PHYSICAL REVIEW B VOLUME 55, NUMBER 19 15 MAY 1997-I

Electrical phase transitions on the alkali-metal-adsorbed Si(001) surfaces

Ki-Dong Lee and Jinwook Chung
Physics Department, Basic Science Research Institute, Pohang University of Science and Technology,
San 31 Hyoja Dong, Pohang 790-784, Korea

(Received 10 December 1996)

The adsorption of alkali metals (AM's) on the Si(001) surface has been studied using high-resolution electron-energy-loss spectroscopy. We find that the metallization at low AM coverages manifests itself with a unique surface plasmon excitation, which turns out to be common to the AM (Li,Na,Cs)/Si(001) surfaces. With increasing AM coverage, these AM-induced metallic surfaces become semiconducting again revealing the characteristic metal-semiconductor transitions (MST's) at the onset of the first ordered structures: (4×1) and (2×3) for Na and Cs adsorption, respectively. We invoke a mechanism leading to a band insulator to understand such a MST accompanying a disorder-order structural transition. In addition, the distinctly different electrical properties of the AM saturated surfaces, semiconducting for Na and metallic for Cs, are attributed to the availability of some excess adatoms beyond 1 monolayer at room temperature. [S0163-1829(97)06419-9]

Adsorption of metallic elements on the semiconductor surfaces has been a subject of intensive studies due to the technological importance in semiconductor industry besides the scientific significance to investigate the basic nature of the interactions involved.[1] Due to the rather simple configuration of the valence electrons of an alkali metal (AM), the adsorption of AM on the Si(001) surface has served as a model system to study adsorbate-derived electrical properties of the metal adsorbed semiconductor surfaces. In fact, recent studies show that the AM/Si surfaces provide ample information regarding the electrical as well as the structural phase transitions depending on AM coverage.[1–10] Previous photoemission studies have shown that a small amount of AM adatoms make the surface metallic by partially occupying an initially empty substrate band[2–7] or a defect-related band.[8] Also, in our earlier high-resolution electron-energy-loss (HREEL) spectroscopy study for the Li/Si(001) surface, we reported evidence for the metallicity of the surface from a prominent loss peak best developed at ~260 meV, which was attributed to a surface plasmon excitation.[9]

Interestingly, such a change in electrical property often accompanies concomitant change in atomic arrangement on the surface. The correlation between the two changes has not been addressed properly or has often been overlooked previously.[5,9] In this paper, we report results of our HREEL spectroscopy measurements of the AM (AM=Na,Cs)/Si(001) surfaces. A semiconductor-metal transition (SMT) at low AM coverages and a metal-semiconductor transition (MST) accompanying a disorder-order structural transition (DOT) have been found to occur commonly on these surfaces for most AM atoms including Li, Na, and Cs. We discuss plausible mechanisms of these electrical phase transitions together with distinctly different electrical properties of the AM saturated surfaces.

We have employed a Lybold ELS-22 spectrometer, which was described elsewhere[11] to measure surface electronic excitations on the Na- and Cs-adsorbed Si(001) surfaces. The experiment was carried out in an UHV chamber with a base pressure better than 3×10^{-11} mbar. The Si(001) single crystal surface (p type, $p=1.5-3.5\ \Omega$ cm) was cleaned through several cycles of flashing at 1175 °C and annealing at 800 °C by resistive heating. The surface thus prepared showed a very sharp and bright (2×1) low-energy-electron diffraction (LEED) pattern with a low background. The cleanness of the sample surface was then examined by x-ray photoemission and HREEL spectroscopy where no impurity peaks were detected. Alkali metals were evaporated by using commercial SAES dispensers that were thoroughly outgassed while the silicon substrate was maintained at room temperature during deposition. The chamber pressure stayed below 1×10^{-10} mbar during evaporation. The AM coverage was controlled indirectly by monitoring the work-function change $\Delta\phi$, which was determined from the shift of a secondary electron tail in x-ray photoemission spectra. The $\Delta\phi$ versus exposure curves measured (not presented) are quite similar with previous measurements within ±0.2 eV.[2,3,6–8] The ELS-22 spectrometer was used with two different primary energies 5 and 20 eV for energy resolutions of 8 and 25 meV, respectively.

The progressive evolutions of the HREEL spectra with AM adsorption on the Si(001) surface are shown in Figs. 1 and 2 for Cs and Na, respectively. The two loss peaks from the clean Si(001) surface S_0 and S_1 are interband transitions from the bulk valence to an empty surface band and from an occupied surface to the bulk conduction band, respectively.[12] In the figures, one immediately notices that a small amount of AM adatoms at the very initial stage of adsorption induces a rather broad shoulder near the elastic peak, which develops into a prominent loss peak denoted as surface plasmons (SP) with increasing AM coverage. The presence of such a loss peak at low AM coverages is in accordance with the presence of some density of states at the Fermi energy in photoemission spectra, revealing the metallic nature of these surfaces.[3–5,8,9] The peak SP tends to shift towards the higher loss energy side upon further increase of the AM coverage reaching eventually 320 and 260 meV for Cs and Na, respectively. It, however, diminishes its intensity gradually before disappearing completely at a certain high coverage ($\Delta\phi=-2.53$ and -1.34 eV in Figs. 1 and 2, respectively). It is noteworthy to find that the surfaces exhibit

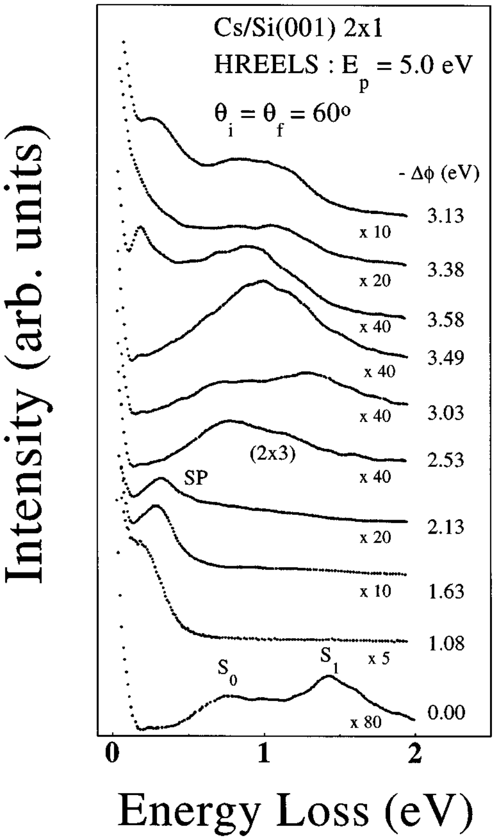

FIG. 1. Series of HREEL spectra showing the progressive change with increasing Cs coverage obtained at a specular geometry ($\theta_i = \theta_f = 60°$). Note that the SP, signaling the metallic phase of the surface, disappears completely as the ordered (2×3) structure appears indicating a reentrant semiconducting phase. The surface becomes metallic again with increasing Cs coverage producing a prominent loss peak near $\Delta\phi = -3.58$ eV and a surface plasmon above the excitation continuum near the elastic peak at saturation as a result of the metallic coupling of the excess adatoms with the underlying adatom layer (see text).

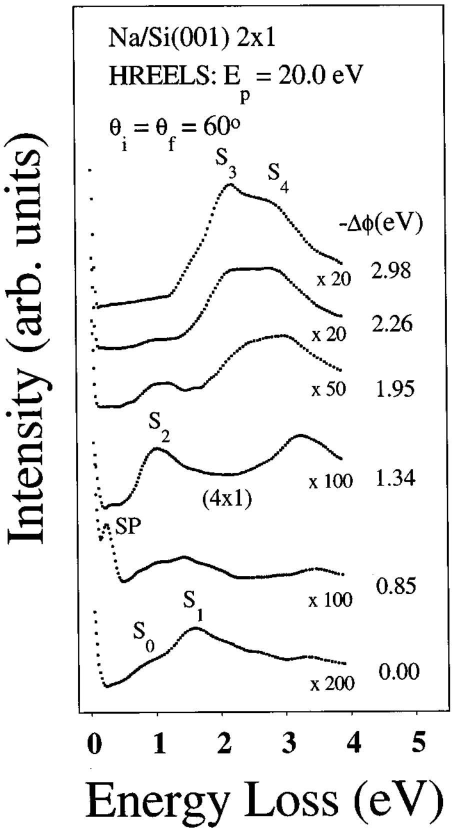

FIG. 2. Corresponding spectra as in Fig. 1 for the Na-adsorbed surface. The overall features at low coverages are quite similar to the Cs-adsorbed surface except for the larger band gap of the reentering semiconducting phase for the ordered (4×1) structure. The semiconducting phase at saturation, however, is in sharp contrast with the metallic phase of the Cs-covered surface.

no AM-derived ordered structures as long as SP prevails, i.e., the surfaces remain disordered producing only the (2×1) LEED pattern. Furthermore, the metallic surfaces become semiconducting again with increasing AM coverage at the onset coverages of the first AM-derived ordered structures. This is seen by the sizable band gaps forming as the surface becomes ordered. The ordered structures and the apparent band gaps of the reentering semiconducting surfaces are (2×3) and ~0.2 eV for Cs and (4×1) and ~0.6 eV for Na. These band gaps agree qualitatively well with the values reported earlier.[13] Such a MST for the AM (Na,Cs)/Si(001) surfaces seems to be of a rather common phenomenon, since a similar MST has also been observed for the Li/Si(001) surface. The ordered structure of the Li/Si(001) surface is a (2×2) with a band gap of ~0.7 eV.[4,9]

Previously, we have shown that the metallization of the Li adsorbed surface is essentially an adsorbate-mediated substrate metallization. In other words, the Li 2*s* electrons partially occupy one of the empty substrate surface bands intrinsic to the clean cold $c(4\times2)$ structure.[9] A general consensus seems to have been made for this explanation in previous photoemission,[2–6] inverse photoemission,[14] and scanning tunneling microscopy[15] (STM) studies contrary to the defect or disorder related interpretations.[8] The loss peak seen from the corresponding metallic Li/Si(001) surface turned out to be a surface plasmon.[9] By the same token adopted for the metallic Li/Si(001) surface at low coverages, we also attribute the metallization of the AM(Na,Cs)/Si(001) surfaces to the substrate metallization. The SP's in Figs. 1 and 2 might then also be surface plasmon excitations of which the energy varies with the AM coverage as for the Li case.[9,10] Because an ordered arrangement of surface atoms is primarily a consequence of the strong lateral interatomic interactions between adatoms, such a DOT due to the increased AM coverages may result in the MST's of the AM/Si(001) surfaces as discussed further below. Although we invoked a substrate reconstruction to account for the relatively strong extra LEED spots from the (2×2) structure of the Li/Si(001) surface, we could not completely rule out a possibility of ordering of the AM layer itself for the ordered structures of the Cs- or Na-adsorbed surface because of the relatively strong scattering factors of these atoms.

We now discuss a mechanism for the MST commonly observed on the AM(Li,Na,Cs)/Si(001) surfaces. The

(2×1) surface at room temperature is known to be a disordered phase of the ordered $c(4\times2)$ low-temperature phase.[16] As Johansson *et al.* pointed out for the Li/Si(001) surface in their recent STM study,[15] AM adatoms may initially sit on the so-called C-defect sites unique to the local $c(4\times2)$ structure. The metallic phase persists as long as the partially occupied surface band remains. As the coverage increases, however, the interaction between adatoms increases accordingly to form a long-range AM-derived ordered structure, which may destroy the local $c(4\times2)$ structure of the substrate. The structure then opens an energy gap at a surface Brillouin-zone (SBZ) boundary by splitting the partially occupied surface band into a completely filled and an empty band above it as in a band insulator.[17] The surface now becomes semiconducting again depending on the size of the gap, which accounts for the MST's observed in this work. It would be interesting to find the gaps shown in Figs. 1 and 2 in photoemission spectra along the azimuth where the SBZ boundary forms.

The semiconducting nature of the first ordered structures of the AM-adsorbed Si(001) surfaces may provide a clue to determine the AM coverage within a single electron picture of band theory. Previously 1/3 (Ref. 18) and 1/4 ML (Ref. 6) have been assigned for the (2×3)-Cs and the (4×1)-Na structure, respectively. Because both surfaces are semiconducting, the assignment of 1/4 ML for the (4×1)-Na surface contradicts its semiconducting nature in the single electron scheme. The theory predicts that the odd number of electrons per unit cell (1 from Na and 4 from Si) of this surface should make the surface metallic. However the even number of electrons (2 from Cs and 6 from Si) for the (2×3)-Cs surface is consistent with the theory predicting a semiconducting phase as observed. The apparent controversy for the the (4×1)-Na surface demands an alternative explanation. One possibility is to invoke many-body effects that may cause a sizable gap, so-called a Hubbard gap, where electron correlation plays a vital role as found in the Cs adsorbed GaAs(110) surface.[19] However, we have not observed any subgap excitations resulting from such a Hubbard gap in our HREEL spectra. Therefore as a simple alternative, we propose 1/2 ML for the (4×1)-Na surface, which provide an even number of electrons per unit cell (2 from Na and 4 from Si) to account for the semiconducting feature of the surface within the framework of the single electron theory.

Further changes of the HREEL spectra with increasing AM coverage beyond the reentering semiconducting phase are also shown for $\Delta\phi\leqslant-1.34$ eV, and $\Delta\phi\leqslant-2.53$ eV for the adsorption of Na and Cs, respectively in the figures. Despite the similar behaviors at low coverages, the two surfaces show strikingly different behaviors at high coverages. In particular, the deeply semiconducting feature of the Na-adsorbed surface near saturation is sharply contrasted with the metallic character of the Cs-adsorbed surface. This is seen by the absence and the presence of the excitation continuum near the elastic peak for the Na- and Cs-adsorbed surface, respectively. For the Na-adsorbed surface a loss peak near 3.5 eV begins to appear at $\Delta\phi=-1.34$ eV at the expense of SP and tends to shift towards the lower loss energy side. At saturation we observe two loss peaks of energies 2.1 and 3.0 eV denoted as S_3 and S_4, respectively. In comparison with recent photoemission and inverse photoemission data reported by Johansson and Reihl,[14] we find that S_3 and S_4 are interband transitions from the two occupied bands and an adsorbate-derived empty surface band. The loss peak at 3.0 eV was mistakenly attributed to an overlayer plasmon previously, which was considered as an indirect evidence for the metallicity of the Na overlayer.[20] The semiconducting character of the Na-saturated surface has also been observed in previous photoemission study.[14]

The metallic feature of the Cs-absorbed surface at high coverages is most clearly demonstrated by a relatively sharp loss peak at 0.18 eV, which begins to appear near the minimum of the work-function change $\Delta\phi=-3.58$ eV. A similar sign for such metallicity has also been observed in photoemission spectra by a finite density of states at the Fermi edge and the need for a large singularity index to fit the Si $2p$ and Cs $4d$ core-level peaks.[7] This loss peak remains almost dispersionless with respect to the momentum transfer parallel to the surface. However, its intensity grows gradually with increasing coverage with a slight change in its energy. Since the work-function change increases beyond the minimum basically due to the excess Cs adatoms above 1 ML, the metallic phase can also be caused by these excess adatoms from the wave-function overlap between the Cs atoms in the two adlayers.[3,14] More specifically, the s electrons from the excess Cs adatoms above 1 ML may form a broad s-$6p_z$ hybridization metallic band with the initially empty $6p_z$ Cs-derived band. The loss peak at 0.18 eV in Fig. 1 may then be a surface plasmon excitation due to Cs s and p electrons in this hybridized metallic band or an interband transition between the metallic band and an empty band 0.18 eV above it. However since the peak persists with the slightly varying energy above the interband excitation continuum near the elastic peak, the peak is more likely a surface plasmon of which the energy varies as the number of conduction electrons increases with coverage. The nondispersiveness of the excitation may be understood by the localized character of the excess Cs adatoms in the second Cs layer. Note that the overlayer plasmon excitation attributed to the Cs $4d$ electrons in Ref. 7 is seen in Fig. 1 as a broad peak with loss energy centered at ~1 eV.

In summary, we find that the metallization of the Si(001) surface at the initial stage of AM adsorption is a general property of the AM(Li,Na,Cs)/Si(001) surfaces and confirms the explanation, attributing it to the substrate rather than an overlayer metallization proposed earlier. The MST accompanying a DOT, observed also commonly for the AM(Li,Na,Cs)/Si(001) surfaces, may occur essentially by splitting a partially filled metallic band to open a sizable band gap as in a band insulator. Additionally the distinctly different electrical phases at saturation, semiconducting and metallic for the Na- and Cs-adsorbed surface, respectively, are ascribed to the availability of the excess AM adatoms in the second layer to form hybridized metallic bonds with the AM adatoms underneath.

We acknowledge partial support by the Basic Science Research Institute Program, Ministry of Education, under Project No. BSRI-96-2440, and also by the Korean Science and Engineering Foundation through the ASSRC program. The support from the Seo-Am Foundation is also greatly acknowledged.

[1] For example, see Inder P. Batra, *Metallization and Metal-Semiconductor Interfaces* (Plenum, New York, 1989).

[2] B. Reihl, R. Dudde, L. S. O. Johansson, K. O. Magnusson, S. L. Sorensen, and S. Wiklund, Appl. Surf. Sci. **56-58**, 123 (1992).

[3] P. Soukiassian, J. A. Kubby, P. Mangat, Z. Hurych, and K. M. Schirm, Phys. Rev. B **46**, 13 471 (1992), and references therein.

[4] K. S. Shin, C. Y. Kim, and J. W. Chung, Appl. Phys. A **60**, 35 (1995).

[5] Y.-C. Chao, L. S. O. Johansson, C. J. Karlsson, Erik Landemark, and R. I. G. Uhrberg, Phys. Rev. B **52**, 2579 (1995).

[6] M. Tikhov, G. Boishin, and L. Surnev, Surf. Sci. **241**, 103 (1991).

[7] Y.-C. Chao, L. S. O. Johansson, and R. I. G. Uhrberg, Phys. Rev. B **54**, 5901 (1996).

[8] Y. Enta, T. Kinoshita, S. Suzuki, and S. Kono, Phys. Rev. B **36**, 1125 (1989).

[9] K. D. Lee, C. Y. Kim, and J. W. Chung, Surf. Sci. Lett. **366**, L709 (1996).

[10] C. Y. Kim, K. S. Shin, K. D. Lee, and J. W. Chung, Surf. Sci. **324**, 8 (1995).

[11] D. H. Baek and J. W. Chung, Appl. Phys. A **59**, 445 (1994).

[12] H. H. Farrell, F. Stucki, J. Anderson, D. J. Frankel, G. J. Lapeyere, and M. Levinson, Phys. Rev. B **30**, 721 (1984).

[13] K. Kobayashi, Y. Morikawa, K. Terakura, and S. Blugel, Phys. Rev. B **45**, 3469 (1992).

[14] L. S. O. Johansson and B. Reihl, Phys. Rev. B **47**, 1401 (1993); Phys. Rev. Lett. **67**, 2191 (1991).

[15] M. K.-J. Johansson, S. M. Gray, and L. S. O. Johansson, Phys. Rev. B **53**, 1362 (1996).

[16] T. Tabata, T. Aruga, and Y. Murata, Surf. Sci. **179**, L63 (1987).

[17] Inder P. Batra, Surf. Sci. **242**, 354 (1991).

[18] T. Abukawa, T. Okane, and S. Kono, Surf. Sci. **256**, 370 (1991).

[19] N. J. Dinardo, T. Maeda Wong, and E. W. Plummer, Phys. Rev. Lett. **65**, 2177 (1990).

[20] Hiroshi Tochihara and Yoshitada Murata, Surf. Sci. **215**, L323 (1989).