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Alkali-metal adsorption on the Si(100) surface studied by low-energy D^+ scattering

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Low-energy D^+ scattering is employed to explore the nature of the bonding of Na, K, Rb, and Cs adatoms on the Si(100) surface in a low-coverage regime (<0.25 monolayers). In contradiction to the commonly accepted picture, the Na-Si bond is found to differ sharply from the others. The D^+ ions, although neutralized almost completely in scattering from Na, survive neutralization considerably in scattering from K, Rb, and Cs. These results indicate that Na has significant covalency with Si, while the others are adsorbed almost completely ionized.

Alkali-metal (AM) adsorption on semiconductor surfaces has been under intense study recently.[1-9] This is motivated both by various technological applications and by a fundamental interest in the metal-semiconductor interface. However, there is still remarkable disagreement as to the nature of the AM-semiconductor bonding.[5] The conventional picture of AM adsorption proposed by Gurney[10] is such that at low coverage an essentially ionic bond is formed due to substantial charge transfer, and depolarization at high coverage eventually leads to metallic or covalent bonding. This picture of bonding has recently been called into question by Ishida and Terakura[3] on the basis of detailed electronic structure calculations, and the polarized covalent bond is proposed as a more appropriate concept. There seems to be a consensus that this type of bonding is formed on a transition-metal substrate,[11] though a simple s-p band metal such as Al(111) can form an intermixing layer with Na.[12,13] The situation is far more controversial for AM adsorption on a Si(100) surface. Published values of charge transfer from AM to Si have varied from 0 to 1,[5] so that the AM-Si bond has been alternatively characterized as strongly ionic or weakly covalent. Most of these studies have revealed that the AM charge is mainly located in the region between the AM overlayer and the top Si surface layer, but the problem lies in partitioning uniquely this charge into a particular center. Thus, the controversy arises from the lack of a convincing way to rationalize ionicity or neutrality in the bond.

In previous papers,[14] we have reported that the charge state or the bond nature of specific surface atoms can be investigated on the basis of neutralization and inelastic scattering of low-energy D^+ (H^+) ions. Specifically, the D^+ ions scattered from simple ionic crystals with purely ionic bonds are found to be neutralized with much smaller probability than those scattered from metals or materials with significant covalency. This has been successfully attributed to the band effect on resonance neutralization,[15] in which the neutralization probability is determined by the competition between the duration of the D^+-surface interaction (10^{-15} sec) and lifetime τ of the D 1s hole given by $\tau=\hbar/W$, where W indicates the valence-band width. If the isolated, closed shells of the perfectly ionized target atoms are relevant to neutralization (narrow band limit), the hole is highly localized either in D^+ or in the target during scattering, so that the neutralization probability becomes at most 0.5. On the other hand, complete neutralization occurs in the case where a target atom bonds to coordinating atoms via metallic or covalent orbital hybridization because the D 1s hole can readily diffuse into the solid. This local-charge-transfer picture arises from the fact that the D 1s orbital is spatially so localized that only the electronic states around the target atoms are responsible for neutralization of D^+. Here we apply this framework to the analysis of the bond nature of Na, K, Rb and Cs adatoms on the Si(100) surface in a low-coverage regime up to 0.25 monolayers (ML). It should be emphasized that D^+ scattering sees the adatoms explicitly, whereas most alternative approaches only infer them. In contradiction to the generally held belief, we find that the Na adsorption results differ sharply from those of K, Rb, and Cs. The D^+ ions are neutralized almost completely in scattering from Na, while D^+ survives neutralization considerably in scattering from the others. These results indicate that the K, Rb, and Cs adatoms are ionically adsorbed on the Si(100) surface while a significant covalent character exists in the Na-Si bond.

Experiments were performed in an ultrahigh-vacuum (UHV) chamber (base pressure 1×10^{-8} Pa) equipped with facilities for low-energy ion scattering (ISS), ultraviolet and x-ray photoelectron spectroscopy (UPS, XPS), and low-energy electron diffraction (LEED). The D^+ ions generated in a discharge type ion source were incident upon a surface with a glancing angle of 80°, and ions scattered with a laboratory scattering angle of 160° were detected with a hemispherical electrostatic energy analyzer. The D^+ dose in each measurement was restricted to below 1×10^{13} ions/cm^2 in order to avoid possible chemisorption of the D^+ beam. The Si(100) wafer (p-type, resistivity 6–8 Ω cm) was cleaned by resistive heating in UHV, yielding a sharp two-domain 2×1 pattern in LEED. The cleanliness of the surface was checked by core-level and valence-band photoemission and ISS with use of a He^+ beam. AM's were deposited on the clean surface held at room temperature from carefully outgassed AM dispensers (SAES getter). The amount of evaporated AM's was directly measured from the XPS peak intensities and was also indirectly determined from the work-function change as a function of the evaporation time. The general shape of the work-function-versus-coverage curve is similar to those found in several other studies.[6,7] As the coverage increases, the LEED pattern changes from 2×1 to 3×2 (4×1), and then it returns to 2×1 for Cs and K (Na) adsorption. The D^+ scattering experiments were performed mainly in the lower-coverage regime exhibiting the 2×1 pattern in LEED.

As mentioned above, the chemical analysis of adatoms proposed here is derived from the comparison of ample experimental results of D^+ energy spectra. Hence, before entering the detailed discussion of AM adsorption, it is worthwhile to show first the spectra for the relevant AM halides to define the extreme case of perfect ionization. Typically shown in Fig. 1 are energy spectra of D^+ ($E_0 = 50$ eV) scattered from (a) NaCl, (b) KCl, (c) RbCl, and (d) CsCl; the samples were polycrystalline thin films thermally evaporated on a H-terminated Si(100) surface.[16] The D^+ ions scattered from the substrate itself are almost completely neutralized, so that all of the detected D^+ ions come from the alkali-halide overlayers. The overall spectral features are similar to those reported before for other ionic compounds;[14] sharp peaks, labeled *A*, appearing around the elastic binary collision energy for individual surface components indicated by arrows on the abscissa, are due to survival of D^+ in single head-on collisions with the outermost-layer atoms, which we refer to as surface peaks. The K surface peak, though almost completely overlapped with the Cl peak in Fig. 1(b), is confirmed to appear independently in the spectra from the other halides such as KI.[17] As can be seen in the Cl surface peak, a well-separated loss peak (labeled *B*) appears at an energy position about 7–9 eV below the position of the elastic peak *A*. The inelastic scattering arises from reionization of once neutralized D^+ ($D^+ \rightarrow D^0 \rightarrow D^+$) and/or electron-hole pair excitation in the Cl 3*p* state during collision.[14] Both contributions yield comparable energy losses, and hence they are overlapped in Fig. 1. The cationic surface peak is also accompanied by such a loss peak, which can be confirmed by increasing E_0.

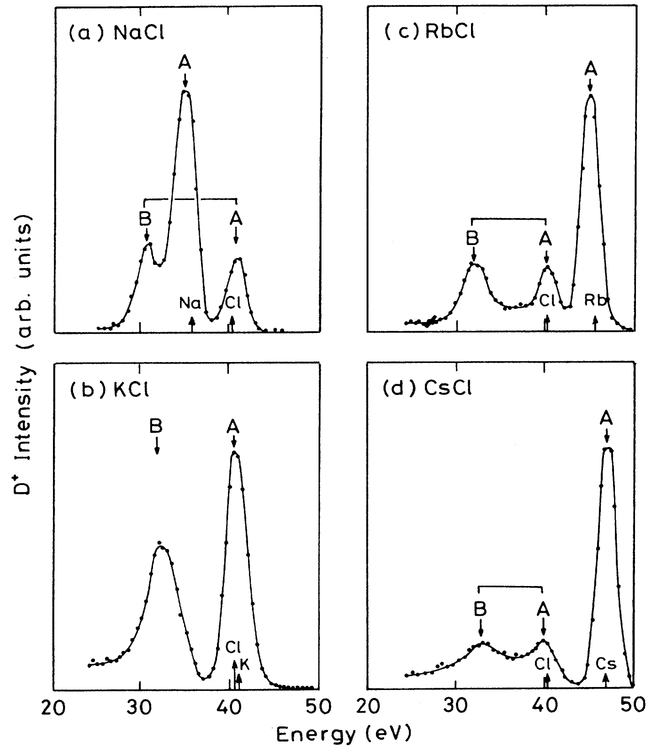

FIG. 1. Energy spectra of $E_0 = 50$ eV D^+ ions scattered from (a) NaCl, (b), KCl, (c) RbCl, and (d) CsCl deposited on the H-terminated Si(100) surface. The measurements were made under the fixed glancing and scattering angles of 80° and 160°, respectively.

In contrast to these results, no significant surface peaks have been recognized for metals and covalent semiconductors.[14] The same is true for some compounds such as $MnCl_2$, $CoCl_2$, and SiO_2,[14] the bonding of which might be characterized as ionic because a considerable amount of charge is expected to be transferred from the cations to the anions. Nevertheless, the band calculation reveals that significant covalency exists due to orbital hybridization between the cationic 3*d* state (sp^3 state) and the Cl 3*p* state (O 2*p* state) for $MnCl_2$ and $CoCl_2$ (SiO_2).[18,19] How can we assign such bonds? Supposedly, the controversy in the nature of the AM-Si bond is essentially identical to this situation. Thus, ionicity or covalency in bonds is a rather crude concept. Here we define ionicity of target atoms as the presence of clear surface peaks in the D^+ energy spectra. In this framework, the bonding of, e.g., SiO_2 is classified as "a highly polarized neutral bond" and can be qualitatively distinguished from the perfectly ionic bond. We believe that our definition of ionicity is among the strictest ones and cannot be reached by most of the other conventional techniques.

On this basis, we have explored the bond nature of AM's on the Si(100) surface. Dots and solid lines in Fig. 2 show representative D^+ energy spectra ($E_0 = 50$ eV) from (a) Na, (b) K, (c) Rb, and (d) Cs adatoms on the Si(100) surface; also shown by dashed lines are the spectral change due to following 2-L O_2 exposure. In each measurement, care is taken to control the AM coverage below 0.2–0.25 ML so that the AM layer breaks up into a set of individual adatoms and no patches of the metallic overlayer are formed.[9] Indeed, the spectral features identical to those in Fig. 2 are obtained for the smaller-coverage regime as well. It is notable that the Na peak is absent at any coverage. Besides the elastic peak *A*, there exist a few energy-loss structures in Figs. 2(b)–2(d). The origin of inelastic scattering will be described later, and we shall focus on the elastic peak *A* first.

One may think that the absence of the Na surface peak is caused by the steric shadowing effect[20] rather than the ion neutralization effect, since, if Na is preferentially located at the subsurface site, the D^+ yield would be decreased remarkably. Very recently, indeed, the commonly accepted assumption that AM's reside on the topmost surface has been questioned for Li/Si(100) (Ref. 8) and Na/Al(111):[12,13] In contrast to the other AM's, Li does not form a metallic overlayer on Si(100) and is intermixed with Si after monolayer formation. On the Al(111) surface, on the other hand, Na occupies an unusual substitutional site even in the low-coverage regime, though Rb resides on the top adsorption site. In these studies, the

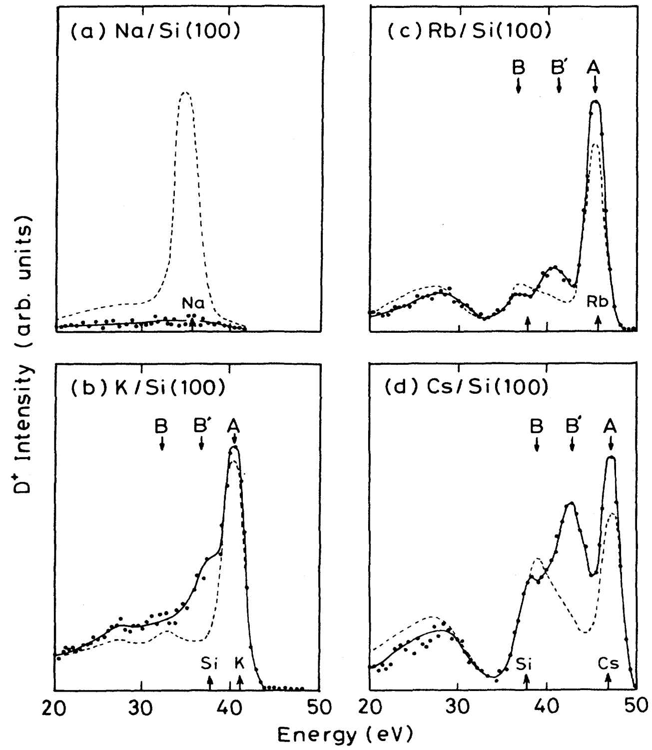

FIG. 2. Energy spectra of $E_0=50$ eV D^+ ions scattered from (a) Na, (b) K, (c) Rb, and (d) Cs adatoms (coverage of 0.2–0.25 ML) on the Si(100) surface; the measurements were made under the same conditions as in Fig. 1. The dashed lines show the D^+ spectra obtained after subsequent exposure to 2-L O_2 gas.

differences have been attributed to the smaller radius of Li or Na relative to the others. By using a polar-and-azimuthal-angle-scan mode of He^+ scattering [so-called impact collision ion-scattering spectroscopy (ICISS)],[20] we have confirmed that both Na and Cs adatoms exists on the outermost surface layer, though the precise adsorption site or the occurrence of the intermixing has not been determined, due presumably to the use of the two-domain sample. In this respect, the molecular-dynamics simulations also conclude that no considerable difference exists in the adsorption sites between Na and K on Si(100).[4] Thus, the difference in the D^+ spectra shown in Fig. 2 should be ascribed to the ion neutralization effect and therefore is indicative of the existence of a crucial difference in the bond nature of AM's on the Si(100) surface.

In order to further evaluate the degree of ionicity of the AM adatoms, oxygen adsorption on these surfaces is quite helpful. If AM's are ionized only in part or neutral species coexist on the surface, oxidation brings about ionization of such adatoms by the formation of more ionic AM-O bonds, leading to a signficant increase in the surface peak. This is in fact the case for the Na result. On the other hand, oxygenation induces only a small change in the intensity of peak *A* for K, Rb, and Cs. These experimental results clearly show that the Na-Si bond has covalency to a certain extent, while the K-, Rb- and Cs-Si bonds are almost perfectly ionic in nature. This tendency is consistent with the difference in the ionization energy; the value of Na (5.1 eV) is a little larger than that of the others (4.3–3.9 eV). Because of this, the Na 3*s* level may be overlapped in part with the Si valence state.

The observed critical difference in ionicity of the AM-Si bond has not been revealed either by any theoretical calculations[2–5] or by other conventional experimental techniques.[6–8] In fact, the LEED and work-function-versus-coverage data appear to have no marked difference between Na and the others, at least as far as the dominant features are concerned. As described, the quantitative value of the charge transfer is in general very difficult to determine. Our definition of ionicity is fairly strict, so that the observed difference in D^+ scattering might correspond only to a small change in the quantity of the AM's charge. There has been some suggestion in recent studies using scanning tunneling microscopy (STM) (Refs. 21 and 22) that the AM atoms form one-dimensional chains perpendicular to the substrate dimer rows and a covalentlike bond is formed. The STM work has provided valuable information about the geometrical arrangement for AM's on Si(100). STM approximately probes the local density of states around the Fermi level. However, the assignment of the alkali-metal *s* electron is not a trivial issue because of the coexistence of partially occupied dangling-bond states. Even in the extreme ionic case, STM may detect AM's decorated with the dangling-bond states,[23] suggesting limited applicability of STM to this subject. The present finding, that AM's with smaller ionization energy are more likely to be ionized, is one of the strong pieces of evidence in support of the Gurney model of the AM adsorption.[10]

Another conspicuous feature in Fig. 2 is the significant energy-loss structures. In previous papers,[14] we have shown that at least two characteristic energy-loss channels exist, one being electron-hole-pair excitation (without changing charge state: $D^+ \rightarrow D^+$), the other being reionization of once neutralized D^+ ($D^+ \rightarrow D^0 \rightarrow D^+$). It is inferred from the well-known electron promotion mechanism[24,25] that both channels are enhanced during collision if the D 1*s* orbital can be promoted due to antibonding interaction with the target core orbital. Since the binding energy of an AM core level becomes closer to that of the D 1*s* level in order of Na (2*p*: 31 eV), K (3*p*: 18 eV), Rb (4*p*: 16 eV), and Cs (5*p*: 13 eV), the degree of the D 1*s* orbital promotion should be increased in that order. As a result, the contribution of inelastic scattering relative to elastic scattering increases in going from Na to Cs, as shown in Fig. 2. We can see two dominant energy-loss peaks. As far as peak *B* is concerned, it can essentially be ascribed to reionization of neutralized D^+ ($D^+ \rightarrow D^0 \rightarrow D^+$). Much more interesting is peak *B'*, which is characteristic of AM's on the Si substrate and cannot be seen for the AM halides shown in Fig. 1. This is the loss peak due to electronic excitation in the Si substrate. Indeed, we have shown that the *e*-*h* pair excitation during collision is concerned not only with the target atoms (AM's) but also with the coordinating atoms (Cl in Fig. 1 and Si in Fig. 2).[14,25] The energy-loss value of 4–5 eV for peak *B'* is essentially the same as that commonly seen in the electron-energy-loss spectra of the AM-adsorbed Si(100) surface,[8] and can be ascribed to individual electronic excitation from the Si valence band to an empty state of AM. This is also shown by the fact that the intensity of peak B' decreases markedly upon O_2 exposure due probably to formation of the more-preferable AM-O bond instead of the AM-Si bond, and accordingly the loss peak position shifts to the lower-energy side as a consequence of excitation of the O $2p$ electron.

Another important contribution of the inelastic scattering in Fig. 2 is the broad spectral background appearing in the energy range below 35 eV. We have assigned the background to reionization of once-neutralized D^+ emerging from the Si substrate ($D^+ \rightarrow D^0 \rightarrow D^+$).[14] The fact that the background is almost completely absent at the clean Si(100) surface and increases with the amount of AM or oxygen adatoms indicates that reionization occurs in the course of small-angle scattering with these adatoms on the outgoing trajectory of D^0. The cutoff energy is located at an energy position about several eV below the exact binary collision energy for Si due to resultant excitation of the D $1s$ electron to an empty surface electronic state, which has been confirmed by increasing E_0 up to 500 eV as well.

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