygenation of the surface is done to check this possibility. As seen in Fig. 2(a), the slight increase of the surface peak intensities for both Sr and F after oxygenation suggests that the ionicity of the Sr-F bonds on the Si(111) surface is not maximal, likely due to the interaction with the substrate electronic state. The absence of a surface peak of Sr in Fig. 2(b) and its remarkable increase after oxygenation indicate that the ionicity of Sr is fairly small on Si(111), probably due to the formation of less ionic Sr-Si bonds.[4]

SrF_2 is known to grow epitaxially when keeping the Si(111) substrate at a moderate temperature.[20] Figure 3 shows the energy spectra of D^+ ions scattered from the Si(111) surface with (a) 0.25 ML, (b) 0.6 ML, and (c) 1.0 ML of SrF_2, deposited at around 950 K. Due to the background, the F peak is almost invisible in Fig. 3(a), but oxygenation increases both F and Sr peaks by the same factor. The intensity of the F peak relative to the Sr peak is small in the lower coverage regime. These facts indicate that the ionicity of Sr is strongly reduced due to the partial loss of the F atoms. Probably, less ionic species such as SrF are formed at the interface.[5,6] The interaction of SrF with the dangling-bond state may further reduce its ionicity. Upon oxygenation, the dangling bond is passivated and the interfacial O atom may act as an electron acceptor, thereby increasing the ionicity (or the surface peaks) of SrF.

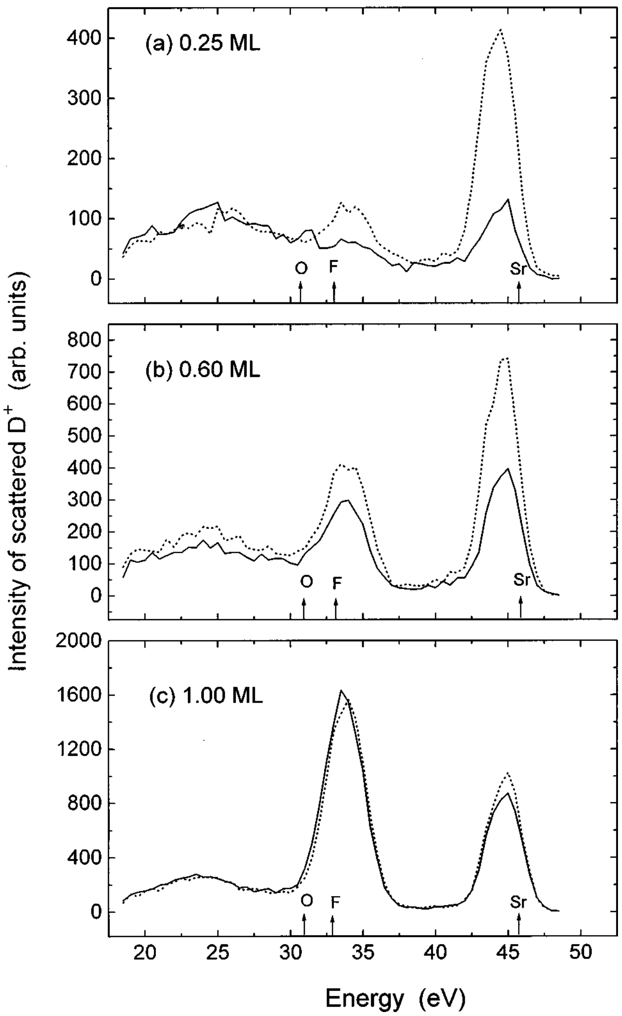

FIG. 3. Energy spectra of D^+ ions ($E_0 = 50$ eV) scattered from the SrF_2-covered Si(111) surface. The deposition was made at a surface temperature of 950 K; (a) 0.25 ML, (b) 0.6 ML, and (c) 1.0 ML. The measurements were made at room temperature. The dotted lines show the spectra after oxygenation (10 L) of the surface.

The D^+ energy spectra from SrF_2 deposited on the clean and adsorbate-covered TiC(111) surfaces are shown in Fig. 4. The deposition of SrF_2 is done at room temperature with the same amount (0.25 ML) as in Fig. 2(a) and the scattered D^+ intensities can be compared relative to each other since both spectra are taken under the same conditions. D^+ ions backscattered from a clean TiC(111) surface are neutralized almost completely, so that the observed D^+ ions in Fig. 4(a) are due to the presence of the adsorbate. As shown by the solid line in Fig. 4(a), no Sr peak is present in the spectrum if SrF_2 is deposited on the clean surface. The spectrum consists mainly of a broad contribution due to multiple scattering from the substrate ($E < 35$ eV). The surface peak of Sr increases in intensity after oxygenation and hydrogenation as indicated by the dotted and short-dotted lines, respectively, in Fig. 4(a). The effect of oxygenation on the recovery of the Sr peak is more pronounced than of hydrogenation. The F peak does not change markedly upon oxygenation and decreases upon hydrogenation. A similar tendency is obtained if SrF_2 is deposited on the oxygen-saturated and hydrogen-saturated TiC(111) surfaces as shown in Fig. 4(b), suggesting that the order of exposure is not very important.

The TiC(111) surface is known to be terminated by Ti

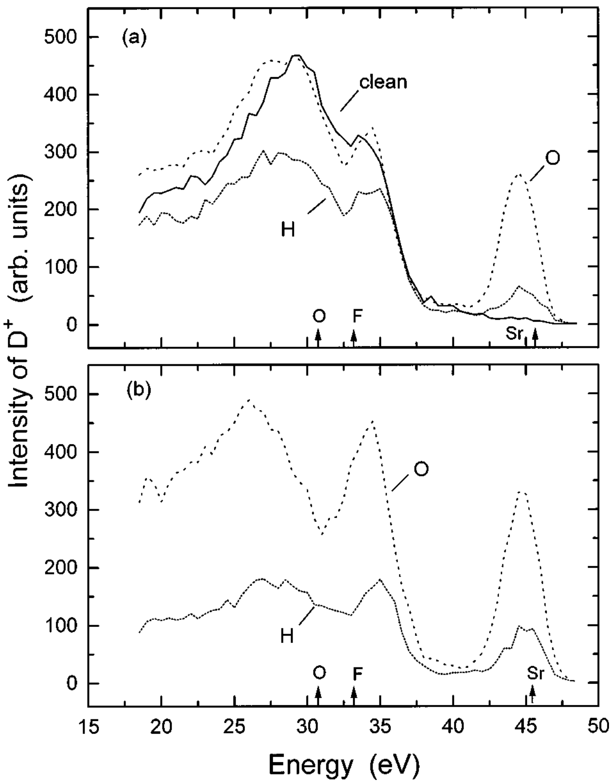

FIG. 4. Energy spectra of D^+ ions ($E_0 = 50$ eV) scattered from the SrF_2 (0.25 ML) adsorbed TiC(111) surface. (a) The spectrum for SrF_2 deposited on the clean TiC(111) surface is shown by a solid line, together with the spectra after the exposure of 10 L oxygen (dotted line) or hydrogen (short-dotted line) gases. (b) Shown by dotted and short-dotted lines, respectively, are the energy spectra of SrF_2 deposited on the oxygen- and hydrogen-saturated TiC(111) surfaces.

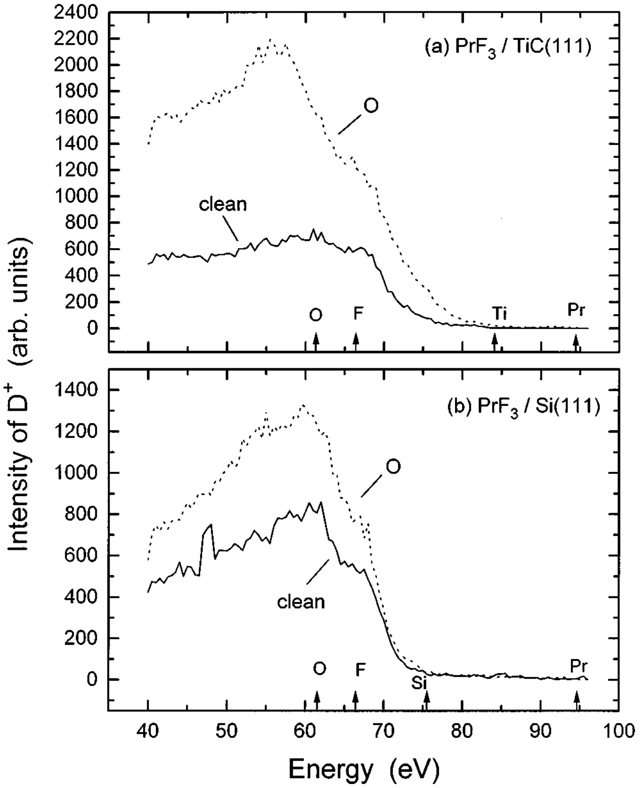

FIG. 5. Energy spectra of D^+ ions ($E_0 = 100$ eV) scattered from 0.27 ML PrF_3 deposited on the (a) TiC(111) and (b) Si(111) surfaces. (a) The deposition is made on the clean (solid line) and oxygen-saturated (dotted line) TiC(111) surfaces. (b) The solid line shows the spectrum of SrF_2 deposited on the clean Si(111) surface and the spectrum after oxygenation (10 L) is displayed by the dotted line.

atoms and its chemical reactivity comes mainly from the dangling-bond state.[15,16] Oxygen and hydrogen are dissociatively adsorbed on the three fold hollow site on which the Ti $3d$ dangling-bond state exists.[17,18] These dangling bonds are saturated with oxygen or hydrogen after exposure of around 1–2 L and the resulting surfaces exhibit a sharp 1×1 LEED pattern.[21] The dangling-bond state of TiC(111) is much more reactive for dissociative chemisorption of H_2, O_2, N_2, and CO than that of Si.[22] Moreover, this particular site also plays an important role in adsorption of cationic species such as Si and Ba.[22] Therefore, it is reasonable to assume that also the SrF_2 molecules preferentially react with the dangling-bond states of TiC(111). The complete absence of the Sr surface peak in Fig. 4(a) indicates that SrF_2 is dissociatively adsorbed and the ionicity of Sr is almost completely reduced. Note that the F peak is still clearly visible despite the complete absence of the Sr peak. The reduced presence of the cationic peak relative to the anionic peak is also observed in scattering from other ionic-compound surfaces with less ionicity such as TiO_2 and MgO.[12] This is ascribed to the formation of a surface ionic molecule ($D^{\delta+}$-$F^{\delta-}$), which suppresses the D $1s$-hole diffusion into the band of the substrate. The surface molecule is, as in Ref. 11, formed during collision of D^+ especially with highly electron negative species. The increase of the Sr surface peak after oxygenation of the SrF_2/TiC(111) surface is caused by recovery of ionic bonding between Sr and F. The formation of oxyfluolides (SrF_xO_y) might also be possible. However, if that were the case, an additional surface peak of incorporated oxygen should appear well separated from the F peak as in the spectra for the SrO surface[23] [see also Figs. 2(b) and 3(a)]. These facts show that the most important role played by coadsorbed oxygen is to passivate the active dangling-bond state, while it is hardly incorporated into the lattice of the adsorbate. Hydrogenation of the SrF_2-adsorbed surface increases the Sr peak intensity as well but the F-peak and background intensities are decreased, as seen in Fig. 4(a). The decrease of the background intensities might be caused by an agglomeration of the SrF_2 into islands upon hydrogenation. In Fig. 4(b), no dissociation of SrF_2 is thought to occur on the oxygen-saturated TiC(111) surface since the dangling-bond state is already passivated. The surface-peak intensities are relatively small on the hydrogen-saturated surface, but subsequent oxygen adsorption results in a spectrum (not shown) quite similar to that for the oxygen-saturated surface, indicating a substitution of hydrogen by oxygen at the interface. These results show that hydrogenation does not perfectly passivate the reactivity of the dangling-bond states and, hence, the partially ionic Sr-F bond is formed on the hydrogen-saturated TiC(111) surface.

In Fig. 5 are shown the energy spectra of the D^+ ions ($E_0 = 100$ eV) scattered from PrF_3 (0.27 ML) deposited on the Si(111) and TiC(111) surfaces. In contrast to SrF_2, the surface peak of Pr is almost completely missing for both surfaces. Moreover, the surface peak of Pr does not emerge after oxygenation. These results indicate that PrF_3 tends to be dissociatively adsorbed and an ionic bond is hardly formed between Pr and F on the surface. The dissociative adsorption (or the absence of the surface peaks) of PrF_3 is seen also for the oxygen-saturated TiC(111) surface. Such a significant difference between adsorption of SrF_2 and PrF_3 can be ascribed to the reactivity of the gas-phase molecules interacting with these surfaces; although the congruent evaporation of SrF_2 and PrF_3 from the furnace is evidenced by the fact that the stoichiometric thick layers can be deposited on an inert substrate like graphite as seen in Fig. 1, PrF_3(g) can be more radical than SrF_2(g) so that the former dissociates immediately even on the oxygen-saturated surface in the very initial stage of adsorption. The underlying mechanism of adsorption and dissociation of such ionic-compound molecules is similar to that of chemisorption of simple covalent molecules on surfaces.

The occurrence of dissociative adsorption or weakening of ionic bonds can be a common feature of ionic compounds interacting with solid surfaces in the very-low-coverage regime. Indeed, this is true for adsorption of alkali halides such as KF, KI, and CsCl.[7,24] On the W(110) and Pt(111) surfaces, the surface peaks for both alkalis and halogens are missing due to covalent-bond formation with the substrate, and the ionicity of the alkalis is not regained completely after oxygenation. On the Si(100) surface, on the other hand, the halogen atoms tend to react with the dangling-bond state and the remaining alkalis form simple ionic bonds with the substrate.[24] As regards adsorption of elemental alkali metals on Si(100), their surface peaks have a much higher intensity than those of alkaline-earth metals,[23] which is related to their lower ionization energy or higher positive ionicity. This dependence on ionization energy is seen even in adsorption of different alkalis,[11] Cs (3.9 eV), Rb (4.1 eV), and K (4.3 eV) are highly ionized on Si(100) but the bonding of Na (5.1 eV) on Si has apparently some covalent character. Sr (5.7 eV) is less ionic than alkalis and tends to form a covalent bond that leads to silicide formation on the surface. Indeed, the formation of the covalent or metallic bonds with the substrate rather than the simple ionic bonds is an indication of the intermixing or the alloy formation.[25,26] Pr is a transition (rare earth) metal with a *d*-electronic state that contributes to increase covalency of the bonds. Probably, Pr tends to form such a stable alloy with the substrate that oxygenation does not recover the ionic bonds.

IV. CONCLUSION

Low-energy D^+ ion scattering has been utilized to investigate the nature of the bonding of SrF_2 and PrF_3 deposited onto the Si(111) and TiC(111) surfaces. SrF_2 is found to react with the active dangling-bond states of the TiC(111) surface and tends to form a covalent Sr-Ti bond rather than the ionic Sr-F bond. Oxygenation or hydrogenation of the TiC(111) surface passivates the dangling-bond states, so that the ionic bond of adsorbed SrF_2 recovers considerably. The dangling bond of Si(111) is less reactive than that of TiC(111) so that SrF_2 can be deposited onto the surface with very little dissociation or decomposition. At an elevated temperature, on the other hand, decomposition of SrF_2 is promoted probably due to preferential reaction between Si and F at the interface. In terms of PrF_3, dissociative adsorption is preferred on both Si(111) and TiC(111) surfaces probably due to a reaction of Pr with substrate atoms. Oxygenation barely restores the ionic bonding of adsorbed PrF_3. It is thus demonstrated that the nature of the local bonding of atoms on surfaces can be investigated on the basis of neutralization of backscattered low-energy D^+ ions. Moreover, we found that dissociative adsorption or bond weakening due to interaction with the substrate-electronic state is a common concept of adsorption not only for simple covalent molecules such as H_2, O_2, N_2, and CO but also for ionic compounds discussed in this work. It should provide further insight into the chemistry of surfaces.

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