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Direct evidence of the occupied valence states for adsorbed Cs atoms on the Si(111) surface

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Metastable deexcitation spectroscopy (MDS) has been applied to detect occupied valence-band features for Cs atoms adsorbed on a Si(111) surface. The MDS spectrum exhibited a clear peak structure of the Cs 6*s*-derived level near the saturation coverage, which is contrary to the concept of full ionization of adsorbed alkali-metal atoms. Direct evidence of the valence-band charge redistribution as a function of Cs coverage is presented.

The adsorption of alkali-metal atoms on solid surfaces has attracted considerable interest because of its work function lowering effect and its catalytic role in surface chemical reactions, which provide several technological applications. A principal objective of the existing experimental and theoretical investigation has been the determination of coverage dependence of the work function within the submonolayer range and the related physical background of this dependence.[1] The conventional model of Gurney[2] describes this adsorption phenomenon as follows: At low coverages the *s* level of an adsorbed alkali-metal atom is broadened and its center of mass is located above the Fermi level forming a resonance. An electric dipole is formed by the ionized absorbate and the electrons screening its Coulomb potential, causing the initial steep decrease of the work function. With increasing coverage, the depolarization field from neighboring dipoles acts to lower the energy of the *s* resonance, thus regaining electrons from the substrate.

Very recently, two different theoretical investigations appeared, both opposed to the conventional model. One is a calculation of the electronic structure of the K/Si(001) surface by Ciraci and Batra.[3] Their conclusion is that adsorbed K atoms are fully ionized irrespective of the coverage. The other investigation was made by Ishida and Terakura with the Na/jellium[4] and the Na/Al(001) (Ref. 5) systems. They assert that the adsorbed alkali-metal atom is almost neutral and that the dipole moment is induced by the atomic polarization due to hybridization of valence-band states. This is essentially in agreement with the concept introduced by Wimmer *et al.*[6]

In order to settle this controversy, it seems to be most important to experimentally clarify the valence-band charge states of adsorbed alkali-metal atoms. Ultraviolet photoemission spectroscopy (UPS) however has provided rather disappointing results on this subject, namely, nearly no occupied electronic structures just below the Fermi level.[7,8] This may be due mainly to the very low cross section for the dipole transition of the *s* state.

Metastable deexcitation spectroscopy (MDS) is an extremely sensitive technique of probing the electronic structure of the topmost atomic layers. When a surface is approached by a metastable excited helium He* (1*s*2*s*), electrons are ejected by either of two different Auger processes.[9] The local work function just over the alkali-metal adsorbate is considerably lower than that over substrate atoms. When the He* atom reaches the former position, electrons are ejected from the adsorbate by Auger deexcitation (AD) of He*. These electrons are strictly distinguished from electrons ejected from the substrate by Auger neutralization (AN) of He^+ previously produced by resonant ionization (RI) of He*. The matrix element for the AD transition of an adsorbate orbital is roughly proportional to its overlap integral with the He* 1*s* orbital.[10] Therefore, the MDS technique can probe the local density of alkali-metal-derived states below E_F at the position of the He* atom hardly being affected by the selection rule, which contrasts with the UPS.

In this Rapid Communication we report the first MDS study of the electronic structure of the adsorbed Cs layer on Si(111) surface. We will show direct evidence that the 6*s*-derived state of the adsorbed Cs atoms are partially occupied, and that its local density of states in the vacuum region varies drastically with increasing Cs coverage.

The experimental apparatus has been described elsewhere.[11] The metastable-atom source works in a pulsed hot-cathode discharge mode. It produces a beam of excited helium atoms (He*) mainly in the triplet state ($2\,^3S$). The beam also includes atoms in the singlet state ($2\,^1S$) of about 10% or less. Since these are efficiently transformed into the $2\,^3S$ state before deexcitation at alkalated surfaces,[12,13] we can regard the present spectra as actually being due to deexcitation of $2\,^3S$ He* (excitation energy 19.8 eV). The mean velocity of He* is around 3×10^5 cm/s. Ultraviolet photons, produced in the pulsed discharge, reach a target earlier than He*. The time-of-flight separation of photons from He* makes it possible to use UPS simultaneously with the MDS.[11] The electron-energy distribution is produced by numerically differentiating the integral spectrum obtained by a retarding-field analyzer. The deposition of Cs onto the Si(111)7×7 surface was made by evaporation with a Cs dispenser (SAES getter). The relative amount of deposited Cs was monitored by Auger electron spectroscopy (AES). Although the residual gas pressure in the chamber was raised up to 6×10^{-7} Pa by operating both the deposition source and the He* beam source, no contaminants were detected in the Auger spectrum.

Figure 1 shows the MDS spectrum of a Cs-adsorbed Si(111) surface at a saturation coverage (effective cover-

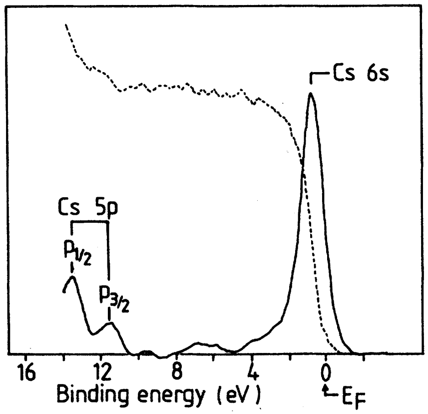

FIG. 1. An MDS spectrum from a Cs-adsorbed Si(111) surface at saturation coverage. The dotted curve is a direct output of the retarding-field analyzer, whereas the solid curve is obtained by differentiating the dotted curve.

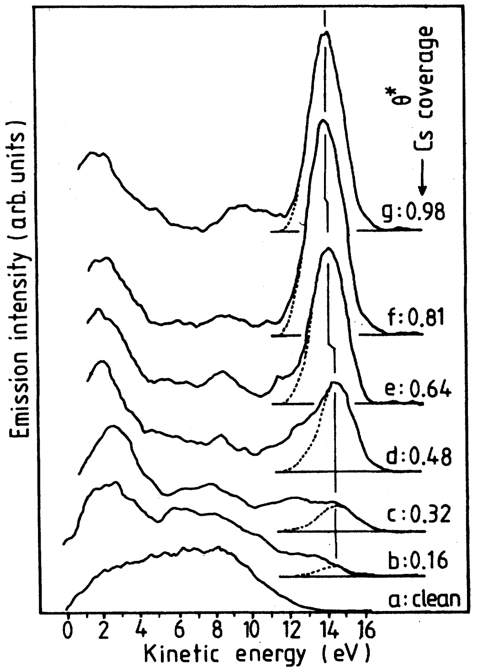

FIG. 2. MDS spectra: Curve *a* from the clean Si(111) surface and curves *b*–*g* from the Cs/Si(111) system. The unity of θ^* is defined as a coverage at which the Auger intensity is saturated (see text and Fig. 3).

age $\theta^* = 1$). The work function of this system is known to decrease by more than 3 eV. Therefore, the electron at the He* 2*s* level cannot tunnel to the unoccupied states of the substrate. The electron emission occurs via the Auger process where the following four one-electron states participate: An occupied state in the surface, He* 2*s*, 1*s*, and a free state in the continuum. The spectrum consists of a sharp peak just below E_F and a pair of peaks in the binding-energy range of 11.5–13.5 eV. A weak structure at 7 eV may be produced by contaminants (mainly oxygen) introduced during Cs deposition. Electron emission scarcely occurred in the energy range of 4–10 eV where the density of electronic states of the substrate Si surface should inherently be located. This means that the adsorbed Cs atom efficiently screens the spread of the substrate electron orbitals leading to the drastic decrease of Auger deexcitation probability for a Si plus He* system. Thus the spectrum of Fig. 1 provides clear evidence that the MDS really probes local electronic structures of only topmost atomic layers.

The peak just below E_F should be derived from the widely expanded Cs 6*s* orbital. Other electronic states which have high amplitude in the bonding region between Si and Cs or in the substrate surface region are considered to scarcely contribute to the AD process. The double-peak structure in the 11.5–13.5 eV region is attributed to the Cs $5p_{1/2,3/2}$ states by comparing with the UPS spectrum.[7] The fact that the Cs 5*p* peak height is much lower than the Cs 6*s* one suggests the matrix-element effect, i.e., the wave functions belonging to higher binding-energy states extend less to the vacuum region which results in lower transition probability to the He* 1*s* level. The appearance of the Cs 6*s*-derived peak in Fig. 1 is clear evidence which confronts the calculation by Ciraci and Batra[3] that the adsorbed alkali-metal layer is fully ionized at the saturation coverage.

In Fig. 2 we show a series of MDS spectra for different Cs coverages. Curve *a* for the clean Si(111) surface corresponds to Hagstrum's and Becker's spectrum by ion-neutralization spectroscopy,[14] which implies the deexcitation of He* via RI+AN process at this surface. Curves *b* and *c* extend to a higher kinetic energy region above the maximum energy of the RI+AN part. This is a sign that the AD process begins to occur at Si-exposed sites competing with the RI+AN process. At low coverages, therefore, the superposition of the AD component of Si and that for the growing Cs layer is important in the energy range of 14–16 eV.

The Cs 6*s*-derived peak drastically increased in intensity from curve *d*. Variation of this peak intensity with increasing Cs coverage is demonstrated in Fig. 3. Although data points in low coverages include uncertainty due to the mingling of Si components, the following discussion and conclusion are not thereby affected. Variation of the Cs-*NOO* Auger intensity versus Cs coverage is inserted in Fig. 3. The fact that the Auger intensity increased in proportion to the coverage and was saturated after a clear break point typically indicates the monolayer adsorption character of Cs. We define the unit effective coverage ($\theta^* = 1$) at this break point. The MDS intensity was already saturated below $\theta^* = 1$. This is due to the apparent decrease of possible impact parameters of He* incidence for each adsorbate when the mean separation between adsorbates is decreased below the sum of the covalent diameters of Cs and He*. The most noticeable point in Fig. 3 is that there exists a clear transition around $\theta_c^* \approx 0.3$. The slope of the coverage dependence of the Cs 6*s* intensity before saturation corresponds to the valence-band charge density per adsorbed atom. Therefore, this result means that the local density of the Cs 6*s*-derived state at the position of the He* nucleus undergoes an abrupt

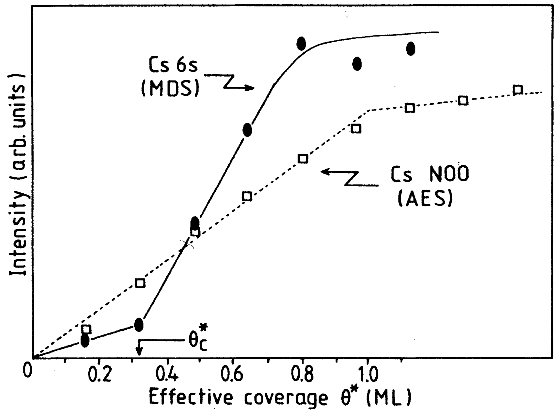

FIG. 3. Variation of the Cs 6*s*-derived peak intensity in MDS and Cs *NOO* Auger intensity as a function of Cs coverage.

change at around θ_c^* from a small value for low coverages to a large one for high coverages. Such valence-band charge redistribution should be a strong factor that controls the work-function variation for alkalated surfaces.

Although the Cs 6*s* peak shape in Fig. 2 does not directly correspond to a real shape of the local density of states, it reflects the density of states convoluted with an experimental error function. The Cs 6*s* peak position slightly shifted towards higher binding energy with increasing Cs coverage. This implies that the shape of the electron density of states near $\theta^* = 1$ is different from that for low coverages. We tentatively explain this phenomenon as follows: At low coverages the Cs 6*s* state forms a resonance whose center of mass is above E_F. The measured spectrum corresponds to a low-energy tail of the resonance, thus exhibiting the peak position to be near E_F. Near the saturation coverage, the interaction between Cs atoms in the adlayer is strong enough to form a two-dimensional band whose density of states is like a step function, leading the averaged peak position to be somewhat lower than E_F.

In conclusion, adsorbed Cs atoms are not perfectly ionized from the limit of zero coverage up to the saturation, confronting Ciraci's and Batra's theoretical viewpoint.[3] The local density of Cs 6*s*-derived states increased abruptly at the effective coverage of about 0.3, which corresponds to coverage-dependent charge redistribution. This result strongly supports the concept of polarization-induced work function change by Ishida and Terakura.[4,5]

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[1] As a review article, see, J. Hölzl and F. K. Schulte, in *Solid Surface Phyics,* edited by G. Höhler, Springer Tracts in Modern Physics, Vol. 85 (Springer, Berlin, 1979), p. 1.

[2] R. W. Gurney, Phys. Rev. **47**, 479 (1935).

[3] S. Ciraci and I. P. Batra, Phys. Rev. B **37**, 2955 (1988).

[4] H. Ishida and K. Terakura, Phys. Rev. B **36**, 4510 (1987).

[5] H. Ishida and K. Terakura, Phys. Rev. B **38**, 5752 (1988).

[6] E. Wimmer, A. J. Freeman, M. Weinert, H. Krakauer, J. R. Hiskes, and A. M. Karo, Phys. Rev. Lett. **48**, 1128 (1982).

[7] H. Tochihara, M. Kuboto, M. Miyao, and Y. Murata, Surf. Sci. **158**, 497 (1985).

[8] Y. Enta, T. Kinoshita, S. Suzuki, and S. Kono, Phys. Rev. B **36**, 9801 (1987).

[9] H. D. Hagstrum, in *Electron and Ion Spectroscopy of Solids,* edited by L. Fiermans, J. Vennik, and W. Dekeyser (Plenum, New York, 1987), p. 273.

[10] W. H. Miller and H. Morgner, J. Phys. Chem. **67**, 4923 (1977).

[11] S. Nishigaki, M. Sugihara, M. Ohara, S. Fukui, K. Matsuo, and T. Noda, Jpn. J. Appl. Phys. **25**, L501 (1986).

[12] J. Lee, C. P. Hanrahan, J. Arias, F. Bozso, R. M. Martin, and H. Metiu, Phys. Rev. Lett. **54**, 1440 (1985).

[13] B. Woratschek, W. Sesselmann, J. Küppers, G. Ertl, and H. Haberland, Phys. Rev. Lett. **55**, 611 (1985).

[14] H. D. Hagstrum and G. E. Becker, Phys. Rev. B **8**, 1580 (1973).