

Metal-overlayer-induced charge-transfer effects in thin SiO₂-Si structures

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The evolution of core-level photoemission spectra has been studied during the initial stages of Cs and In overlayer growth on thin SiO₂ layers on Si(111) substrates to probe the influence of the metal-SiO₂ interaction on the charge state of the resulting structure. The Si 2*p* soft-x-ray photoelectron spectra on the SiO₂ and the Si substrate, which have been recorded simultaneously, show substantially different shifts to higher binding energy for the two components of the structure for Cs adsorption on the SiO₂ surface, but only small uniform shifts for In overlayers. The Si 2*p* core-level spectra have been analyzed by simulating the spectra with a model that separates the Cs-covered SiO₂ structure into thin layers with a constant dipole field gradient applied across them. Accordingly, the metal-induced Si 2*p* core-level shifts of the Si substrate are interpreted in terms of Si band-bending changes as a result of charge transport from the metal layer to the SiO₂/Si interface. The differential Si 2*p* shifts, which lead to a larger separation of substrate and oxide peaks on cesiated SiO₂/Si than on the pristine SiO₂/Si structure, are discussed in terms of a Cs-induced dipole field across the SiO₂ layer. It is proposed that the different behavior of Cs and In overlayers may be related to the different electronegativity and, consequently, to the different adsorbate dipoles of the two metals.

I. INTRODUCTION

The widespread use of metal-insulator-semiconductor (MIS) structures in modern device technology has stimulated extensive research to unravel the basic chemical and physical interactions between metal overlayers and thin oxide layers on semiconductors.¹ On SiO₂-Si structures, for example, it has been found that silicide-forming metals with mean electronegativities < 1.5 reduce the SiO₂, and this has been explained and substantiated by thermodynamical analysis.² Recently, we have investigated the chemical interactions of thin layers of SiO₂ on Si(111) substrates with rare-earth metal overlayers, which are of interest as possible gate materials in MIS-based chemical sensors³ or solar cell devices.⁴ Using core-level spectroscopies to monitor the chemical state of the elements, the reduction of thin SiO₂ layers by the rare-earth metal overlayers and the concomitant formation of metal oxides and silicides has been unequivocally demonstrated.⁵⁻⁷ In addition to chemical reactivity, however, differential chemical shifts of the Si 2*p* x-ray photoelectron spectroscopy (XPS) core-level signals of the Si substrate and the SiO₂ layer have been observed during the growth of the first metal monolayer on the outer SiO₂ surface.⁶ These effects have been tentatively associated with band bending and band lineup changes at the buried SiO₂-Si interface. A problem in the latter experiments, however, was the pronounced chemical reactivity of the rare-earth metals with SiO₂, which tended to blur the core-level spectra, thereby obliterating distinctions between different models of explanation of the Si 2*p* core-level shifts. Similar though less pronounced core-level effects have also been reported by Sarapatka in a study of XPS on Pd and Pb on

SiO₂-Si,^{8,9} but the differential Si 2*p* shifts have not been addressed specifically by this author.

In order to investigate metal-induced charge transport and Si band-bending evolution during the initial stages of MIS structure formation we have studied in this work model MIS systems with nonreactive metal overlayers on thin layers of SiO₂ on Si. It was hoped that in this way chemical effects might be disentangled from physical effects, i.e., that band bending and/or band alignment changes might be accessible to investigation. We have chosen for this study two metals of different electronegativities, namely, In and Cs, with values of 1.78 and 0.79, respectively, on the Pauling electronegativity scale. Both metals do not form stable bulk compounds with Si, and their oxides have much lower heats of formation than SiO₂.¹⁰ Thus, from thermodynamic considerations In and Cs are not expected to reduce SiO₂ layers, but the bonding interactions between In and Cs and the SiO₂ surface are expected to be of a different type (e.g., more covalent versus more ionic). We have used soft-x-ray photoemission (SXPS) techniques in conjunction with synchrotron radiation to study the evolution of the Si 2*p* core levels of the Si substrate and the SiO₂ layer during the initial stages of metal overlayer growth on the outer SiO₂ surface.

Our results demonstrate that the two metals In and Cs behave quite differently with respect to their interaction with the SiO₂-Si structure: whereas In metal deposition has very small effects on the Si 2*p* core-level energy positions, Cs overlayers induce pronounced differential core-level shifts. The latter data will be discussed in terms of charge injection from Cs adatoms and the buildup of a dipole field across the SiO₂ layer, whereas the differences

between In and Cs will be related to the more "ionic character" of the Cs adsorbate bonding.

II. EXPERIMENT

The experiments with use of synchrotron radiation were carried out at the TGM6 beamline of the synchrotron radiation laboratory BESSY in Berlin. The electron spectrometer system was equipped with a hemispherical electron energy analyzer (VSW HA 50) and the usual facilities for sample surface preparation, cleaning, and characterization. The spectral resolution of the system was ~ 0.3 eV at $h\nu=120$ eV. The sample manipulator allowed heating and cooling (~ 120 K) of the samples. Work-function changes ($\Delta\Phi$) were monitored using the slow secondary electron cutoff as measured in photoemission, with a small positive bias on the sample (typically 5 V) to improve the cutoff.

Two types of oxide layers on *n*- and *p*-type Si(111) substrates ($2.5\text{--}5\ \Omega\text{cm}$) have been used in the experiments: (i) the so-called "native oxide," which consists of $10\text{--}15\text{-\AA}$ -thick layers of amorphous SiO_2 formed by a chemical passivation procedure of the manufacturer (Wacker-Chemitronic); (ii) *in situ* thermally oxidized Si(111) surfaces, which were prepared following the procedure described by Himpfel *et al.*¹¹ to yield 15-\AA -thick SiO_2 layers. The "native oxide" samples were gently degassed and then carefully heated to 550°C in a vacuum to remove surface contaminants.⁶ Indium was evaporated onto the oxide surfaces from a W coil evaporator which was surrounded by a liquid-nitrogen-cooled Cu shroud, and metal coverages and mean film thicknesses were measured with a quartz film thickness monitor (Inficon). Note that $\sim 2\text{-\AA}$ In corresponds to 1 ML as defined by the number of Si atoms on an unreconstructed Si(111) surface. Cs was deposited from a SAES getter source and Cs coverages were monitored by $\Delta\Phi$ measurements. The Cs surface coverages are expressed in this paper in terms of fractions of the room-temperature saturation coverage $\Theta/\Theta_{\text{sat}}$. In the absence of specific Cs coverage information on SiO_2 and using guidance from Cs-on-Si(111) experience¹² it is assumed that the Cs saturation coverage on amorphous SiO_2 at room temperature corresponds approximately to a densely packed Cs adlayer.

In the course of the experiments with synchrotron radiation it was noted that the evolving MIS structures with Cs were sensitive to photon irradiation: the observed core-level binding-energy shifts were somewhat reduced upon prolonged irradiation with light. It was therefore attempted to minimize the irradiation time and to move to a different part of the sample for each XPS spectrum; however, the reported binding-energy shifts constitute minimum values since the radiation influence during the recording of one spectrum cannot be completely excluded.

III. RESULTS

A. Indium on SiO_2 -Si

Si $2p$ core-level spectra of $\sim 15\text{-\AA}$ thermal SiO_2 on *p*-Si(111) as a function of In coverage are displayed in Fig.

1. The spectra have been recorded with $h\nu=121$ eV and they are normalized to constant photon flux. A smooth polynomial background has been subtracted from the original data and the relative binding energy scale refers to the Si bulk $2p_{3/2}$ peaks as the energy zero. On In deposition a small shift to higher binding energy (BE) of the order of 0.1 eV is observed for the Si substrate and the SiO_2 $2p$ core levels, but we note that the shifts are the same for both substrate and oxide peaks. The situation is very similar for In on native SiO_2 layers and on *n*-type samples. The effects of In deposition onto the SiO_2 -Si surface are therefore not pronounced concerning the charge state and the chemical state of the structure; however, another interesting point has to be noticed. The attenuation of the SiO_2 XPS signal intensity with In coverage is unexpectedly small, amounting to only $I(\Theta_{\text{In}}=12\ \text{\AA})/I_0 \approx 0.6$ for the nominally 6 ML of In. It appears therefore that the In overlayer forms islands and does not wet the SiO_2 surface. The coalescence of nonreactive metals into islands on SiO_2 -Si has also been observed directly in previous work by Pretorius, Harris, and Nicolet² in secondary electron micrographs.

B. Cesium on SiO_2 -Si

Figure 2 shows the Si $2p$ SXPS spectra of native SiO_2 on *n*-Si(111) for various Cs coverages up to room-temperature saturation coverage. As in Fig. 1 the spectra have been background subtracted and normalized to constant photon flux. The inset shows the course of the work function upon Cs adsorption. The Si $2p$ substrate peaks shift with increasing Cs coverage to higher BE, up

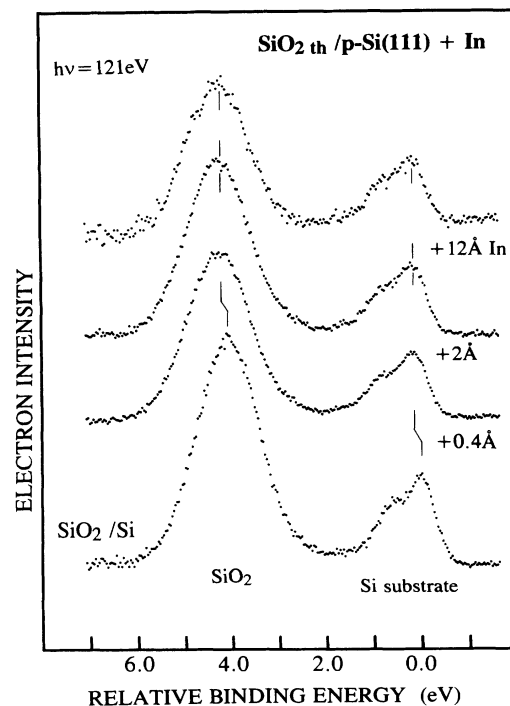


FIG. 1. Si $2p$ core-level spectra of thermal SiO_2/p -Si as a function of In coverage.

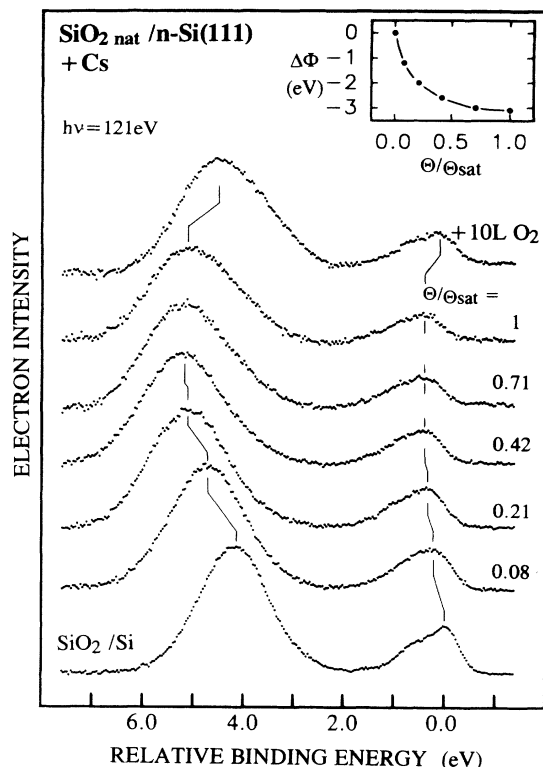


FIG. 2. Si 2*p* XPS spectra of native SiO₂/*n*-Si as a function of Cs coverage and 10-L O₂ exposure (top spectrum). The inset shows the work function change upon Cs deposition. The Cs coverage is referred to the saturation coverage at room temperature.

to 0.4 eV at $\Theta/\Theta_{\text{sat}}=1$, but the oxide Si 2*p* structure shifts by a much larger amount up to 1.0 eV. The corresponding work-function change of the SiO₂ surface is -3.1 eV up to Cs saturation. Exposing the saturated Cs/SiO₂ surface to gaseous O₂ partly reverses the Si 2*p* core-level shifts—see the top spectrum of Fig. 2. The oxide Si 2*p* structure broadens considerably on Cs adsorption, from ~ 1.6 eV on the pristine SiO₂ surface to ~ 2.1 eV after Cs saturation.

In Fig. 3 Cs 4*d* SXPS spectra are displayed as a function of Cs coverage Θ_{Cs} for the sequence of Fig. 2. No background subtraction has been applied here, and the background intensity increase at the low BE is due to overlapping with Cs Auger transitions. Similar to the Si 2*p* XPS peaks, the Cs 4*d* core-level signals shift gradually to higher BE with increasing Θ_{Cs} , by 0.5 eV at $\Theta/\Theta_{\text{sat}}=1$, and this shift can also be reversed by exposure to O₂ from the gas phase (top curve of Fig. 3).

Similar results to those reported above on *n*-type substrates have been obtained for native SiO₂ layers on *p*-type Si samples. However, *quantitatively* somewhat different results were obtained on thermally grown oxide layers. This is illustrated in Fig. 4 for 15 Å of thermal SiO₂ on *p*-Si(111), where Si 2*p* SXPS of the pristine surfaces are compared to those of surfaces covered with small amounts of Cs. In this experimental sequence Cs has been deposited onto the cooled oxide surface (~ 120 K). The two bottom spectra compare the clean room-

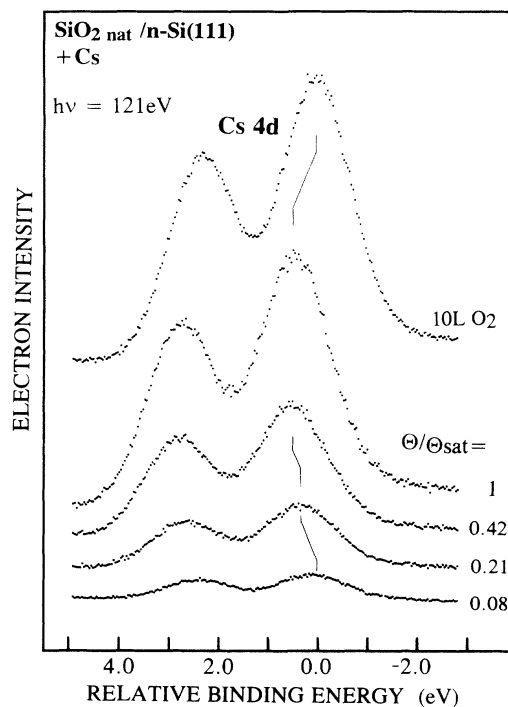


FIG. 3. Cs 4*d* XPS spectra following Cs deposition onto native SiO₂/Si and after exposure to 10 L O₂ (top spectrum).

temperature SiO₂-Si surface with the 120-K surface: a uniform -0.3 -eV shift to *lower* BE is observed for the Si 2*p* XPS peaks of both substrate and oxide layer. This shift is reflected as an increase in the $\Delta\Phi$ curve (not shown) and is due to a reduction of the Si band bending as a result of the increase of the surface photovoltage effect at the lower temperature.^{13,14} With Cs coverage the substrate Si 2*p* features shift to *higher* BE, by 1.0 eV for $\Theta/\Theta_{\text{sat}}\approx 0.3$, but the oxide Si 2*p* structure of the same surface shifts by 2.5 eV to higher BE. Thus, the separation between bulk Si and SiO₂ 2*p* core-level energies is increased by ~ 1.6 eV on the cesiated structure. The experimental data of Fig. 4 have been simulated according to the model described in Sec. IV, and the solid lines through the data points are the resulting theoretical fits. For two spectra (bottom and top) the components of the fits are indicated. The inset of Fig. 4 illustrates the results of the modeling procedure in terms of changes of the Si band bending and of the proposed dipole field across the SiO₂ layer as discussed below.

IV. DISCUSSION

The Cs-induced Si 2*p* BE shifts of the Si substrate are most naturally explained by a change of the Si band bending, which is mediated by electron transport from the Cs overlayer to the SiO₂/Si interface. This results in the additional population of interface states and in a band flattening on the *n*-type substrate. The fact that on *p*-type Si the shifts occur in the same direction, leading to an increase of band bending in this case, supports the view that electron injection *from the Cs overlayer to the interface* causes the band-bending change. The interaction of

O₂ with the Cs-SiO₂/Si structure leads to a partial reversal of the band-bending change. Adsorbed oxygen acts as an electron acceptor and changes the dipole layer at the Cs-SiO₂ surface. The result of this is a partial depopulation of the SiO₂/Si interface states which have been filled during the Cs adsorption step. Similar effects of adsorbed oxygen on the band bending have also been reported on other metal-SiO₂/Si systems.^{6,8}

The shift of the Cs 4*d* core levels follows the direction of the Si 2*p* movements; however, the close quantitative correspondence between the Cs and the Si substrate core-level shifts must be considered as fortuitous. Shifts of metal core-level XPS peaks as a function of coverage are commonly observed during the buildup of metal overlayers on semiconductors, and they are due to the combined effects of initial-state, final-state, and environmen-

tal (ensemble) changes during the metal overlayer growth. The change of the electrostatic potential at the SiO₂ surface as a result of band-bending alteration and of the other effect discussed below provides only additional factors for core-level shifts which cannot, however, be separated from each other in a simple way.

The Cs-induced change of the Si band bending cannot account for the differential Si 2*p* core-level shifts observed between the Si substrate and the SiO₂ layer. Two models may be offered to explain the situation: (1) the Cs-SiO₂ interaction produces a dipole field across the SiO₂ layer and a concomitant shift of the oxide core levels; and (2) the band lineup at the SiO₂/Si interface is modified following Cs deposition onto the outer SiO₂ surface. The experimental verification of model 1 requires examination of the width of the SiO₂ Si 2*p* XPS peaks: indeed, as mentioned in Sec. III, a broadening of ~0.5 eV is observed on the SiO₂-derived core-level feature. A change of band alignment at a heterojunction interface requires the modification of the dipoles at the interface,¹⁵⁻¹⁷ for which in turn structural or chemical changes in the interfacial region are necessary in order to modify the so-called extrinsic charge neutrality levels.¹⁵

In order to decide between the two models and to obtain reliable data on the band bending and the Cs-induced shifts, the spectra were analyzed using a line-shape analysis procedure based on the Levenberg-Marquart algorithm, where the core-level spectrum is assumed to consist of a Lorentzian line shape, convoluted with a Gaussian function. The background below the spectrum is modeled using a third-order polynomial. The spectrum of the clean SiO₂ surface can be described by a single spin-orbit pair representing the bulk emission and another one representing emission from the SiO₂ layer, which are separated by roughly 4.1 eV. The Gaussian broadening for these lines are 0.5 and 1.6 eV. The first value is determined by the instrumental resolution in the experiment, while the latter is the intrinsic Gaussian broadening of the SiO₂ peak.¹¹ Both components of the spectrum from the clean surface have a symmetric line shape as expected for a semiconducting sample. However, upon Cs adsorption on the SiO₂ surface the core-level emission from the SiO₂ layer becomes more and more asymmetric with increasing Cs coverage, where the tailing is towards the lower BE side of the peak. Furthermore, the separation between the Si bulk component and the peak of the SiO₂-related structure in the spectra increases with Cs coverage. To understand these two features of the series of spectra, it was assumed that the SiO₂ component consists of emission from several layers, each of which is located at a different energy. Thus the SiO₂ region of the spectra was separated into four components, each representing a single layer of SiO₂ in the (111) direction; the exact crystallographic structure of the SiO₂ layer on the Si(111) surface is not known, but the results of the fitting procedure show only minor variations with the number of layers used for the model, and a continuum model leads to similar results. The emission from each layer was calculated using a discrete layer attenuation model, where the attenuation length of 8.5 Å for SiO₂

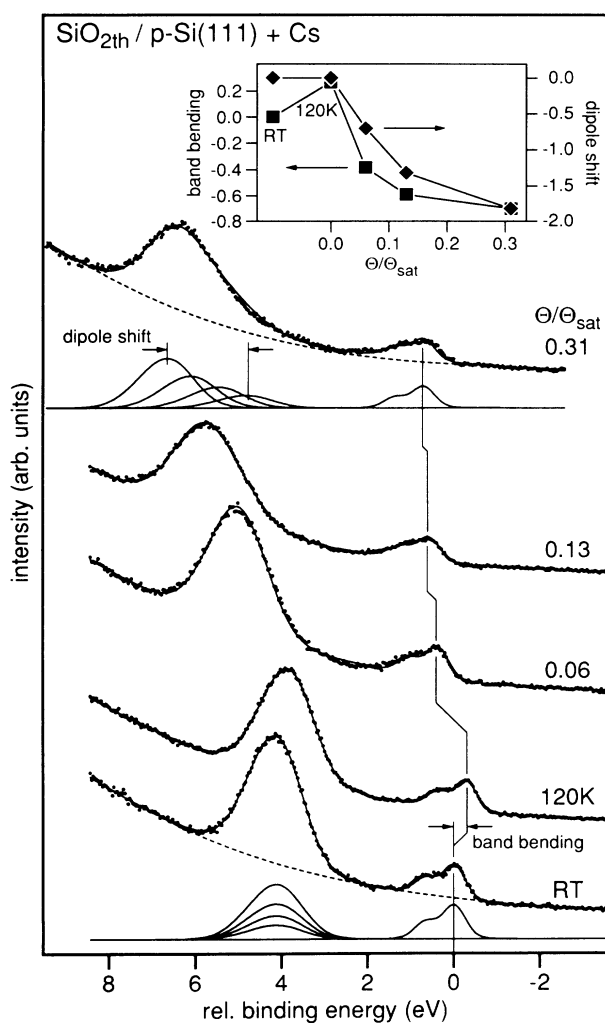


FIG. 4. Si 2*p* XPS spectra of thermal SiO₂/p-Si as a function of Cs coverage deposited at 120 K. The solid lines through the data points represent the fits obtained using the layer model with a linear dipole field across the SiO₂ layer as discussed in the text. The individual layer components of the simulation are given for the top and the bottom spectrum. The inset summarizes the Cs-induced band bending and the dipole shift within the SiO₂ layer as a function of Cs coverage.

and 4.0 Å for Si as well as the relative photoemission intensity $\sigma_{\text{SiO}_2}/\sigma_{\text{Si}}=1.8$ at the photon energy of 120 eV were taken from Himpsel *et al.*¹¹ We thus arrive at a model containing only three parameters: the energetic position of the Si bulk component, which is easily determined, the absolute intensity of the Si/SiO₂ core-level emission (the relative intensities were fixed according to the model), and, most importantly, the relative shift in the energy of the SiO₂ components. The top spectrum in Fig. 4 is shown with all components used for the fit, i.e., the four SiO₂ components and the Si bulk component. The data are given by the dots, while the fit to the data is represented by the solid line. With increasing Cs coverage the position of the Si bulk component is now allowed to vary, due to the band-bending change at the interface, but the relative shift between the Si bulk component and the SiO₂ component with lowest intensity, i.e., the one at the Si/SiO₂ interface, is kept fixed (which is equivalent to a fixed band offset at the Si/SiO₂ interface). Instead we allow a binding energy “gradient” to occur in the SiO₂ layer, which is equivalent to the existence of an electric field across this layer. Using a potential linearly dependent on distance from the surface, i.e., a constant binding energy offset between the single components, the best fit to the experimental data is obtained. The fit is superimposed one each spectrum, and the constituent components are given for the top spectrum in Fig. 4. Based on this procedure we are able to determine the resulting Cs-induced band bending at the SiO₂/Si interface, and the dipole shift of the SiO₂ components within the SiO₂ layer as a function of the Cs coverage. These data are shown in the inset. We thus conclude that Cs adsorption on the SiO₂ surface induces a dipole field across the SiO₂ layer, as well as a change in the band bending in the Si at the SiO₂/Si interface. However, the band offset at the buried interface is not changed.

A pictorial representation of our model describing the situation at the Cs-SiO_{2,th}/p-Si structure is given by the band diagrams in Fig. 5. Diagram (a) for the pristine SiO₂/Si system has been adapted from Ref. 18 using a work function of 5.2 eV for SiO₂ (Ref. 19) and assuming somewhat arbitrarily that the Fermi level is pinned to a near-midgap position. Diagram (b) describes the established Cs-SiO₂/Si structure where the experimentally evaluated Si 2*p* XPS core level changes and the change of the work function have been incorporated. Note that the observed differential Si 2*p* shift between the Si substrate and the thermal SiO₂ layer is made up by an electric dipole field contribution of 1.8 eV.

The formation of In overlayers on SiO₂/Si is accompanied by only a small uniform shift to higher BE (~ 0.1 eV) of both substrate and oxide Si 2*p* peaks, and this is indicative of a small In-induced change of the Si band bending. In view of the Cs results these small effects are remarkable and it may be worthwhile to speculate on the differences between the two systems. The electronegativity of In and Si is similar, and the In-Si interaction is probably described best by a covalent type of bonding.²⁰ Thus, there is no or little charge transfer to be expected and the In adsorbate dipole should be weak. Consequent-

ly the injection of electrons from the In layer into interface states at the SiO₂/Si interface is less favorable than in the case of Cs which is characterized by a more ionic situation.¹²

IV. SUMMARY

The initial stages of the formation of SiO₂/Si model MIS structures with thin Cs and In metal overlayers have

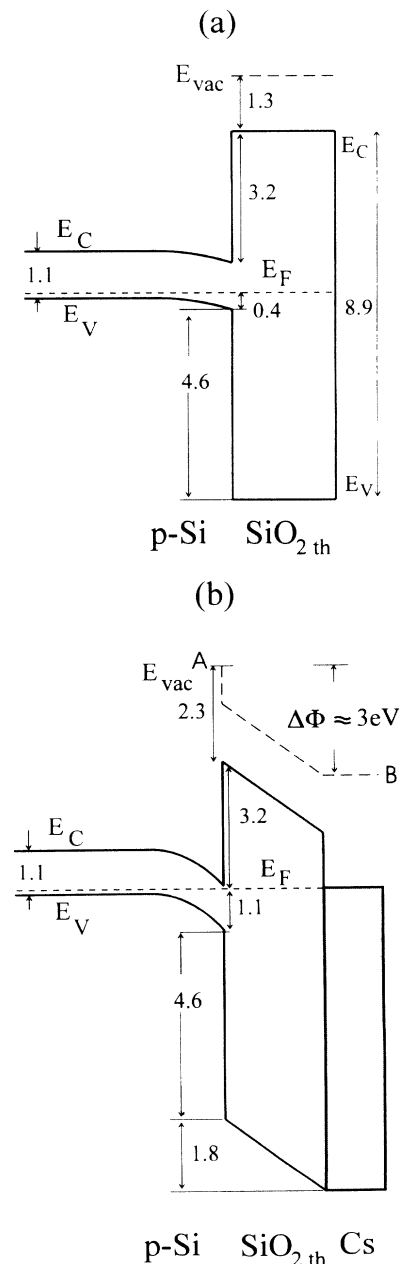


FIG. 5. Schematic band diagrams of the pristine SiO₂/p-Si structure (a) and of the Cs-covered MIS structure (b) illustrating band-bending changes as well as the electric-field gradient across the SiO₂ layer as a result of Cs deposition (numbers in eV). *A* and *B* in diagram (b) refer to the work function of the pristine SiO₂/p-Si structure before and after Cs deposition at low temperature.

been followed by SXPS core-level spectroscopy using synchrotron radiation. The simultaneous observation of Si 2*p* core-level signals from the Si substrate and the SiO₂ layer allowed us to probe both the outer metal-SiO₂ and the buried SiO₂/Si interfaces. For the Cs-SiO₂/Si system large Si 2*p* core-level shifts have been observed, with the oxide Si 2*p* signals shifting by a larger amount to higher BE than the Si substrate peaks. The spectra have been analyzed and simulated in terms of changes of the band bending of Si at the SiO₂/Si interface and of a dipole field across the SiO₂ layer. The latter is mediated by the Cs-SiO₂ surface interaction. The In overlayers induce only small uniform Si 2*p* core-level shifts which are explained

in terms of Si band-bending changes. The differences between the effects of In and Cs overlayers on SiO₂/Si structures are related tentatively to the different bonding situations of the two metals on Si, namely, covalent versus ionic, and to the resulting different adsorbate dipole layers.

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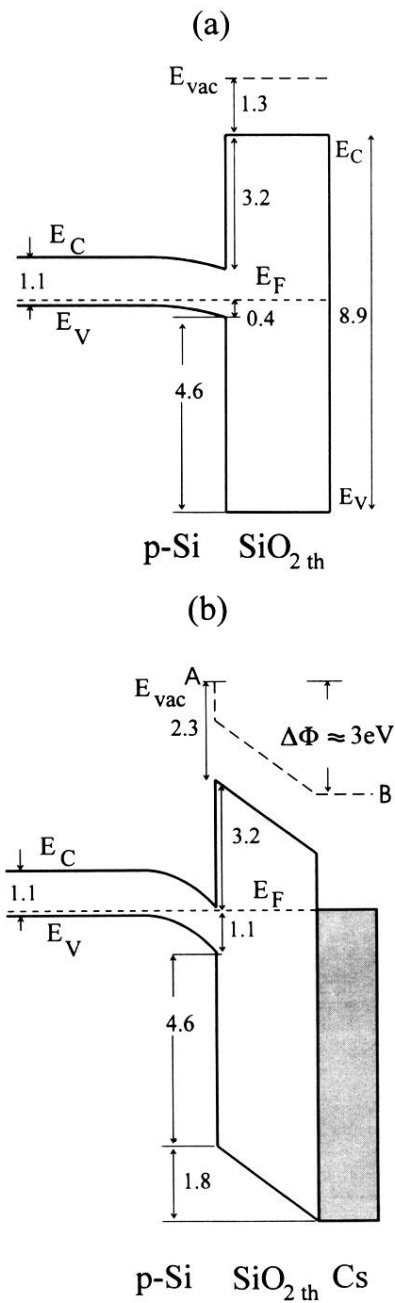


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