Potassium adsorption on metal and semiconductor surfaces studied by low-energy D$^+$ scattering

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We report on neutralization and inelastic scattering of low-energy D$^+$ ions at the K-adsorbed Si(100), Pt(111), and W(110) surfaces. The D$^+$ ions scattered from the K adatoms are neutralized almost completely on the Pt(111) and W(110) substrates, although they are observed intensively with a much smaller neutralization probability on the Si(100) surface. These results strongly suggest that K is ionically adsorbed on the Si(100) surface but is essentially neutral on the Pt(111) and W(110) surfaces, which is derived from the fact that the diffusion of the D $1s$ hole leading to neutralization of D$^+$ is extremely enhanced if the target bonds to ligands via metallic or covalent orbital hybridization, while the contrary is true if the bonding is ionic. The ionic K-Si bond results from the preferential donation of the K $4s$ electron to the active dangling-bond states or the bulk conduction-band states of the Si substrate, whereas the K adatoms are in the polarized neutral state rather than ionized on the metal surfaces due to charge redistributions. It is also found that the oxygen coadsorption results in the formation of the ionic K-O bond on the K/Si(100) surface, but the covalent K-Pt bond is retained irrespective of oxygenation on the K/Pt(111) surface. The fact that oxygen does not strongly interact with K implies that the catalytic promoter effect of K is less poisoned during reaction on the Pt(111) substrate.

I. INTRODUCTION

In recent years, there has been a great interest in alkali-metal (AM) adsorption on metal and semiconductor surfaces. This interest is motivated in part by technological applications such as the significant reduction of the surface work function and the catalytic promotion in surface chemical reaction. In particular, if the work function of the semiconductor is lowered by adsorption of AM's (and subsequent addition of oxygen) to such an extent that the vacuum level falls below the bulk conduction band, then the system is said to be driven in the negative-electron-affinity state.[1] This system has an important application as high-efficiency electron emitters. Furthermore, AM's or their additives are known to be important promoters in heterogeneous catalysts for Fischer-Tropsch synthesis,[2] ammonia synthesis,[3] and other reactions.[4] However, the AM-induced effects on these reactions are not fully understood yet. The point still under debate is that the molecular dissociation is mediated by either an indirect through substrate AM-molecule interaction or a direct interaction between AM and molecules involving overlap of the molecular orbitals.[5-7] On the other hand, it has been suggested that the mechanism underlying the promotion of the catalytic process is electrostatic in nature.[8,9] Thus the effective range of the AM promoter is a subject of current discussion. The principal question related to these interests is what is the most likely chemical state of AM's on a clean surface as well as during reaction.

The AM's are highly electropositive elements and hence their weakly bound s electron is intuitively considered to be donated to the conduction band of the substrates,[10] the resultant AM ions being responsible for the formation of a dipole layer or the lowering of the work function. This picture has been refined by considering the broadening of the AM s level into a partly occupied surface resonance and consequently some degree of covalency has been introduced.[11,12] In more recent theoretical works for $c(2 \times 2)$ Cs on W(100),[13] the notion of charge donation is less important and the bonding is metallic with very little charge transfer from Cs to the substrate. Other theoretical works for Na on Al(001) (Ref. 14) and AM's on jellium[15] also find that the dipole layer comes from the polarization of the AM valence electrons and the adatom is neutral in any coverage. Experimentally, the occupancy of the AM s level at low coverage is still significantly controversial: The AM s-derived feature is difficult to detect in the studies of ultraviolet photoelectron spectroscopy (UPS) for K/Al(111) (Ref. 16) and K/Ag(100) (Ref. 17) with less than half a monolayer coverage, while in metastable-deexcitation-spectroscopy (MDS) study of K/Cu(110) (Ref. 18) the contribution from the K $4s$ electron to the density of state close to the Fermi level has significantly been observed even in the low-coverage limit. Very recently, the covalentlike bond for Cs, K, and Na on W(110) (Ref. 19) or the metallic Na-Al bond accompanying the substitution of the Al(111) substrate[20] have been reported even at submonolayer coverage. The situation is far more controversial for semiconductor substrates.[21-29] Published values of charge transfer have varied from 0 to 1, so the AM-semiconductor bond has been alternatively characterized as strong ionic or weak covalent. This is probably because the amount of covalency or ionicity in the bond cannot be qualitatively stated with much confidence due to a large spatial overlapping between AM and substrate wave functions.

In this paper, we employ low-energy D$^+$ scattering as a probe of the electronic properties of potassium adsorbed on Si(100), Pt(111), and W(110). We have revealed in previous papers[30] that neutralization of D$^+$ is closely

related to the chemical states of solid surfaces. The proposed mechanism is summarized briefly in what follows: One of the early indications of uniqueness of H^+ or D^+ scattering was reported by Eckstein and co-workers[31] in comparison with the results of He^+ scattering. The He^+ ions scattered from outermost surface atoms are more likely to survive neutralization and form so-called surface peaks in their energy distribution. However, the surface peak is usually completely absent for H^+ or D^+ scattering from metal surfaces. This is remarkable if one considers the similarity of the electronic structure between the H^+ and He^+ ions. It is commonly recognized that electron capture occurs via one-electron resonance (RN) and two-electron Auger (AN) processes and that the relative role of these processes depends sensitivity upon the energy position of the vacant ionic level relative to that of the valence band. In fact, AM ions with vacant s levels close to the Fermi level are neutralized via RN. Rare-gas ions such as He^+, on the other hand, have the ground $1s$ level (-24.6 eV) well below the valence band, so that an electron is captured via the AN process. As for H^+ (D^+), the ground $1s$ level (-13.6 eV) and the excited $2s$ level (-3.4 eV) seem to be involved with AN and RN, respectively. However, uniqueness comes about because the $1s$ level position is located just around the bottom of the valence band as shown in Fig. 1(a). In this configuration, RN takes place since the $1s$ level can significantly be promoted in the vicinity of a surface. There are two origins of the electronic level promotion: one being the image charge effect and the other being the antibonding interaction with a target core orbital in the collisional regime. The latter concept has been established in connection with reionization of neutral He^0,[32,33] where the level promotion is found to be essentially the atomic process determined by the combination of projectile and target atoms and occurs for all target atoms expect for those which have a filled d shell with binding energy shallower than the $1s$ level. In this respect, Tsuneyuki, Shima, and Tsukada[32] have pointed out that neutralization of H^+ ions is substantially dependent on the valence-band structure (band effect). In this picture, as shown in Fig. 1(a), the $1s$ level crosses the valence band from the bottom and the resonance condition is met over the wide energy range of the band until the close encounter with target atoms is reached, which is in apparent contrast to the ordinary RN relevant to the shallow AM s or D $2s$ levels. Then the neutralization probability is determined by the competition between the duration of the D^+-surface interaction ($\sim 10^{-15}$ sec) and the lifetime τ of the hole given by[34]

$$\tau = \hbar / W , \qquad (1)$$

where W indicates the valence-band width. If the isolated, closed shells of the surface electronic states are relevant to neutralization (narrow-band limit), the hole diffusion is so highly suppressed that the neutralization probability is at most 0.5, while complete neutralization occurs when the hole can diffuse immediately into the wide band.

In the present studies, we focus on large-angle scattering of D^+ involving single head-on collision with the top-

most surface atoms as schematically shown in Fig. 1(b). It should be emphasized that the single-collision event can be separated from other complicated scattering trajectories in the energy spectra of scattered ions. Since the deviation of the incoming and scattered ion trajectories from the surface normal is as small as 10°, D^+ contributing to the surface peak interacts only with the electronic states around the specific target atoms. This effect also issues from the localized nature of the D $1s$ orbital. In the local charge-transfer approach, therefore, the above-mentioned band picture can be alternatively stated that the hole diffusion is enhanced significantly if target atoms bond to coordinating atoms via metallic and covalent orbital hybridization but is suppressed if those are ionic. Especially in scattering from cations of simple ionic compounds, the hole is highly localized in deuterium and hence the intensive surface peak due to survival of D^+ can be observed. Inversely, the absence of the surface peak in scattering from metals and covalent semiconduc-
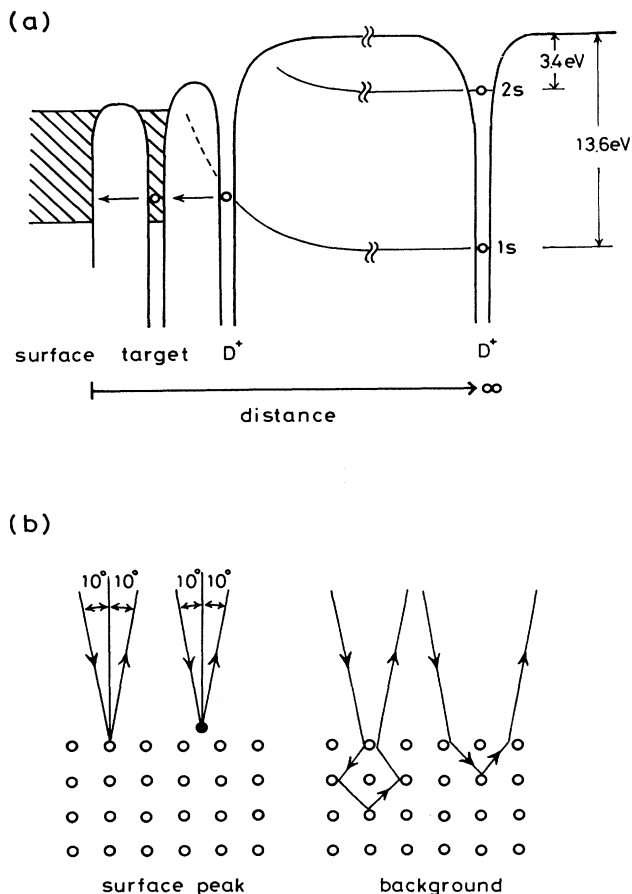
(a)

(b)

FIG. 1. (a) Energy-level diagram for neutralization of D^+ associated with a promotion of the $1s$ and $2s$ levels in the vicinity of a surface followed by diffusion of the hole into the band. (b) A schematic of various ion trajectories contributing to the surface peak and the background of the D^+ energy spectra. The experiments were performed under the large-angle scattering condition with incidence and detection angles of 10° relative to the surface normal.

tors is obvious. In this framework, the appearance of the marked surface peaks in the D^+ energy spectra can be the experimental evidence for ionicity of specific target atoms. We have deduced this principle from a large number of experimental results[30,35] for ionic crystals with purely ionic bonds (NaCl, NaI, KF, KI, RbCl, CsF, CsCl, $SrCl_2$, CaF_2, SrF_2, BaF_2, $CdCl_2$, Sb_2O_3), simple, transition, and noble metals [Ba, Ag, Mo(111), TA(111), W(110), Pt(111)], and materials with significant covalency [diamond (100), Si(100), Si(111), Ge(100), SiO_2, $MnCl_2$, $CoCl_2$]. As regards AN, it can also make an important contribution to D^+ neutralization but should have nothing to do with such an efficient neutralization process that leads to complete absence of the surface peaks because of the fact that covalent insulators like diamond, $MnCl_2$, $CoCl_2$, and SiO_2 yield no surface peaks despite that AN for these surfaces should be suppressed due to existence of a large band gap.[30] The charge-transfer process between D^+ and surfaces is in reality complex.[35] Beside neutralization described here ($D^+ \rightarrow D^0$), reionization ($D^+ \rightarrow D^0 \rightarrow D^+$) as well as resonance neutralization to the D $2s$ level ($D^+ \rightarrow D^*$) takes place. However, the latter processes will be shown to have less bearing on the bond nature of the surface.

On this basis, we have investigated the nature of the bonding of K on the Si(100), Pt(111), and W(110) surfaces in a low-coverage regime (< 0.2 ML) (ML denotes monolayer).[35] It is found that the surface peak of D^+ scattered from the K adatom is almost completely absent on the Pt(111) and W(110) surfaces due to RN ($D^+ \rightarrow D^0$), though it is intensively observed with a much less neutralization probability on the Si(100) surface. These results strongly suggest that K is ionically adsorbed on the Si(100) surface but is essentially neutral on the Pt(111) and W(110) surfaces. The ionic nature of the K-Si bond can be ascribed to the preferential donation of the K $4s$ electron to the active dangling bond state or the bulk conduction-band state of the Si substrate. The neutrality in the K-Pt and K-W bonds may arise from the covalent orbital hybridization. The neutralization of D^+ is enhanced in the high K coverage regime due to additional neutralization ($D^+ \rightarrow D^*$) if the surface work function is reduced below 3.4 eV. Oxygenation of the K/Si(100) surface is indicative of the formation of the ionic K-O bond while the charge state of K is suggested to be less affected by the coexistence of oxygen on the Pt(111) surface. Neutralized deuterium emerging from the substrate can be reionized ($D^+ \rightarrow D^0 \rightarrow D^+$) in the course of the small-angle scattering with the adatoms on the outgoing trajectory.

II. EXPERIMENT

The experimental setup has been described elsewhere[33] and only the features important to this experiment are briefly summarized here. The sample chamber was evacuated down to an ultrahigh vacuum (UHV) condition (1×10^{-8} Pa) and equipped with facilities for low-energy ion scattering (ISS), low-energy electron diffraction (LEED), and ultraviolet photoelectron spectroscopy (UPS). The D^+ ions with kinetic energy E_0 ranging from

10 eV to 1 keV were generated in a discharge-type ion source and were mass analyzed by a Wien filter. The ion source was attached to the sample chamber through three differentially pumped vacuum chambers containing lens systems so that the pressure in the sample chamber was kept below 2×10^{-8} Pa during the measurements. The D^+ dose in each measurement was restricted to below 5×10^{12} ions/cm^2 in order to minimize the surface decomposition and possible chemisorption of the D^+ beam. The positive ions reflected under the scattering geometry shown in Fig. 1(b) were analyzed by a hemispherical electrostatic energy analyzer operating with a constant energy resolution of 1 eV.

The Si(100) wafers (p-type, n-type) were cleaned by resistive heating in UHV, yielding a sharp two-domain 2×1 pattern in LEED. A monohydride Si(100)-(2×1) surface was also prepared by adsorption of atomic hydrogen from a hot tungsten filament placed in front of the surface, the termination of the surface dangling bond being confirmed with UPS. The Pt(111) and W(110) surfaces were prepared with a standard oxygen treatment. The surface cleanliness was checked by means of LEED, UPS, and ISS with use of He^+ ions. Potassium was deposited on these surfaces held at room temperature from a carefully outgassed chromate dispenser (SAES getter). The amount of evaporated potassium was indirectly controlled by measuring the work function change $\Delta\Phi$ as a function of the evaporation time with use of UPS. The general shape of that curve was similar to those found in several other studies.[5,28]

III. EXPERIMENTAL RESULTS

The energy spectra of $E_0 = 50$ eV D^+ obtained at the Si(100) surface with increasing K coverage are shown in Figs. 2(a)–2(c). The spectrum from the clean Si(100) surface shows almost nothing in the D^+ yield, indicating that D^+ is neutralized almost completely. However, if K is deposited only with a very little coverage, a marked change is seen in the spectra. The surface peak appearing around the elastic-binary-collision energy for D-K scattering, shown by the arrow on the abscissa, evolves accompanied by an extended background with increasing the coverage. The surface peak stems from survival of D^+ in single head-on collision with K and the spectral background arises from reionization of neutral D^0 ($D^+ \rightarrow D^0 \rightarrow D^+$) scattered from the substrate as schematically shown in Fig. 1(b). The coverage of K relative to the saturation value is estimated to be 0.21 from the reported work-function versus coverage curve at $\Phi = 3.4$ eV.[28] With further increasing coverage, both surface peak and background begin to decrease and, at saturation coverage, the D^+ ions are neutralized almost completely again as shown in Fig. 2(c). A remarkable change occurs if the K-saturated surface is exposed to oxygen with an amount of 1 L (1 L=1 langmuir=1.3×10^{-4} Pa s) as typically shown in Fig. 2(d), where both the K surface peak and background reappear dramatically in the spectra. It is notable that the width of the K surface peak in Fig. 1(d) is narrower than that in Fig. 1(b).
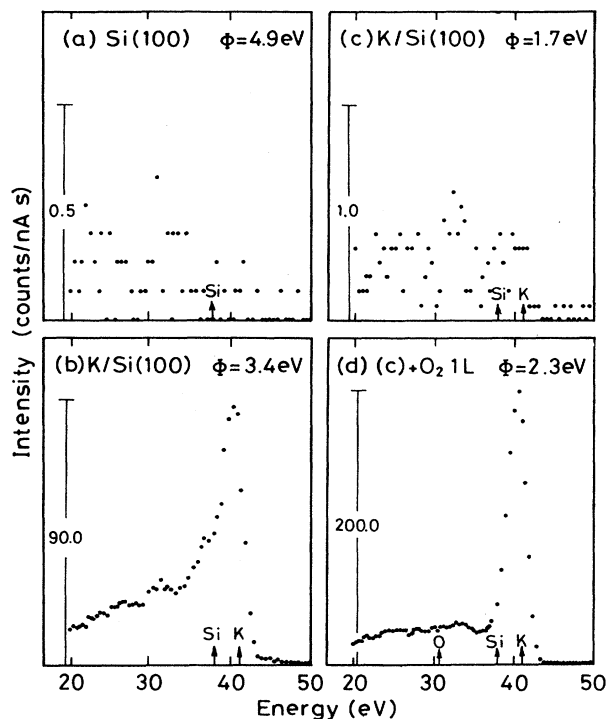
The K adsorption is performed on the H-terminated

FIG. 2. Energy spectra of $E_0 = 50$ eV D^+ ions scattered from (a) the clean Si(100) 2×1 surface with work function (Φ) of 4.9 eV, (b) the K-adsorbed Si(100) surface with $\Phi = 3.4$ eV, (c) the K-saturated Si(100) surface with $\Phi = 1.7$ eV, and (d) the K-saturated Si(100) surface exposed to 1 L O_2. The measurements were made under the scattering geometries shown in Fig. 1(b). The spectral intensity is normalized relative to each other through beam currents. The energy corresponding to elastic binary collision with each surface component is indicated by arrows on the abscissa.
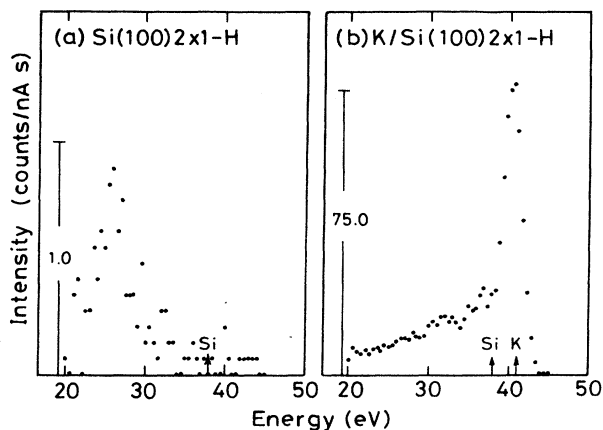

FIG. 3. Energy spectra of $E_0 = 50$ eV D^+ ions scattered from (a) the H-terminated Si(100) 2×1 surface and (b) the H-terminated Si(100) surface obtained by subsequent deposition of K with the same amount as in Fig. 2(b). The intensities are normalized through beam currents.
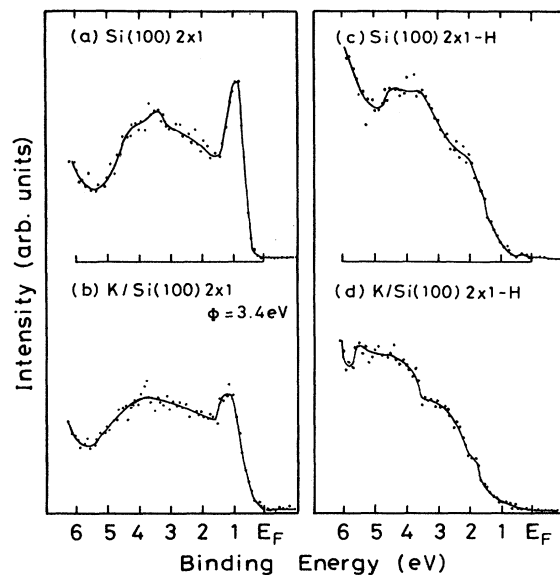

FIG. 4. Normal-emission UP spectra (HeI) for (a) the clean Si(100) 2×1 surface, (b) the K-adsorbed Si(100) 2×1 surface with work function of 3.4 eV, (c) the H-terminated Si(100) 2×1 surface, and (d) the H-terminated Si(100) surface obtained by subsequent K deposition with the same amount as in (b).

Si(100)-(2×1) substrate as well in order to investigate the role of the Si dangling bond in the K adsorption; the results obtained by using a $E_0 = 50$-eV D^+ beam are shown in Fig. 3 for (a) the H-terminated Si(100) surface and (b) the H-terminated Si(100) surface obtained by consecutive K adsorption with the same deposition time as in Fig.
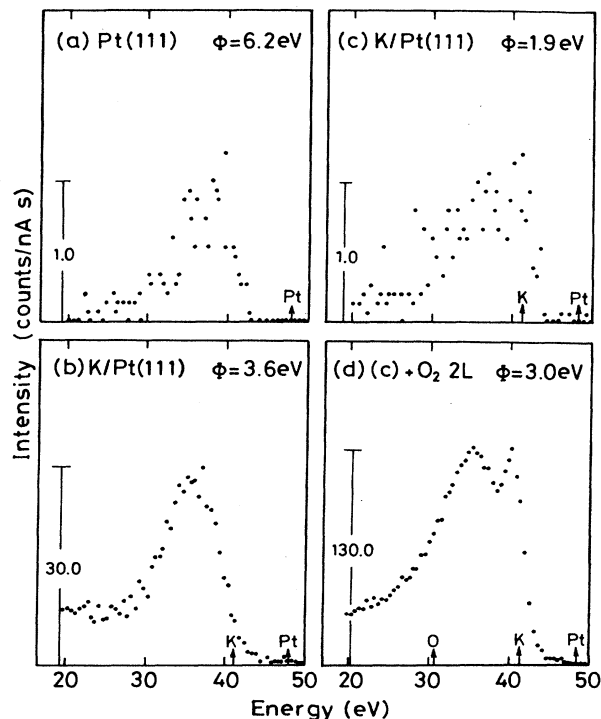

FIG. 5. Same as in Fig. 2 for the Pt(111) substrate.

2(b). The termination of the dangling bond during hydrogenation followed by K adsorption has been confirmed from the normal-emission UPS spectra (He I) shown in Fig. 4; the occupied portion of the dangling-bond states just below the Fermi level at the Si(100)-(2×1) surfaces disappear completely at the H-terminated surfaces both with and without the K adatoms. The energy spectra of D^+ shown in Figs. 3(a) and 3(b) are quite similar to those in Figs. 2(a) and 2(b), respectively. A small structure appearing around $E = 25$ eV in Fig. 3(a) probably comes from the contamination of oxygen during hydrogenation. The spectral intensity increases initially with increase of the K coverage and begins to decrease at approximately the same deposition time as in Fig. 2.

Shown in Fig. 5 are the D^+ energy spectra obtained at the Pt(111) surface with increasing K coverage. Similar to the Si surfaces, the neutralization rate of D^+ is quite high at the clean surface. The K adsorption increases the D^+ yield but no clear K surface peak appears. The D^+ spectrum, typically shown in Fig. 5(b), is attributable to the background due to reionization $(D^+ \rightarrow D^0 \rightarrow D^+)$. This is derived from the fact that the energy distribution quite similar to that in Fig. 5(b) is obtained at the O-chemisorbed Pt(111) surface as well, indicating that the background originates from the substrate and is almost independent of the adsorbates [see Fig. 1(b)]. The absence of the K surface peak in Fig. 5(b) is remarkable in comparison with the results of the Si substrate. The K coverage at $\Phi = 3.6$ eV is estimated to be 0.14 ML from the literature.[5] With increase of the coverage, the background decreases and the result obtained at the saturation coverage is shown in Fig. 5(c). By exposing this sur-
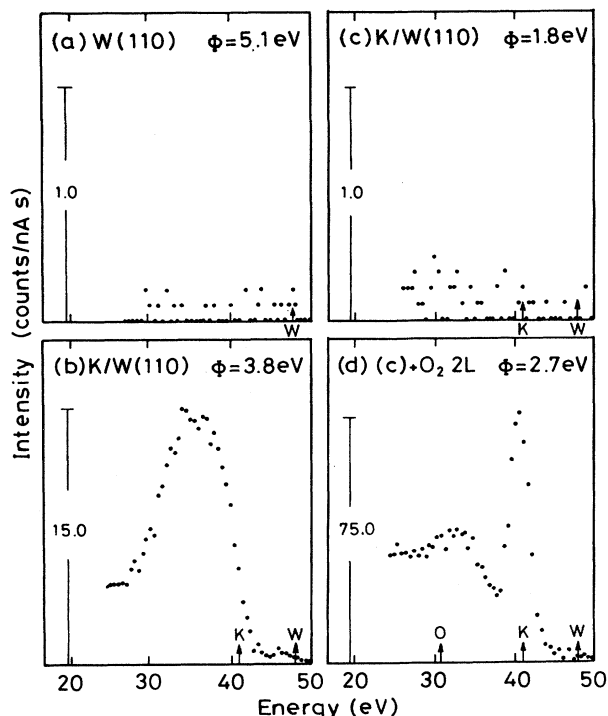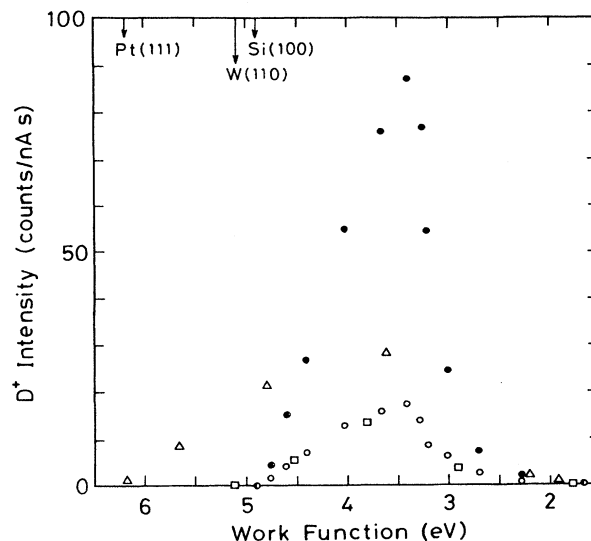

FIG. 7. The K-induced intensity change of the scattered D^+ ions ($E_0 = 50$ eV) as a function of surface work function. The D^+ intensities with energy of 40.5 eV (corresponding to the K-surface-peak position) and 30 eV (the background position) obtained at the Si(100) surface are indicated by solid and open circles, respectively. The background intensities with energy of 36 eV obtained at the Pt(111) [W(110)] surfaces are plotted by open triangles (squares) as well.
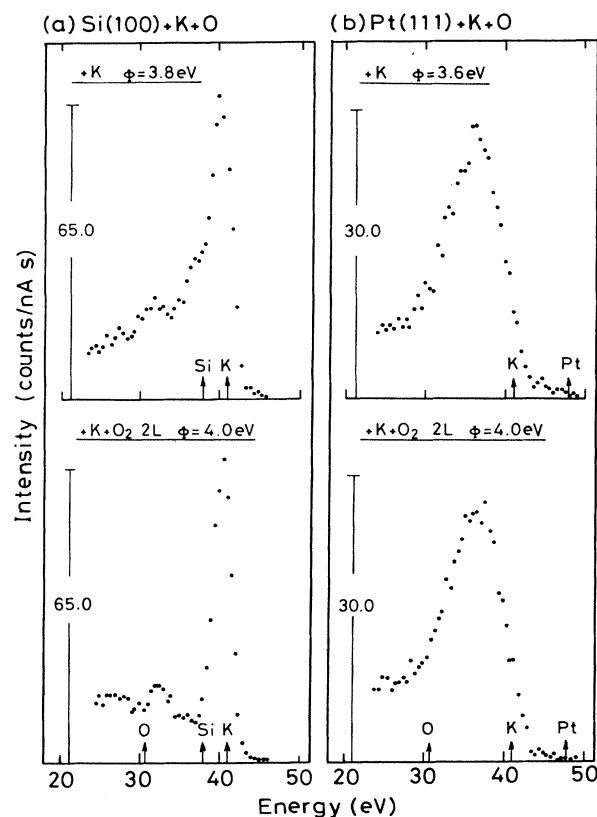

FIG. 8. Effects of the oxygenation on the energy spectra of $E_0 = 50$ eV D^+ ions obtained at the K-adsorbed (a) Si(100) and (b) Pt(111) surfaces exhibiting the work function of 3.8 and 3.6 eV, respectively.

FIG. 6. Same as in Fig. 2 for the W(110) substrate.

face to a 2-L O_2 gas, both K surface peak and background appear markedly as shown in Fig. 5(d). A quite similar spectral change induced by K adsorption is obtained for the W(110) substrate and the results are displayed in Fig. 6.

Plotted in Fig. 7 are the intensities of the K surface peak (at $E = 40.5$ eV; solid circles) and the background (at $E = 30$ eV; open circles) for the Si(100) substrate, together with the background intensities at $E = 36$ for the K/Pt(111) (open triangles) and K/W(110) (open squares) surfaces, as a function of the surface work function. Both surface-peak and background intensities increase initially and then decrease in the high-K-coverage region. The work-function value at which the D^+ yield begins to decrease is measured to be about 3.4 eV. That the threshold corresponds well to the binding energy of the excited D $2s$ level indicate that the onset of the RN to the excited state ($D^+ \rightarrow D^*$) is responsible for the marked decrease of the D^+ yield in the high coverage region.

Oxygenation has a remarkable effect on the D^+ spectra collected from the K-saturated surfaces of Si(100), Pt(111), and W(110), but little change occurs if the K coverage is small enough. In the case of the Si(100) substrate, shown in Fig. 8(a), though the width of the K surface peak is reduced due to oxygen chemisorption, the overall spectral intensity is almost unchanged. Similarly as shown in Fig. 8(b), very little change is seen due to oxygenation of the K/Pt(111) surface. It should be em-

phasized that the absence of the K surface peak in Fig. 8(b) is obviously in remarkable contrast to the results of the oxygenation of the K-saturated surface shown in Fig. 5(d). For this system, the K surface peak emerges upon oxygenation provided that the K coverage is increased to be about 0.3 ML or more. One may think that the absence of the surface peak in Fig. 8(b) stems from the shadowing effect by coadsorbed O. But this assumption is discarded because of the fact that the K surface peak is recognized in He^+ scattering for all surfaces shown in Fig. 8.

Shown in Fig. 9 are the oxygen-induced changes of (a) the surface work function and (b) the spectral intensities of $E_0 = 50$ eV D^+ at the K-saturated Si(100) surface. The work function initially decreases due to oxygenation, and then increases. At the turning point, the Φ_{min} state is obtained with O_2 exposure of 0.3 L. The D^+ yields corresponding to both the K surface peak (solid circles) and background (open circles) do not appear unless the Φ_{min} state is reached, and then increase markedly with further O_2 exposure.

IV. DISCUSSION

A. The charge state of potassium on Si(100), Pt(111), and W(110)

At the early stage of K adsorption, the D^+ spectra from the K/Si(100) surface contrast sharply with those from K on the metal substrates. The K surface peak conspicuously appears on the clean and H-terminated Si(100) substrates while, on the Pt(111) and W(110) substrates, only the background due to reionization is increased with the K adatom. As described in the Introduction, the presence of the surface peak can be the experimental measure of ionicity in bonds. In reality, however, ionicity or covalency in bonds is a rather crude concept. This is in fact the case for some compounds such as $MnCl_2$, $CoCl_2$, and SiO_2. The bonding of these compounds 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 calculations[36,37] reveal that significant covalency exists due to orbital hybridization. How can we assign such bonds? Supposedly, the controversy in the nature of the chemisorptive bond of AM's is essentially identical to this situation. On the basis of our definition of ionicity, the bonding of, e.g., SiO_2 is classified as "a highly polarized neutral bond" and is qualitatively distinguishable from the perfectly ionic bond of the simple ionic compounds. Presumably, this type of bond is formed for K on the Pt(111) and W(110) surfaces. On the other hand, appearance of the remarkable K surface peaks on the Si(100) substrate is indicative of the high ionicity of the K adatoms.

The neutrality of the AM adatoms on metal substrates has been pointed out theoretically by Ishida and Terakura.[14] They found that the AM adatoms are essentially neutral even in the low-coverage limit because the covalentlike bond is formed due to charge redistribution. Experimentally, the MDS data on K/Cu(110) by Woratschek et al.[18] appear to have consensus if the ob-
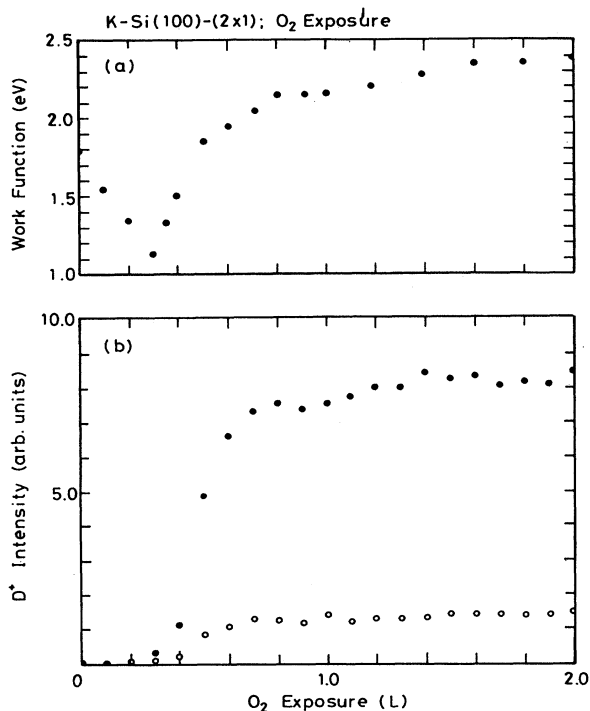

FIG. 9. Effects of oxygen adsorption on the K-saturated Si(100) 2×1 surface. (a) The work function is plotted against the amount of O_2 exposure. (b) The intensities of the D^+ spectra ($E_0 = 50$ eV) at $E = 40.5$ eV corresponding to the surface peak (solid circles) and $E = 30$ eV corresponding to the background (open circles) are plotted against the O_2 exposure.

served density of state (DOS) close to the Fermi level really comes from the AM s-derived states. This interpretation, however, is quite controversial since the enhancement in DOS is not clearly observed in the UPS data[16,17] below half a monolayer coverage, which has been ascribed to the low excitation cross section of s-electronic states by photons. Very recently, however, Hemmen and Conrad[38] have proposed that this strong emission is characteristic of MDS coming from the decay of a core-excited negative He$^-$ ion. Furthermore, it seems probable that at a very low-coverage region DOS near the Fermi level is not necessarily related to the AM electrons because any electronic states at the low work-function patches induced by the AM adatoms may contribute to the Penning process. Therefore, these studies seem to be not definitive for concluding the occupation of the AM s state.

Another experiment directly dealing with the charge state of AM's has recently been made by Riffe, Wertheim, and Citrin.[19] They found that the Cs, K, and Na overlayers on W(110) with coverage of saturation and 1/3 of saturation are neutral with covalent or metallic bond as the surface core-level photoemission of W $4f$ shows very little shifts due to AM adsorption. Our results on K/Pt(111) and K/W(110) conclude that this picture of bonding is correct even for a much lower-coverage region where the K layer breaks up into a set of individual adatoms (<0.2 ML).

Very recently, the common picture of AM adsorption that no intermixing occurs with the substrate are called into question for Na adsorption on the Al(111) surface.[20,39,40] If K were adsorbed in a substitutional site of W(110) or Pt(111) surfaces, the coordinating substrate atoms would also make a significant contribution to neutralization during the D$^+$-K collision and hence the absence of the K surface peak might not be a strong evidence for covalency in bonds. In reality, since the substitution still leaves the center of the AM atoms rather protruding from the top layer of the substrate due to a large AM radius, the direct contribution from the substrate electronic states may be marginal.[20] Moreover, the intermixing is reported only for the Na/Al(111) system, representing a rather special case.[40] Indeed, the close-packed transition-metal surfaces such as W(110) or Pt(111) are unlikely to react with AM's.[41]

As regards the Si substrate, the K-metal picture may not be necessarily applicable to the K-Si interactions. It is argued[24,42] that the presence of active dangling bonds on semiconductor surfaces either delays or suppresses the overlayer metallization. In fact, Ciraci and Batra[24] have claimed that the K adatom is perfectly ionized due to preferential donation of the K $4s$ electron to the active dangling-bond state. Our result is consistent with these theoretical predictions in the low coverage regime. For the saturation coverage, unfortunately, the charge state of K cannot be inferred only from our results because of the dominance of the additional neutralization to the excited 2s level (D$^+$ $\rightarrow$ D*). Enta et al.[28] concluded from angle-resolved ultraviolet photoemission spectroscopy that the K-saturated Si(100) 2×1 surface is semiconducting with 1 monolayer (ML) coverage. More recently,

Johansson and Reihl[29] have shown, based on the inverse photoemission spectroscopy, that the K overlayer becomes metallic at saturation coverage since the empty surface state of K crosses the Fermi level at about the same coverage where the work function reaches its minimum. At lower K coverage, they concluded that a covalentlike K-Si bond is formed since the K $4s$ level is postulated to be hybridized with the dangling-bond states of the Si substrate and the empty surface state is assigned mainly to the K $4p_z$ level. Our result, however, is incompatible with these interpretations. All of the valence electronic state belonging to K is suggested to be located well above the Fermi level at the low-coverage region.

According to the calculations by Ciraci and Batra,[43] donation of the K $4s$ electron to the bulk conduction-band states of semiconductors also leads to ionization of the K adatoms. This possibility has been checked for the K adsorption on the H-terminated Si(100) surface. The ionization of the K adatom is testified by the presence of the K surface peak in Fig. 3(b). The fact that passivation of the active dangling bond does not affect the charge state of the K adatoms suggests that the K adatoms can also be ionized on compound-semiconductor surfaces with no dangling-bond states.

B. Resonance neutralization to the excited state (D$^+$ $\rightarrow$ D*)

As described in the Introduction, though the neutralization discussed above (D$^+$ $\rightarrow$ D^0) is characteristic of deuterium, the RN to the D $2s$ level (D$^+$ $\rightarrow$ D*) is essentially identical to the well-established RN of the AM ions.[44–47] Because of the large spatial distribution of the $2s$ orbitals, this process may be less sensitive to the local target-substrate bonding and is concerned mainly with the work function of the surface. This is also supported by the fact that the neutralization probability is independent of the trajectories or the individual scattering events of AM ions.[45] Of particular interest in this respect is that, in the low AM coverage regime (<0.25 ML), the charge transfer is governed by the local electrostatic potential of the individual AM adatoms rather than the average of the overlayer. In fact, the effective range of the AM-induced field has been studied so far with use of AM-ion scattering,[46,47] where the ion yield from the substrate decreases with increasing the amount of the AM adatoms. In these studies, the ions scattered from the AM adatoms or its vicinity are assumed to be neutralized almost completely because of the downward shift of the ionization levels induced by the strong electrostatic potential.[8,48] Our result is apparently in contradiction to this picture. The presence of the K surface peak clearly indicates that the D$^+$ ion does survive neutralization in scattering from the K adatom itself. The D$^+$ intensity versus Φ curves in Fig. 7 show that the D$^+$ ion feels a "local" work function induced by the individual K adatoms rather than the strong electrostatic field leading to almost complete neutralization. It should be emphasized that the D$^+$ ions corresponding to the K surface peak hit the center of the K adatoms in a single head-on collision [see Fig. 1(b)] so that ion neutralization is much less complicated by the troublesome trajectory-dependent part of

the neutralization. The concept of the local work function is established in various electron spectroscopies.[49] The macroscopic work function Φ determined by, e.g., UPS provides only an average of alkali and clean sites while the local work function varies in the vicinity of the surface as function of the lateral distance from the AM adatoms. In a low-coverage regime, therefore, the local work function felt by D^+ scattered from K may be smaller than the average Φ values shown in Fig. 7. Another factor determining the neutralization probability of D^+ is the upward shift of the D $2s$ levels due to the image-charge effect. Thus the coincidence of the D $2s$ binding energy and the change in the neutralization probability at $\Phi = 3.4$ eV might be rather accidental.

Another example of the local work function is provided by oxygenation of the K overlayers shown in Figs. 2(d), 5(d), and 6(d). It is notable that the D^+ yield recovers remarkably although the average work function Φ of these surfaces is as small as below 3.0 eV. This is because oxygenation changes the local work function as well as the structure of the K overlayers and hence the surface is rather patchy in the work function. A more detailed change in the D^+ yield due to oxygen chemisorption is presented in Fig. 9 for the K-saturated Si(100) surface. The oxygenation does not increase the D^+ yield until the Φ_{min} state is reached and then increases the yield rapidly with increase of the exposure. The initial lowering of the work function is thought to be achieved by submergence of oxygen under the outermost K layer. Such an atomic configuration enhances the effective dipole moment and hence the neutralization rate is retained with a large value. However, once the subsurface site is saturated, the other chemisorption site probably leading to passivation of the active dipole moment of K begins to be occupied. Since the D^+ ions scattered from such sites avoid neutralization, the D^+ yield increases rapidly with increasing the number of the sites. Indeed, the K adatoms contributing to the surface peak of Fig. 2(d) should be bonded to O, which can be inferred from inelastic scattering of D^+. We have shown in previous papers[30,33] that ions scattered from solid surfaces inevitably induce electron-hole-pair excitation in the target as well as coordinating atoms. And the local target-ligands bond can qualitatively be estimated from the energy-loss value of the surface peak. The broader K surface peak in Fig. 2(b) stems from the overlapping of inelastically scattered D^+ due to e-h pair excitation in the Si substrate, whereas the narrower K surface peak in Fig. 2(d) comes only from the elastic scattering since the electronic excitation in the K-O bond results in a larger energy loss (~ 7 eV) due to excitation of the O $2p$ state. In a low-coverage regime, on the other hand, similar spectral change is recognized in Fig. 8(a) though the surface peak intensity is almost unchanged upon oxygenation. That the passivation of the K adatom has very little effect on the K peak intensity clearly shows that the RN to the $2s$ level ($D^+ \rightarrow D^*$) is negligible when $\Phi > 3.4$ eV.

C. The catalytic-promoter effect of K on molecular dissociation

The coadsorption of AM's and simple molecules on transition-metal[5-7] or Si (Refs. 50–52) surfaces has been a favored topic in connection with the promoter effect of AM's on molecular dissociation. But no unified description of the role played by AM's exists except for a common recognition that filling of the antibonding molecular orbitals is promoted. As far as the AM-induced oxidation promotion of Si is concerned,[50-52] various mechanisms have been proposed so far, but the fundamental interest in this subject can be summarized in whether the promoter effects of AM's are local or nonlocal. To this end, the knowledge of the charge state of AM's as well as the charge-exchange interaction between AM's and the impinging molecular or atomic projectiles on a surface is of crucial importance. In the Si case, the K adatom is ionized in the low-coverage regime and hence the direct interaction played by the K $4s$ electron can be ruled out. In the measurements of the produced SiO_2 amount by Michel et al.[50] and the initial sticking coefficient by Ernst and Yu,[52] a linear relationship between the reaction rate of O_2 and the amount of the promoters (K and Cs) has been reported. Only for the local mechanism, the linear behavior may be expected. Considering the ionization of the K adatoms in the low-coverage region, we conclude that the K-O_2 interaction is electrostatic in nature based on the local-work-function picture proposed by Norskov, Holloway, and Land[8] and Lang, Holloway, and Norskov.[9] The local dipole field increases the filling of the antibonding molecular level and the resultant $O_2^{\delta-}$ ion readily bonds to the K^+ adatom. The reported local character of the catalytic effect can be explained by the model that the formation of the $K^+O_2^{\delta-}$ precursor is of importance for the O_2 dissociation and the resultant ionic K-O bond strongly passivates the catalytic activity of the K^+ adatom. With further increasing the AM coverage exceeding about 0.5 ML, the direct interaction may occur if the overlayer becomes metallic,[29] which might be responsible for the change in the slope of the O_2 sticking coefficient at about 0.3 ML of Cs on the Si(100) surface reported by Ernst and Yu.[52]

Similar to the Si case, the O_2-dissociation rate is markedly enhanced by the K adatom on transition-metal surfaces;[5] although the initial sticking coefficient of O_2 on clean Pt(111) is about 0.05, it becomes unity with preadsorbed K. However, the K-O_2 interaction on the metal substrate should be different from that on the Si substrate since the K adatoms are substantially neutral. The oxygen chemisorption of the K-saturated Pt(111) and W(110) surfaces increases the K surface peak intensity as shown in Figs. 5(d) and 6(d), respectively, but the intensity of the K surface peak relative to the background is fairly small compared to that on the Si(100) surface shown in Fig. 2(d). This implies that the K adatoms on the metal substrates are ionized only in part due to oxidation. Furthermore, if the K coverage is small enough, the K surface peak is not increased by the oxygen chemisorption as shown in Fig. 8(b). If the K adatoms were ionized by oxygen, the K surface peak should appear in Fig. 8(b). In this case, the O_2 molecule may also be dissociated due to the interaction with the active dipole field of the K adatom but the resultant O atom preferentially bonds to Pt rather than K. The covalent K-Pt bond may be retained because of the lack of the direct ionic interaction between

K and O. With increasing K coverage above 0.3 ML, the O_2 molecule can interact with patches of the metallic K overlayer. Only in such a dense region, the direct K-O_2 interaction leading to the ionic K-O bond may take place as evidenced by the appearance of the surface peak. Thus it is suggested that one of the key ingredients determining the K-O_2 interaction at the surface is the charge state of the K adatom or the nature of the K-substrate bonding.

The findings here also offer the basis for understanding the promoter effect of AM's on heterogeneous catalysts under industrial conditions. It is known that the promoter is presented not only as elemental K but also as the form of KOH or other compounds on transition-metal surfaces.[5] The fact that the ionic K-O bond is not formed in the low-K-coverage region on Pt(111) implies that ionic salts can also be dissociated on metal surfaces and the covalent bond is formed with the substrate. We have confirmed this issue for adsorption of KF, KI, and RbCl on the W(110) surface.[53] Even if the dissociation of the AM compounds occurs on the transition-metal substrate, the dipole field may not be activated when the anionic species coexist close to AM's. In such a case, thermal activation of the surface leading to separation of these two species or preferential desorption of the anionic molecule may be necessary to promote the catalytic reactivity around the AM sites.[5] Thus the lack of the strong ionic interaction between the adatoms is suggested to have significance for emergence of the catalytic promoter effect.

D. Reionization $(D^+ \rightarrow D^0 \rightarrow D^+)$

The origin of the spectral background has been investigated for the oxygen-chemisorbed Mo(111) and Ta(111) surfaces,[30] as well as some ionic compounds such as SiO_2, LaF_3, and KI. We have assigned the background to reionization of neutral D^0 on the basis of the fact that the D^+ spectra obtained with D^0 incidence are essentially identical to those obtained with D^+ incidence except for the surface peaks. The energetically extended background structure cannot be attributed to the single head-on collision with surface atoms and comes from multiple scattering from the solid [see Fig. 1(b)]. The fact that deuterium scattered from the substrate [Si(100), Pt(111), and W(110)] is completely neutralized $(D^+ \rightarrow D^0)$ and that the background is increased in intensity with the amount of the K or O adatoms indicates that reionization $(D^+ \rightarrow D^0 \rightarrow D^+)$ arises from the small-angle scattering with the adatoms on the outgoing trajectory of D^0. Reionization results in excitation of the D 1s electron to the empty surface electronic state, so that the high-energy cutoff of the background as typically shown in Figs. 5 and 6 is located several eV below the elastic collision energy corresponding to the substrate atoms. This has been confirmed for many surfaces with different beam energies as well.[30] The occurrence of reionization is an experimental evidence of the promotion of the D 1s level at the surface as schematically shown in Fig. 1(a). The promotion is thought to be mediated by the image-charge effect or the antibonding interaction with a target core

orbital in the collisional regime. The latter is in fact the case for reionization of He^0.[32,33] However, there seems to be a marked difference between reionization of D^0 and He^0. The surface peak is pronounced for reionization of He^0 though the background from the bulk is rather small.[33] The difference arises from the smaller cross section of reionization for He^0 than for D^0 since the larger ionization energy of He^0, exceeding that of D^0 by 11 eV, necessitates a much closer approach to the target atom to achieve enough promotion. The background intensity increasing almost linearly with the K coverage shown in Fig. 7 implies that the range of the interaction is limited within the vicinity of the adatom. Indeed, the rapid decrease in the background intensity for $\Phi < 3.4$ eV is an indication that reionization has a more local character than the resonant neutralization to the 2s level $(D^+ \rightarrow D^*)$.

V. CONCLUSION

On the basis of neutralization $(D^+ \rightarrow D^0)$ and inelastic D^+ scattering, the nature of the bonding of the K adatom on the metal and semiconductor surfaces has been investigated in the low-K-coverage regime (< 0.2 ML). The D^+ ions are found to be scattered from the K adatoms with a much less neutralization probability on the Si(100) surface than on the Pt(111) and W(110) surfaces, indicating that the K adatom on the Si substrate is highly ionic while that on the metal surfaces is essentially neutral. The ionization of the K adatom can be ascribed to the preferential donation of the K 4s electron to the active dangling-bond states and/or the bulk conduction-band states of silicon. The neutrality of the K adatom may come from the covalent orbital hybridization with the substrate metal atoms. It is also found that the bond nature of K with the substrate is crucial for understanding the K-O_2 interaction at the surfaces. The O_2 dissociation rate is enhanced probably due to the local dipole field induced by the K adatom for both metal and semiconductor surfaces. The O_2 dissociation is thought to be mediated by the $K^+ O_2^{\delta-}$ precursor on the Si(100) substrate and ceases if K is passivated due to formation of the ionic K-O bond, while, on the other hand, since the resultant O atom is not ionically bonded to K on the Pt(111) surface the catalytic promoter effect can be restored easily by thermal activation. The neutralization of D^+ is enhanced in the high-K-coverage regime because of the additional neutralization to the excited 2s level $(D^+ \rightarrow D^*)$. The neutralization occurs at the low work-function patches induced by the active dipole moment of the K adatom. Inversely, the D^+ ions are not neutralized completely even at the K-saturated surface if the K adatom is passivated locally due to slight oxygen chemisorption.

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