Metallization, surface photovoltage, and quantum-well-type resonance for K-covered Si(100) observed via valence-band photoemission

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The development of metal character in the surface region of K-covered Si(100) is monitored via the appearance of a Fermi edge in photoemission spectra recorded at low photon energies ($\hbar\omega < 60$ eV). The Fermi-edge intensity shows an onset at a coverage close to that required to obtain the work-function minimum typical for this adsorption system. For clean, cooled (~ 70 K) Si(100) substrate (n-type, 2 Ω cm), the light source used for photoemission nearly eliminates the surface band bending, but upon K deposition the band bending reappears and then has nearly the same magnitude as for the uncovered Si(100) surface left in darkness. The changeover from flat bands to full band bending occurs over a narrow monolayer coverage interval at coverages somewhat higher than required for the observation of a Fermi edge. Upon continued deposition a photoemission peak is observed which is assigned to a quantum-well-type resonance formed by alkali-metal valence electrons propagating back and forth in the overlayer between the vacuum barrier and the overlayer-substrate interface.

I. INTRODUCTION

During the last several years a number of surface-sensitive methods have been used to probe the structure and electronic properties of metal-semiconductor interfaces.[1] As far as electronic properties are concerned, the issues of main interest are the development of metal character and Schottky-barrier formation upon metal adsorption on a semiconductor substrate. For this it is necessary to monitor the overlayer metallization as well as the surface band bending and how it is affected by the incident light at different metal coverages, preferably at different sample temperatures.[2-4] Alkali-metal overlayers are of particular interest as model systems. One reason is that these are believed to form an abrupt interface with semiconductor substrates such as Si(100).[5-8] Other reasons are the simple electronic structure of the adsorbed metal and the relatively large amount of reference data available from the results obtained when the same experimental probes are used to study alkali-metal adsorption on metal substrates.

In the last few years Si(100) covered with K has been a favorite system for investigations of metal-semiconductor interfaces. This system was the subject of photoemission[9-12] and inverse photoemission measurements,[13] thermal desorption spectroscopy,[14,15] scanning tunneling microscopy (STM) analysis,[16,17] and surface optical second-harmonic generation.[18] On the theoretical side there have been electronic structure calculations made with the main aim of predicting the onset of metal character in the surface region.[19,20] Here we will report on angle-resolved photoemission measurements on the Si(100)/K system. In previous work similar measurements have been made with higher photon energies than used here ($\hbar\omega < 6$ eV).[9-12] At the higher photon energies used previously the obvious advantage was that the entire valence band could be probed. With the low photon en-

ergies used here, little information is obtained about the electronic energy bands of the Si(100) substrate. The reason why the present measurements are still quite useful is the large cross section for the emission of alkali-metal valence electrons obtained at low photon energies.[21] Important characteristics, such as the Fermi-edge intensity which is used to monitor the onset of metal character, and the position at the Fermi edge which is used to monitor the surface band-bending changes, are conveniently measured at low photon energies. Low photon energies are also useful for the observation of the thin-film quantum-well states or resonances which may be formed by alkali-metal valence electrons confined to the overlayer.[22-26] This type of quantum confinement will produce states or resonances with more or less well-defined energy depending on the thickness homogeneity, and on how well the electrons propagating back and forth in the overlayer are reflected at the interfaces. Previously for metal overlayers on semiconductor substrates, quantum-well states have been observed for few systems.[27-31]

Aside from the observation of a quantum-well-type state for a K overlayer on Si(100), the results of main interest in the present work are the onset of metal character in the monolayer coverage range, the independence of the band bending on the metal coverage, and the strong monolayer coverage dependence of the surface photovoltge when K is absorbed on a cooled (70 K) Si(100) surface.

II. EXPERIMENT

All experiments are carried out under ultrahigh vacuum (UHV) conditions with a base pressure of $\sim 1 \times 10^{-10}$ torr. The Si(100) sample (n-doped, 2 Ω cm, $20 \times 10 \times 0.4$ mm^3) is cut from a commercial mirror polished wafer and then chemically etched before mounting it in the vac-

uum chamber. In vacuum, the sample is cleaned by cycles of Ar^+ sputtering (600 eV, 2 μA) followed by annealing ($\sim$1200 K) with a direct current through the sample. The low-energy electron-diffraction (LEED) pattern showed a 2×1 structure characteristic of the reconstructed clean Si(100) surface. The crystal temperature during annealing is measured with a thermocouple and/or a pyrometer. Sample cooling is achieved by LHe flow into two copper cylinders connected to the sample holder with two Cu braids. The temperature of the sample upon cooling ($\sim$70 K) is estimated via the work-function change observed upon Xe absorption, which has been studied earlier.[9] K is evaporated onto Si(100) from a glass ampoule broken in UHV. The light source is a Hg lamp and a monochromator. A 10-mW He-Ne red laser is used to study the intensity dependence of the surface photovoltage. The intensity is varied by changing the angle between two polarizers instead in the light beam. The photoemission spectra are recorded with a cylindrical mirror-type analyzer accepting a beam of electrons with an angular spread of around 2°.

III. RESULTS AND DISCUSSION

A. Work-function changes and metallization

The work-function change ($\Delta e \Phi$) for cooled Si(100) crystal ($\sim$70 K) as a function of the K coverage (indicated by the evaporation times in minutes) is plotted in Fig. 1. At low-K coverages the work function drops rapidly and almost linearly with the coverage. Upon further K evaporation it increases after passing a pronounced minimum ($\Delta e \Phi_{min} \sim -3.2$ eV). The work function saturates at a value close to the work function for the bulk K ($\Phi_K = 2.26$ eV). The $\Delta e \Phi$ curve is similar to that reported by Pervan et al.[9] and Michel et al.[10] At low-K coverages the work-function change is measured from the low-energy cutoff of the photoemission spectra, while at
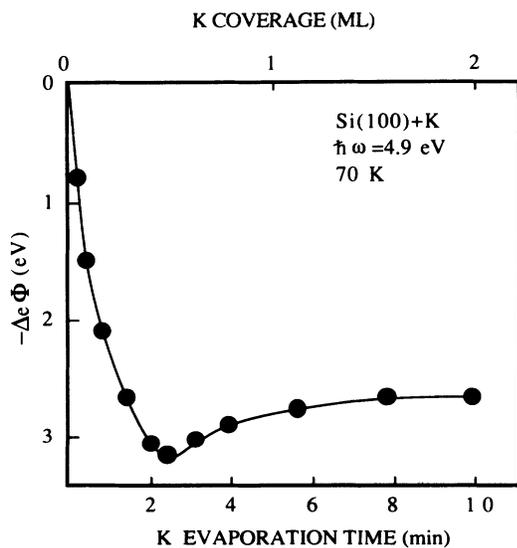
higher-K coverages the work-function change is measured from the spectrum width. The reason for the latter procedure is that rigid shifts of the photoemission spectra toward higher kinetic energies are observed when the K coverage is high enough that the Si(100)/K interface obtains metal character. At evaporation times close to that needed to obtain the minimum work function, a Fermi edge appears in the spectra which indicates metal character. For zero parallel wave vector ($k_{\parallel} = 0$) the photoemission intensity at the Fermi edge increases with the K coverage, and then, at low enough photon energy, it saturates after passing a maximum (Fig. 2). Based on similar observations reported for Na-covered Cu(100) (Ref. 21) and Na-covered Si(100),[3,4] this behavior is interpreted in terms of the surface photoelectric effect. For these two systems the maximum intensity is obtained at approximately one full monolayer of alkali-metal coverage. We therefore associate the intensity maximum at E_F with the evaporation time needed to form one full K monolayer on Si(100). With the sample kept at room temperature (RT) the photoemission intensity at the Fermi edge increases monotonically, and saturates only slowly at much higher evaporation times than required for saturation to be obtained when the sample is kept at low temperature. Based on the above determination of the K coverage, the work-function minimum is reached at almost one-half K monolayer, which is in agreement with recent results reported by Pervan et al.[9] and Michel et al.[10]

B. Surface photovoltage (SPV)

For K coverages high enough that the K overlayer obtains metal character, rigid shifts of the photoemission spectra are observed toward higher kinetic energies as more alkali metal is adsorbed (Fig. 3). The origin of the shift is the change in the surface band bending of the Si(100) sample, i.e., the surface photovoltage (SPV). The coverage dependence of the SPV is shown in Fig. 3. For

FIG. 1. The work-function change for the Si(100) substrate as a function of the K coverage. The substrate temperature is $\sim$70 K.
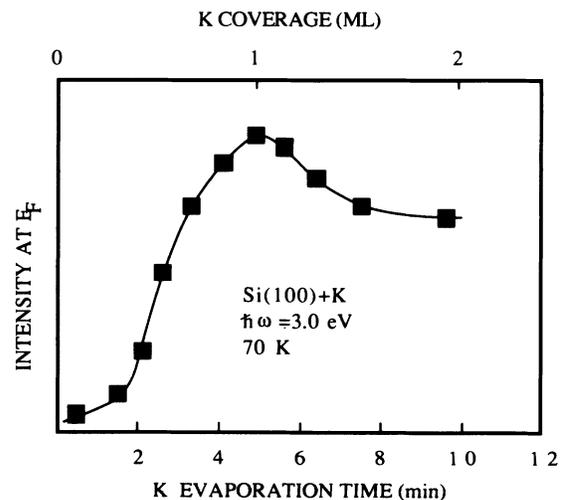

FIG. 2. Photoemission intensity at the Fermi edge E_F as a function of the K coverage. The intensity maximum is associated with the K evaporation time needed to form one full K monolayer on Si(100). The photon energy is 3.0 eV. The emission angle is zero, i.e., $k_{\parallel} = 0$.
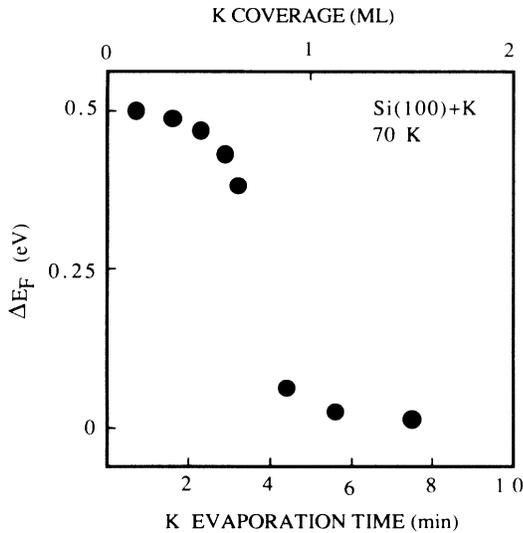
K COVERAGE (ML)

FIG. 3. The shift of the Fermi-edge position observed in the photoemission spectra vs the K coverage. The shift is associated with the increase in band bending (decrease in the SPV) as the K coverage increases.

the clean Si(100) surface at ~ 70 K the intensity of the uv light source used for photoemission is high enough nearly to flatten the bands (maximum SPV). This is due to the low relaxation rate of the carriers at low temperature.[32−34] The band bending is an equilibrium phenomenon, and this equilibrium is shifted by incident light such that the band bending is reduced. The mechanism responsible for this is that the incident light creates electron-hole pairs. Due to the electric field in the band-bending region, electrons and holes will move in opposite directions. The resulting charge separation will thus reduce the field producing the band bending. The relaxation is regarded as a thermally activated process, and will proceed slow enough at ~ 70 K that the band bending is nearly eliminated for the clean Si(100) sample when this is subject to the modest light intensity from the monochromator. Even with small amounts of K on Si(100), the bands remain flat. In the coverage range where the overlayer obtains metal character, the relaxation rate becomes strongly enhanced, which means that the light intensity is no longer sufficient nearly to flatten the bands. Instead, the bands bend upwards again as more K is adsorbed. At around one full K monolayer the total shift is around 0.5 eV, which means that the band bending is similar to that observed for the clean Si(100) sample via the rigid spectral shift observed upon cooling the crystal from RT to ~ 70 K.

Although the band bending is thus close to its full value at a high-K monolayer coverage, when light from the monochromator is incident on the sample the light sensitivity of the SPV is still much higher than for the clean Si(100) crystal held at RT. This is shown by directing light from a 10-mW He-Ne red laser onto the spot probed by the electron spectrometer. For the clean Si(100) sample held at RT this produces a SPV of only around 70 meV, while for Si(100) covered by a full atomic

layer of K held at ~ 70 K the SPV is close to its maximum value (~ 0.5 eV). This means that using the auxiliary light source one obtains the opportunity to observe the intensity dependence of the SPV. For this, two polarizers were inserted in the light beam, and the angle between them was varied. The SPV shows the expected nonlinear dependence (Fig. 4). Similar measurements for the clean Si(100) sample are impractical. At low temperatures such low light intensities would be required that the time needed to record a photoemission spectrum would be very long, while at RT very high light intensities would be necessary. The present results could be of practical interest, since they show that the light sensitivity of the SPV can be controlled not only by temperature but also by the metal coverage. The observation that the SPV has approximately the same saturation value for the K-covered Si(100) surface as for the clean Si(100) surface is different from that of a previous study, where the band bending was found to decrease with increasing K.[10]

An increased relaxation rate for the band bending upon metal adsorption has been observed previously.[3,35] Particular to the present case is that the change from flat bands to full band bending occurs over a small monolayer coverage range. The metal-adsorption-induced decrease of the SPV has been discussed in terms of a short circuiting of the barrier due to conductive paths created by the metal adsorbate.[34] It has been suggested, for example, that such shorts may be present at the edges of the sample. In the present case such an edge effect may be ruled out by the observation that the rigid shift of the photoemission spectrum used to monitor the SPV is only observed when the auxiliary light source is directed toward the spot on the surface that is probed by the photoelectron spectrometer. The conducting paths are thus more local, and are either produced or activated by the metal adsorbate as the overlayer obtains metal character. One possibility is that the paths are associated with defects penetrating the dipole layer. The defects may be present for the clean crystal, but will then be of negligible importance if their surface area is only a small fraction of the total surface. With a metal-like overlayer, even if this is
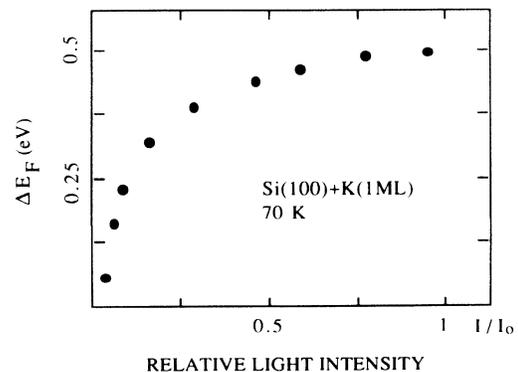

RELATIVE LIGHT INTENSITY

FIG. 4. Change of the surface photovoltage, measured as a shift of the Fermi edge in the photoemission spectra after deposition of around one full K monolayer, vs relative light intensity. The light source responsible for the SPV is a 10-mW He-Ne red laser.

not conductive over macroscopic dimensions, a modest number of defects may provide conductive paths reaching a large fraction of the crystal surface area. Using a STM to probe the SPV, it has been found that defects do affect the local SPV.[36]

In qualitative terms the SPV observed for the alkali-metal-covered surface at high monolayer coverage can be accounted for by assuming that the relaxation of the surface barrier is dominated by a resistive current i_R, proportional to the surface photovoltage V, such that $i_R = C_1 V$, where C_1 is constant. This current is then, for the illuminated sample, equal to the photogenerated current i_{ph}, due to the field acting on the optically excited electron-hole pairs in the surface barrier region. To a first estimate this gives $i_{ph} = C_2 I(V_0 - V)$, where C_2 is a constant, I is the light intensity, and V_0 is the band bending without illumination of the sample. The light intensity dependence of the surface photovoltage is thus given by $V^{-1} = V_0^{-1} + C I_0 I^{-1}$, where C is a constant and I_0 is the maximum light intensity of the laser lamp (~ 10 mW). This simple estimate agrees well with the measurements (Fig. 5).

C. Quantum-well states (QWS)

After an evaporation time about three times longer than required to obtain the minimum work function, a well-defined peak at ~ 1.0 eV below E_F appears in the photoemission spectra recorded at normal emission (Fig. 6). The peak appears rather abruptly between 6- and 7-min evaporation time. We ascribe this peak to a K valence-electron resonance that results from the quantized motion of the valence electrons normal to the overlayer. The peak is due to a resonance since the energy lies below the valence-band edge at the surface, i.e., $E_F - E_{VBM} = \sim 0.55$ eV. As seen in Fig. 6, the K reso-
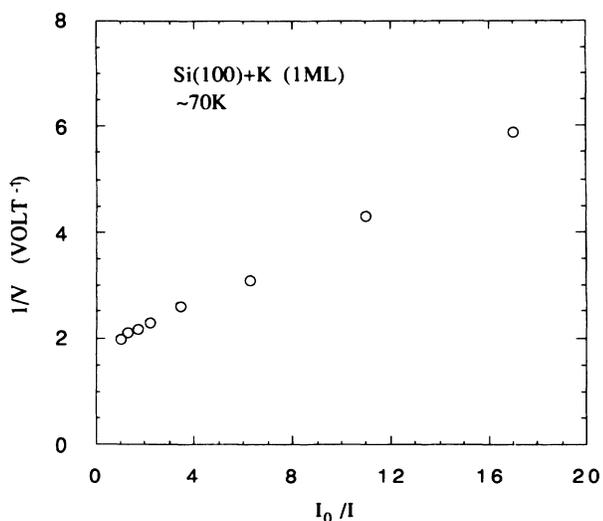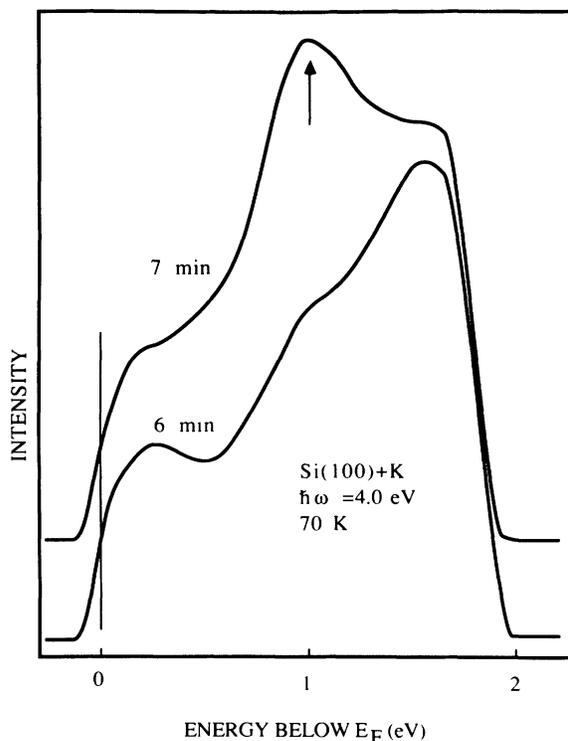

ENERGY BELOW E_F (eV)

FIG. 6. Angle-resolved photoemission spectra for K-covered Si(100) recorded at normal emission using a 4.0-eV photon energy. The emission peak located ~ 1.0 eV below E_F (indicated by an arrow), which appears after around 7 min of K evaporation, is associated with a K quantum-well-type resonance.

nance emission peak is superimposed on a relatively high background. Similar behavior was observed for the resonance and discrete states observed for Na overlayers adsorbed on cooled Si(100).[3,4,30] The background emission indicates that the K and Na overlayers cannot be considered perfect quantum wells. This probably means that the overlayer has a homogeneous thickness only over a part of the surface. For quantum-well-type states in metal overlayers on metal substrates, a lower background emission has been observed.[22-26]

No resonance is observed for K adsorbed on Si(100) when the substrate is held at RT (293 K) or at LN_2 temperature (~ 100 K) during K evaporation. This is ascribed to different growth modes for K at different substrate temperatures. In the case of Na adsorbed on Si(100), quantum-well-type states did not appear when the sample was held at RT, but were observed with the sample cooled with LN_2 (~ 100 K) or with LHe (~ 70 K).

When K evaporation is continued beyond 7 min, the resonance peak broadens, weakens, and then disappears (not shown). We ascribe this to nonhomogeneity in the K overlayer thickness. For Na adsorbed on cooled Si(100), by contrast, a well-defined emission peak appears again in the spectra if Na is further adsorbed, but with energy shifted toward E_F.

As found for the Si(100)/Na system,[4] the K resonance emission peak vanishes if the temperature is increased to

FIG. 5. Plot of the inverse of the surface photovoltage ($1/V$) vs the inverse of the relative light intensity (I_0/I), where I_0 is the maximum light intensity of the laser. The experimental data in Fig. 4 agree well with the simple estimate given by $V^{-1} = V_0^{-1} + C I_0 I^{-1}$. The points in the figure fit well on a straight line, as predicted the above relation.

around RT. If the temperature is lowered again to ~ 70 K the peak does not reappear. However, for the recooled sample the peak can be made to appear again by additional deposition of K. If K is evaporated on Si(100) at RT and the temperature is then decreased to 70 K, the K resonance appears in the spectra if the cooling is followed by further K evaporation.

In the present work no emission peak due to K valence electrons is observed at low monolayer coverages on Si(100). In previous work an electron emission peak close to E_F was observed via He* metastable, deexcitation spectroscopy at low coverages for K-covered Cu(110) (Ref. 37) and for K-covered Si(100).[38,39] This peak was ascribed to emission of K valence electrons. However, recently the interpretation of such spectra has been revised,[40] and the peak at the Fermi edge is now not ascribed to the emission of electrons out of alkali-metal valence resonances.

IV. CONCLUSIONS

The work-function change of Si(100)/K shows a clear minimum at around half a full monolayer. The K cover-age is estimated from the intensity dependence of the photoemission spectra at the Fermi edge. Interface metallization is monitored via the appearance of a Fermi edge in the photoemission spectra which is present for coverages above around 40% of a full monolayer. The surface photovoltage shows a strong K-coverage dependence in the monolayer range, indicating a drastic increase in the relaxation rate when the overlayer obtains metal character. The band bending remains nearly independent of the K coverage. A quantum-well-type resonance for K is observed in the photoemission spectra when the substrate is kept at low temperature at an evaporation time three times that required to obtain the minimum work function.

ACKNOWLEDGMENT

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