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The Schottky barrier height of caesium on n-Si(111)-7 × 7 surfaces

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Abstract. The adsorption of Cs on Si(111)-7 × 7 surfaces at 170 K was studied by x-ray photoelectron spectroscopy. The growth mode was determined as layer-by-layer growth. Si(2p) core-level spectra show an initial shift to higher binding energies of 70 meV for small Cs coverages. As the Cs overlayer becomes metallic, the Si(2p) core level shifts to lower binding energies by 70 meV with respect to that for the clean surface. The barrier height of Cs/n-Si(111)-(7 × 7)¹ Schottky contacts is obtained as 0.49 ± 0.05 eV. This result agrees well with the prediction of a model based on metal-induced gap states and electronegativity.

Silicon is the most important semiconductor for industrial purposes and the Si(111)-7 × 7 surface is probably its most studied surface. Schottky contacts on silicon are of fundamental importance in the development and performance of electronic devices. Hence, theoretical understanding of the basics of these interfaces is essential. Since Schottky's [1] first explanations of the rectifying behaviour, numerous models have been invoked to explain the barrier heights on these contacts. Heine [2] considered the metal-induced gap states (MIGS) to provide the fundamental mechanism that determines the barrier heights of Schottky contacts. In order to predict the barrier heights as a function of material-specific values, Mönch developed the MIGS-and-electronegativity model [3]. In this model the Schottky barrier heights on a particular semiconductor depend linearly on the electronegativity of the metal. Due to their low electronegativities, alkali metals are most suitable for use in testing this chemical trend of the barrier heights.

The Cs/Si(111)-7 × 7 interface at room temperature (RT) has been well explored. X-ray standing-wave studies [4, 5] have been carried out to investigate the geometric structure. The electronic structure was examined by photoemission [6–11] and inverse photoemission spectroscopy [7, 9], while scanning tunnelling microscopy [12] was used for investigating both geometric and electronic aspects.

In contrast to the cases for Li and Na, only a Cs monolayer adsorbs on semiconductor surfaces at room temperature [6]. Although the saturation coverage of Cs on Si(111)-7 × 7 surfaces shows metallic behaviour [9], no metallic Cs layer is obtained. Only small clusters of Cs atoms are formed on the surface and these clusters are large enough to show metallic

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behaviour, but their electronic structure differs from that of bulk Cs. From second-harmonic-generation studies [13], it is known that multilayer growth can be achieved at low temperatures. Hence, low-temperature experiments are necessary to obtain continuous metallic Cs films.

In this paper we present the results of an x-ray photoelectron study of Cs multilayer adsorption on Si(111)- 7×7 surfaces at 170 K and we determine the Schottky barrier height of this Schottky contact.

The experiments were performed in a two-chamber stainless-steel ultrahigh-vacuum (UHV) system with a base pressure of $\sim 6 \times 10^{-9}$ Pa. The analysis chamber was equipped with a hemispherical electron energy analyser, a Mg/Zr double-anode x-ray source for photoelectron spectroscopy (XPS), a differentially pumped, windowless discharge lamp with a concave grating monochromator for ultraviolet photoemission spectroscopy (UPS) and a rear-view optics for low-energy electron diffraction (LEED). The instrumental resolution of the hemispherical analyser was 150 and 270 meV with UPS and XPS, respectively. An additional four-grid LEED optics was installed in the preparation chamber.

The samples, cut from n-type Si(111) wafers ($n = 3 \times 10^{15} \text{ cm}^{-3}$), were first oxidized under 1 bar of O_2 at 900 °C for 30 min, then dipped into hydrofluoric acid, which was diluted by a buffered $\text{HF}:\text{NH}_4\text{F}:\text{NH}_4\text{OH}$ solution (pH = 9), and eventually transferred into the UHV system. This *ex situ* preparation resulted in H-terminated Si(111):H- 1×1 surfaces. Hydrogen was then desorbed by heating the samples to 800 °C for about 3 min. Following this procedure, sharp 7×7 LEED patterns were observed. The samples were then transferred to the analysis chamber where their cleanliness was monitored by XPS. The sample holder was connected by a copper rope to a liquid-nitrogen-filled reservoir. The samples were cooled to 170 K. Cs was evaporated from well-outgassed commercial dispensers (SAES Getters) onto the cooled surfaces. The dispensers were heated to 1040 K by a current of 6.5 A and the evaporation time was controlled by a mechanical shutter. The adsorption of Cs on Si(111)- 7×7 was followed by XPS. In order to measure the changes in band bending, Mg $K\alpha$ radiation ($h\nu = 1253.6 \text{ eV}$) was chosen because of its higher bulk sensitivity (escape depth $\lambda \approx 18.3 \text{ \AA}$ [14]) with respect to Zr $M\zeta$ radiation ($h\nu = 151.2 \text{ eV}$, $\lambda \approx 4.4 \text{ \AA}$). After the first as well as the last Cs deposition on each Si sample, the O(1s) core-level line was monitored. As on the clean Si surface, no oxygen contamination was detected.

Figure 1 shows the intensities of the Cs($3d_{5/2}$) core-level lines as a function of Cs evaporation time, measured for two different samples. The data may be fitted by two straight lines, whose behaviour indicates layer-by-layer growth. The kink reflects the completion of the first continuous Cs layer at an evaporation time of 75 s. The Cs($3d_{5/2}$) intensity at this point is in good agreement with the intensity measured at the saturation coverage of Cs on a sample kept at RT (not shown), which is known as one adlayer [6]. After the completion of the first layer, the slope is reduced due to a lower sticking coefficient and the attenuation of the signal intensity from the first layer by the subsequent layer. This behaviour is known from studies of Cs adsorption on various semiconductor surfaces [15–20].

Figure 2 shows the energy position of the Si($2p_{3/2}$) core-level lines as a function of the Cs evaporation time. The Si($2p_{3/2}$) core level shifts to lower kinetic energies until it reaches a minimum at an evaporation time of ~ 30 s. After longer evaporation times it shifts to higher kinetic energies and reaches a constant value after ~ 100 s at $\Delta W_{kin} = 70 \pm 40 \text{ meV}$, with respect to the clean surface.

In order to obtain the position of the Fermi level in the band gap from the XPS data, its position at the clean (7×7)-reconstructed Si(111) surface was determined by UPS. Figure 3 shows the energy distribution curve of such a surface recorded with monochromatized He I radiation of 21.2 eV. The well-known surface states S_1 to S_3 [21] of the Si(111)- 7×7 reconstruction are resolved. The energy position of the Fermi level was obtained from a

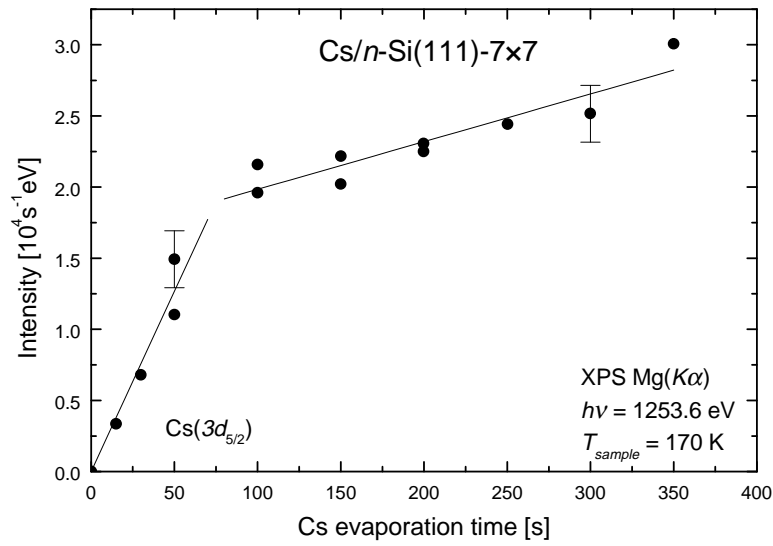


Figure 1. Intensities of Cs(3d_{5/2}) core-level lines for two 170 K Si(111)-7 × 7 samples as a function of Cs evaporation time. The lines drawn are the results of linear regressions of the experimental data in the corresponding ranges of evaporation times.

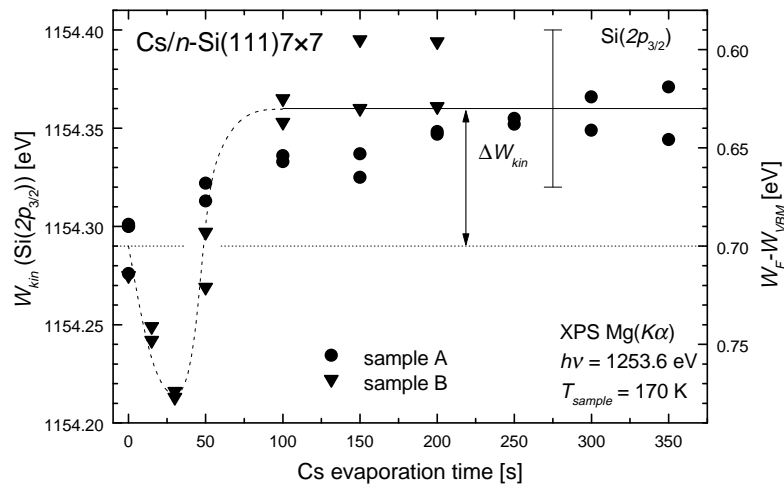


Figure 2. The energy position of the Si(2p_{3/2}) XPS core-level lines and the resulting position of the Fermi level as a function of Cs evaporation time. The dashed line is drawn to guide the eye. The dotted and solid lines are least-squares fits for the clean surface and the saturation region, respectively.

measurement with the molybdenum sample holder. From the energy distance between the valence-band maximum (vbm) and the surface state S₂, $W_{S_2} - W_{vbm} = 0.15$ eV [21], the position of the Fermi level was obtained as 0.7 ± 0.03 eV above the vbm. This value agrees

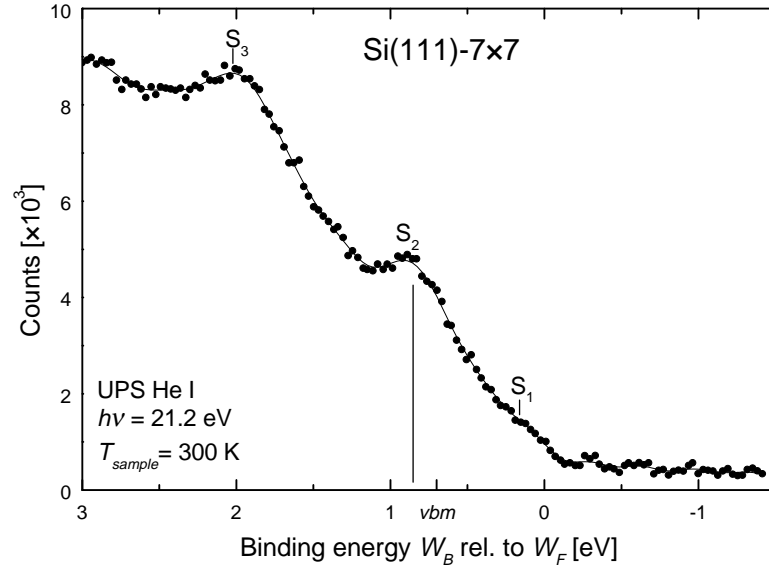


Figure 3. Valence-band spectra of a clean Si(111)- 7×7 surface at room temperature. The structures labelled S_1 to S_3 are due to emission from surface states of the (7×7) -reconstructed surface.

well with previously published data [22]. Taking this value as the reference, the positions of the Fermi level with respect to the vbm as a function of the Cs evaporation time are obtained, as shown on the right-hand axis of figure 2. The Fermi level first moves to 0.77 eV above the vbm and assumes a coverage-independent position at $W_{vbm} + 0.63 \pm 0.07$ eV for high Cs exposures.

The position of the Fermi level inside the band gap as a function of Cs evaporation agrees well with calculations by Klepeis and Harrison [23]. The Fermi level moves from the pinning position at the clean surface towards the conduction-band minimum (cbm); this behaviour is explained by Cs-induced surface states of donor type. In an early study, Mönch determined these states to lie at 0.76 eV above the vbm [24]. In contradiction to these results, Magnusson *et al* [10] and Paggel *et al* [25] found the Fermi level to move towards the vbm after RT adsorption of Cs and Na, respectively. In order to decide whether this discrepancy is due to the different surface preparations or the different temperatures, further investigations are necessary.

At Cs coverages above one monolayer, the position of the Fermi level is determined by the Schottky contact. For n-type doped semiconductors, the Schottky barrier height is the energy difference between the Fermi level (W_F) and the cbm, i.e.,

$$\Phi_{Bn} = W_{cbm} - W_F = W_g - (W_F - W_{vbm}). \quad (1)$$

The barrier heights of Schottky contacts on n-type doped semiconductors vary in the same way with temperature as their band gaps [22]. With the RT band gap of Si, $W_g = 1.12$ eV, our data give a RT barrier height of $\Phi_{Bn} = 0.49 \pm 0.07$ eV for Cs/n-Si(111)- $(7 \times 7)^i$ contacts. In contrast to this value, Magnusson *et al* reported $\Phi_{Bn} = 0.67$ eV [10] from their RT studies. At saturation coverage at RT, they found the Cs layer to consist of planar and metallic clusters of nine Cs atoms within each of the triangular subunits of the 7×7 unit mesh. Since the electronic properties of small clusters definitely differ from the properties of bulk metals [26, 27], the

electronic features of the interface might be different, too. Even for thin two-dimensional metal layers the electronic properties of the interface depend slightly on the layer thickness [28]. But these effects are one order of magnitude smaller than the accuracy of our measurement and, therefore, they can be neglected.

The electronic properties of bulk metal–semiconductor interfaces are described by the continuum of the MIGS. The barrier height is determined by the charge-neutrality level (cnl) of the MIGS and the charge transfer between the metal and semiconductor across the interface. According to Mönch [29], the barrier height turns out to be

$$\Phi_{Bn} = \Phi_{cnl} + S_x(X_m - X_s). \tag{2}$$

Tersoff [30] calculated the cnl position of silicon to be at 0.36 eV above the vbm. The charge transfer between the metal and the semiconductor is described by the difference $X_m - X_s$ of their electronegativities. The slope parameter S_x results from the electronic contribution ϵ_∞ of the static dielectric constant of the semiconductor [29]. Using Miedema’s electronegativity scale [31], equation (2) gives

$$\Phi_{Bn} = 0.76 \text{ eV} + 0.101(X_m - 4.7 \text{ eV}) \tag{3}$$

for silicon. Figure 4 shows the barrier heights of the Cs/n-Si(111)-(7 × 7)ⁱ Schottky contact and those for various other metals and silicides on silicon surfaces [32]. The solid line is the prediction (3) of the MIGS-and-electronegativity model, while the dashed lines are least-squares fits to the barrier heights on (7 × 7)ⁱ-reconstructed and (1 × 1)ⁱ-reconstructed Si(111) interfaces, respectively. The difference between these two lines was explained by the dipole associated with the stacking fault of the 7 × 7 surface [33, 34]. The predicted slope agrees

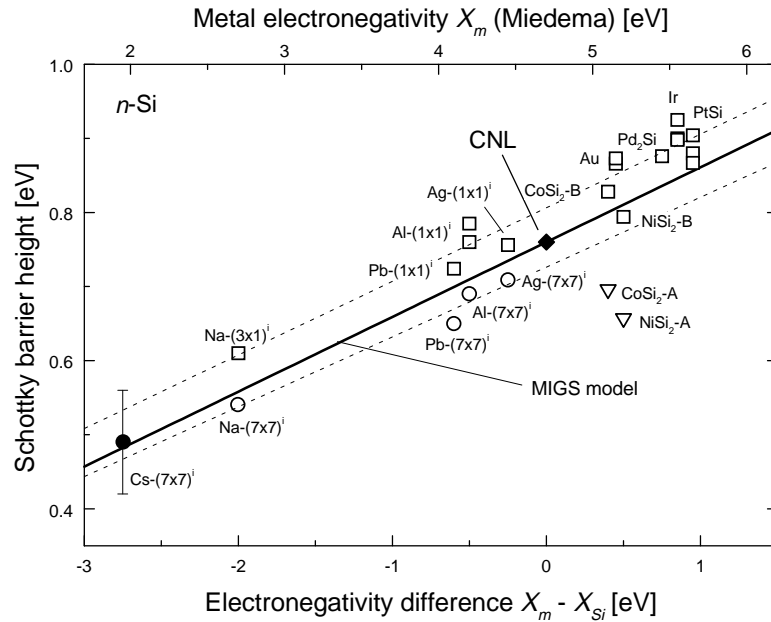


Figure 4. Barrier heights of the Cs/n-Si(111)-(7 × 7)ⁱ and other metal–silicon and silicide–silicon contacts versus the difference $X_m - X_{Si}$ of the Miedema electronegativities of the metals and Si. The \circ , \square data and dashed lines are adopted from [32].

well with the experimental results for both surface reconstructions. The barrier height of Cs/n-Si(111)-(7 × 7)ⁱ Schottky contacts, as determined in our study, confirms the prediction made by the MIGS-and-electronegativity model as well as agreeing with the chemical trend given by previous experimental results for (7 × 7)ⁱ-reconstructed metal–Si(111) interfaces.

In summary, Cs shows layer-by-layer growth on Si(111)-7 × 7 surfaces at 170 K. Hence, three-dimensional Cs-metal layers are obtained. Therefore, the resulting metal–semiconductor interface can be described by the MIGS-and-electronegativity model. This is validated by the good agreement between the barrier height predicted by this model and the experimental result $\Phi_{Bn} = 0.49 \pm 0.07$ eV from our studies.

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