Evaluation of alkali-induced band-bending inhomogeneity and charge transfer trend from core-level analysis

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We present a method for evaluating the spatial inhomogeneity of adsorbate-induced band bending on semiconductors from the substrate core-level lineshape. As a case study we consider the first stages of accumulation layer formation due to K adsorption on the H:Si(111) surface at 300 K. The observed Si 2p core-level lineshape variation is accounted for considering each randomly distributed adatom as a source of a screened Coulomb potential. We determine the coverage dependence of the band-bending distribution, and the parameters characterizing the local K-induced potential.

In recent years, several works have pointed out the importance of taking into account the band-bending inhomogeneity in the study of Schottky potential barrier formation (that is, upwards band bending) at metal/semiconductor interfaces. In particular, Tung[1] has shown that inhomogeneity of the Schottky barrier height (SBH) can strongly affect the electron transport properties at these interfaces, while a direct measurement of SBH fluctuation has been performed by Palm *et al.*[2] by means of ballistic electron emission technique. Moreover, Cimino *et al.*[3] have qualitatively shown that SBH fluctuation can deeply affect the substrate core-level photoemission peak lineshape. In this paper we address the issue of a quantitative determination of the band-bending potential distribution in the case of accumulation layer formation. In fact, the occurrence of a huge downward band-bending (of almost 1 eV) at specific metal/n-type semiconductor interfaces has been reported for coverages as low as 0.1–0.2 ML,[4–6] at variance with the cases of depletion layer formation on n-doped semiconductors, for which maximum band-bending usually occurs at the monolayer. Obviously in these cases the approximation of a laterally uniform adlayer is rather poor and the band-bending potential inhomogeneity could play a major role in the determination of the barrier properties. It is therefore relevant for the study of accumulation layer formation to be able to determine the band-bending inhomogeneity at these interfaces. Here we describe a quantitative method for the evaluation of the distribution of the local band-bending value from the substrate core-level lineshape, in the case of accumulation layer. As a case study, we present the analysis of the lineshape modification of the Si 2p core-level upon K adsorption on the H:Si(111)(1×1) surface in the submonolayer regime. The H:Si(111)(1×1) surface is particularly suitable for this kind of investigation because of its high intrinsic homogeneity and low defects density, which is reflected in the sharpness of the Si 2p core-level photoemission spectra, besides its high stability. As we shall see, the adsorption of K atoms produces, even for the lowest coverages, a huge broadening of the Si 2p lineshape.

We introduce a model which considers a random distribution of adatoms, each treated as a source of a screened Coulomb potential. The core-level lineshape analysis is performed taking into account the distortion of each component (bulk- and surface-related) due to the spatially varying band-bending potential. At variance with the work of Ref. 3 which treated the spatial dependence of the band-bending potential in the Schottky approximation, we explicitly take into account the local character of the potential and the electronic screening. The output of this analysis is a description of the spatial variation of the band-bending potential on the mesoscopic scale for each K deposition step, along with an evaluation of the local potential parameters (i.e., charge transfer and effective screening length of the K-derived electrons). The spatial variation of band bending results to be quite relevant at this interface, confirming our initial statement on the influence of overlayer disuniformity on the band-bending inhomogeneity. Besides, this work demonstrates the importance of band-bending inhomogeneity in the analysis of the evolution of core-level lineshape during interface formation.

The experiments were performed in the ultrahigh-vacuum chamber of the SuperEsca beamline at the ELETTRA Synchrotron radiation facility[7] in Trieste, Italy. Core-level photoelectron spectra were obtained at a photon energy of 247 eV, collecting the electrons at the emission angle of 38° with a double-pass 150 mm hemispherical electron analyzer and an overall resolution of about 50 meV. The Si crystal was n-doped and nondegenerate ($n = 4 \times 10^{15}$ cm^{-3}). The hydrogenated Si(111) surfaces were prepared *ex-situ* by a proper chemical treatment[8] and introduced in the experimental chamber *via* a fast entry lock. Surface quality and cleanliness were checked by ultraviolet [$h\nu(HeI) = 21.218$ eV] valence band and x-ray photoemission measurements. The K
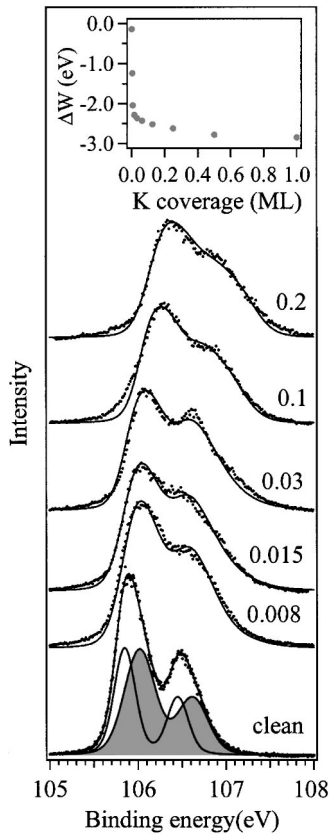
FIG. 1. Si 2p core-level peaks (filled circles) as a function of K deposition along with their best-fit curves (solid line). Spectra are taken with a photon energy of 247 eV and an angle of emittance of 38°. For the clean surface, the surface (S, shadowed) and bulk (B) Voigt-doublet components are also shown. The values of the spin-orbit separation and of the branching ratio are 0.602 eV and 0.53 ± 0.01, respectively. The Lorentzian width is 37 meV for both components, while the Gaussian width is of 110 meV for B and 180 meV for S. Numbers in the figure indicate K coverage in monolayer. Spectra are vertically shifted for convenience and normalized to the photon current. In the inset the change of the work function is displayed as a function of K coverage.

coverage calibration were performed considering the evolution of the work function, of the mean band bending and of the K 3p core-level intensity. We refer to a monolayer (ML) as the saturation coverage of potassium on the H:Si(111) surface at room temperature.[6]

The Si 2p core-level lineshape of the clean H:Si(111)(1 ×1) surface has been studied by several groups,[9–12] which, in order to reproduce its asymmetric shape, have proposed different deconvolutions, each involving several components. We performed a best-fit analysis of the clean surface Si 2p core-level doublet in two different ways. First, we considered a best-fit with two Voigt doublet components, obtaining the curve shown in Fig. 1, where the two components are related to bulk (B) and surface (S) Si atoms, respectively. Then, following the indication of Ref. 12, we added a further component S_1. For both procedures the energy shift between bulk and surface components results to be $\Delta E_{BS} = 0.17 \pm 0.05$ eV, while the energy difference between S_1 and B (ΔE_{BS_1}) is 0.45 ± 0.05 eV, in substantial agreement with the literature.[9,11,12] By introducing the third component only a small improvement in the best-fit quality is obtained. For the

sake of clarity therefore in the following we consider the simpler two-component best-fit as a starting point for the analysis. In fact, while the component S is clearly related to the Si atoms of the surface, the origin of the third component S_1 is not yet unambiguously determined, so that its unknown evolution as a function of K coverage would introduce some degree of arbitrariness in the analysis.

The evolution of the Si 2p core level with K coverage is shown in Fig. 1 together with the work function change (reported in the inset). As can be observed from the shift towards higher binding energy of the whole spectrum, the potassium deposition induces a downward surface band bending that reaches the largest value of about 0.55 eV around 0.2 ML, in agreement with the literature.[6,13] Moreover, the Si 2p core-level shape changes dramatically upon K adsorption already for depositions of few hundredths of a monolayer, and in such a low coverage regime, this change cannot be reasonably explained by the local interaction between Si and K adatoms. In fact, an attempt to fit the core-level peaks introducing components related to K-bonded Si atoms leads to unrealistically high values of their intensity. On the other hand, it is known from high-resolution electron energy-loss measurements[14] that K adsorption does not affect the long range order of the hydrogenated surface, nor induces H atoms desorption. It is therefore necessary to introduce a different mechanism to explain the Si 2p lineshape change. In the following, the observed evolution of the Si 2p core-level is quantitatively reproduced considering the inhomogeneity of the band-bending potential due to the sparse adatom distribution. We calculate the spatial variation of the band-bending potential induced by the randomly deposited adatoms and attribute to each Si atom in the photoemitting volume the value of the potential energy at its site. The core-level lineshape is then built up summing the contribution of all Si atoms in the photoemitting volume, each shifted in energy by the local value of the band bending. As a first step in this analysis we find a proper expression for the spatial dependence of the adatom-induced potential. The bonding between K and surface Si atoms is known to be strongly ionic,[6,15] with a net electronic charge transfer from the adatoms to the substrate. In the low coverage limit, each K atom can thus be treated as an almost completely ionized donor impurity, partly screened by the surrounding electrons. We therefore associate to each adatom i a screened Coulomb potential

$$\phi_i(\rho,z) = \frac{A e^{-\sqrt{(\rho-\rho_i)^2+(z+z_K)^2}/\kappa}}{\sqrt{(\rho-\rho_i)^2+(z+z_K)^2}}, \quad (1)$$

where (ρ,z) is the position vector of the Si atoms of the crystal, ρ_i is the bidimensional vector of the surface adatom position and z_K is its vertical distance from the surface, assumed to be 3 Å. A is a constant related to the value of the adatom positive charge, and κ is the electronic screening length. As the Si sample is nondegenerate, the screening length of the dopant electrons is of several hundreds Å,[16] having therefore a negligible influence on the spatial dependence of the potential. On the other hand, the screening of the K-derived electrons can be more relevant. In fact, even if its exact evaluation deserves a full quantum-mechanical calculation, a rough estimate of an effective screening length
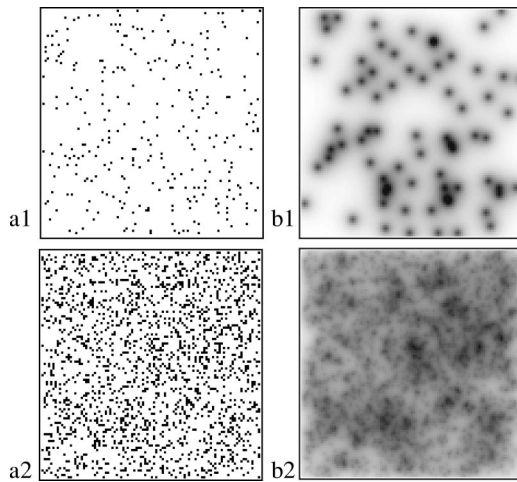
FIG. 2. Left panels: random distribution of adatoms, represented as black dots, on the (400 Å×400 Å) surface mesh, corresponding to a K coverage of 0.03 ML (a1) and 0.2 ML (a2). Right panels: corresponding distribution of the band-bending potential values on the surface layer, for 0.03 ML (b1) and 0.2 ML (b2). Darker regions correspond to higher values of the potential.

can be obtained calculating the value of the Bohr radius associated with the donor state level $r_0 = \epsilon\hbar^2/e^2 m^*$.[17] Taking $m^* = 0.2m_0$ and $\epsilon = (\epsilon_b + 1)/2 = 6.5$ (Ref. 18) a value of 15 Å is obtained, which is more than one order of magnitude smaller than the dopant screening length.

The following step in order to reproduce the observed core-level lineshapes is to introduce the distribution of K adatoms on the surface. As far as we know, no morphological study of the alkali/H:Si(111) system has been performed yet. LEED observations, showing a progressive reduction of the (1×1) pattern sharpness upon K deposition, without appearance of any superstructure, suggest that potassium grows disorderly on the H:Si(111) surface.[14] In absence of a more direct knowledge of the surface morphology, we therefore consider a random distribution of K-adatoms on the surface. A squared mesh of 400×400 Å^2 (corresponding to 10^4 Si unitary surface cells) is introduced, on which the K adatoms are randomly distributed,[20] as shown in the left panels of Fig. 2 for two different coverages. We then consider the effect of the randomly deposited adatoms on a crystal slab constituted by six (400×400 Å^2) layers, which represents the effective photoemission volume. Each layer is defined by the value of $z = a_\perp \cdot h$, where $a_\perp$ is the mean distance between layers and $h = 0, \ldots, 5$. For each adatom distribution, the total band-bending potential energy in each point (ρ, z) of the crystal slab is given by $E(\rho, z) = e\Phi(\rho, z) = e\Sigma_i \phi_i(\rho, z)$, where the sum runs over all the adsorbed adatoms on the squared mesh. The results of this calculation for the surface layer and for two different coverages are shown in the right panels of Fig. 2 as image plots, where darker regions correspond to higher band-bending potential energy values. The distribution of potential energy values thus obtained is the main ingredient for calculating the Si 2p experimental lineshapes. For each coverage, in fact, the Si 2p core level is built up summing the contributions of all the Si atoms of the crystal slab. Each atom contribution is given by the clean crystal surface (if $h = 0$) or bulk (if $h = 1, \ldots, 5$) component, shifted in energy relative to the clean surface position by the value of the total
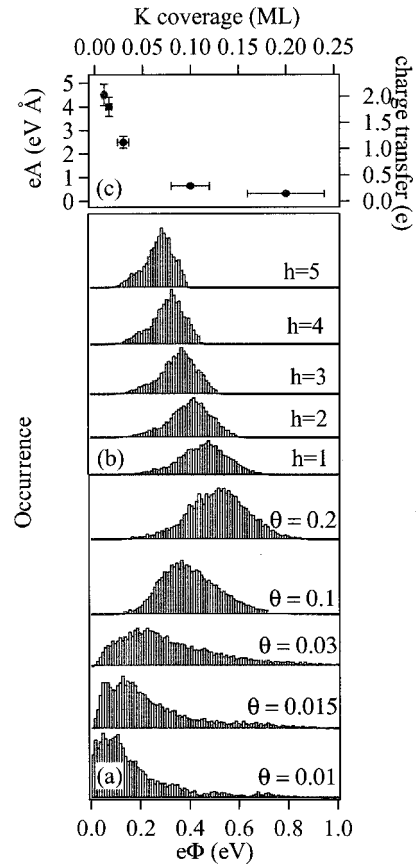

FIG. 3. Panel (a): Histograms of the distribution of the total band-bending potential on the surface layer, for successive K coverages. Panel (b): The same, for each of the five bulk layers of the slab, at the fixed coverage $\theta = 0.2$ ML. Histograms are vertically displaced for convenience. Panel (c): Value of the parameter eA (left scale) and of the charge transfer (right scale) as a function of K coverage, as determined by the fitting procedure and assuming $\epsilon = 6.5$.

band-bending energy $E(\rho, z)$ in that site. Furthermore, the intensity of the contribution of atoms coming form the hth layer is weighted by a factor accounting for the electron escape depth $\lambda = 7$ Å.[21] In order to reproduce the experimental data we only vary, for each coverage, the proportionality factor A and the screening length κ in Eq. (1). The best-fit curves obtained for each coverage with this procedure are compared with the experimental data in Fig. 1, showing a good agreement in both lineshapes and energy positions. The small discrepancy on the lower binding energy side of the spectra could be explained by the presence of a further component, already reported in literature,[12] probably caused by a small amount of K-induced surface defects. In panel (a) of Fig. 3 is reported the distribution of potential energy values over the surface layer, as determined by the fitting procedure: The histograms are built up by counting the number of Si atoms for each potential energy value. In the first stage of deposition the distribution is peaked around zero, indicating that most of the surface is unaffected by the adatoms induced potential, while for coverage greater than 0.03 ML the number of atoms unaffected by the band bending vanishes. The mean value of the band bending potential energy distribution increases with coverage, reaching almost 0.55 eV for 0.2 ML, while its width remains of ~0.3 eV. The distributions

of potential energy in the bulk layers, shown in panel (b) of Fig. 3 for 0.2 ML, are narrower and centered on lower values relative to that of the surface, indicating that bulk layers are more homogeneous than the surface and less affected by the band bending.

The factor eA is related to the amount of charge transfer from the K-adatoms to the substrate. As shown in Fig. 3, panel (c), left scale, it decreases from 4.5 eV Å at the lowest coverage to 0.3 eV Å for 0.2 ML, probably due to the coverage dependent adatom depolarization. This effect is confirmed by the coverage dependent shift towards lower binding energy of the K 3p core level (not shown here). The corresponding decrease of $\phi_i(\rho,z)$ is not in contradiction with the total band bending increase, as this last is given by the progressively increasing overlap between the potentials induced by the adatoms. This observation shows the importance of taking into account the surface inhomogeneity in the evaluation of band bending evolution, especially in the submonolayer regime. Assuming the realistic value of $\epsilon = 6.5$, the initial charge transfer would be of about two electrons per adatom, decreasing to 0.14e at 0.2 ML [Fig. 3, panel (c) right scale]. This anomalous initial value could indicate that already at very low coverage the adlayer is formed by K atom dimers rather than by isolated adatoms. This hypothesis is not in contrast with the ionic character of the adsorbates, as it is well known that alkali metals on III-V(110) semiconductor surfaces, for example, form long dimer chains at extremely low coverage, despite their long range repulsive interaction.[22,23] Even if a precise treatment of the island nucleation process is clearly beyond the scope of the present work, we observe that a modification of the model in this

sense (i.e., replacing each adatom by a dimer and renormalizing the coverage accordingly) is also consistent with the experimental data and leads the value of charge transfer back to a more physical range. The best-fit value of κ is of 15 Å for the lower coverages, increasing to 25 Å for $\theta = 0.2$ ML, in substantial agreement with the Bohr radius estimate. The increase in the screening length with coverage points towards a progressive delocalization of the donated electrons due to the increase in the mean band-bending value and the formation of a bidimensional electron gas inside the accumulation layer.[13]

In conclusion, we propose a method for evaluating the band-bending potential inhomogeneity from the substrate core-level lineshape, in the case of accumulation layer formation. This analysis provides the distribution of potential values at the interface, as well as the values of the significant parameters characterizing the local band-bending potential. As a case study we investigated the K deposition on the H:Si(111) surface, and treated the local band bending as a screened Coulomb potential originated from the partially ionized adatoms, randomly distributed on the surface. The spatial variation of band bending, due to the overlayer disuniformity, results to be quite relevant at this interface, with a mean value increasing with K coverage and an almost constant width of ~ 0.3 eV. The relevant parameters characterizing the local band-bending potential are the charge transfer and the electronic screening length. The latter plays a fundamental role in the determination of the potential inhomogeneity and it would be therefore extremely interesting to compare the effective value determined in this work with the results of a full quantum-mechanical calculation.

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