Final-State Effects in Photoemission from Metal-Semiconductor Interfaces

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In this Letter we stress the importance of final-state effects in photoelectron spectroscopy. In particular, we address the problem of Schottky-barrier formation, as studied via core-level shifts in photoemission. We have calculated the shift of the core-level distribution when a semiconductor surface is covered with a metal, using a wave-vector-dependent image-screening model. We conclude that final-state effects, which are generally neglected in this context, are in fact quite important. This conclusion is supported by experimental observations reported in the literature.

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After decades of intensive studies, the mechanism behind the Schottky-barrier phenomenon remains a subject of debate. On the experimental side, much of the recent information is derived from studies of core-level photoemission. At an early stage it was found that barrier heights deduced from core-level shifts are practically the same as those observed by electrical methods [1]. Consequently, photoemission has been accepted as a method for investigation of the microscopic details of Schottky-barrier formation. It is worthwhile to note, however, that this conclusion was based on results with submonolayer metal coverages, i.e., before it was realized that the final Fermi-level pinning is modified at the formation of a metallic overlayer [2–7]. As the great majority of studies so far have been made on nonideal interfaces, it is justified to question the experimental support for detailed equivalence between photoemission and electrical measurements. On the contrary, in the few cases when well-defined (i.e., atomically abrupt and crystallographically ordered) metal-semiconductor interfaces have been formed, significant differences were reported [8–10].

According to the textbook treatment of the rectifying metal-semiconductor junction [11], the barrier can be divided into two parts. One part is related to the interface Fermi-level pinning, and the other to the image potential. For n-type semiconductors the two contributions have opposite signs, so the effective barrier peaks typically 50 Å from the image plane (i.e., away from the metallic region). Further away from the interface the band bending dominates, but closer to the interface the image potential becomes important. Recalling that the photoemission method probes essentially the first 10 Å or so from the interface, it is crucial to examine the influence of the image potential on photoemission results—this effect is generally neglected when extracting the barrier height. In this Letter we discuss the effects of nonlocal metal-induced screening on a localized charge, such as the core hole in the final state of the photoemission process. It should be stressed that the point of our interest is equally relevant whether the actual interface states responsible for the Fermi-level pinning are defect states [1] or metal-induced gap (MIG) states [12].

We have modified our earlier calculations [13] to take into account the wave-vector dependence in the model dielectric function, for both the semiconductor and the metal. This implies that the image potential saturates at the interface. The model consists of two semi-infinite dielectric media, described by dielectric functions $\varepsilon_1(q)$ (semiconductor) and $\varepsilon_2(q)$ (metal or vacuum) [14]. The core hole is approximated with a static point charge Q situated at a distance z_0 inside the semiconductor. We calculate the induced (image) potential energy in the semiconductor, ϕ_1, for both the semiconductor/vacuum and the semiconductor/metal systems. Using space-translational invariance and time independence we solve

$$-\nabla^2\phi^D = 4\pi Q\delta(\mathbf{r}+z_0\hat{\mathbf{z}}), \tag{1}$$

$$\phi(q) = \phi^D(q)/\varepsilon(q), \tag{2}$$

subject to the boundary conditions

$$\phi_1(q,z=0) = \phi_2(q,z=0), \tag{3}$$

$$\left.\frac{\partial\phi_1^D(q,z)}{\partial z}\right|_{z=0} = \left.\frac{\partial\phi_2^D(q,z)}{\partial z}\right|_{z=0}. \tag{4}$$

The potentials ϕ^D and ϕ correspond to the **D** and **E** fields, respectively. For the semiconductor we use [15]

$$\varepsilon_1(q) = 1 + k_1^2/(c+q^2), \tag{5}$$

and for the metal

$$\varepsilon_2(q) = 1 + k_2^2/q^2, \tag{6}$$

where k_1^{-1} and k_2^{-2} are the Thomas-Fermi screening lengths in the semiconductor and the metal, respectively. All dielectric matrices used have in common that local-field effects are neglected. Inclusion of local fields would require the use of dielectric matrices of the form $\varepsilon(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}')$, where $\mathbf{G},\mathbf{G}'$ are reciprocal-lattice vectors. The effect of a nondiagonal dielectric matrix is to put the screening charge in the bond regions. Using a diagonal dielectric matrix implies spherical averaging of the

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screening charge in the bond regions. Using a diagonal dielectric matrix implies spherical averaging of the screening charge density. Local-field effects are known to be important [16]. However, in this case we consider quantities averaged over q and are thus less sensitive to details in the dielectric matrix. We then find the following for ϕ_1:

$$\phi_1^{M,V}(q,z)=B^{M,V}\left[\frac{e^{qz}}{\varepsilon_1}+\frac{k_1^2 e^{\kappa_1 z}}{2\kappa_1(\kappa_1-q)}\right]+\frac{2\pi Q}{q}\left[\frac{k_1^2 e^{\kappa_1 z-qz_0}}{2\kappa_1(\kappa_1+q)}+\frac{k_1^2 q e^{-\kappa_1|z+z_0|}}{\kappa_1(\kappa_1^2-q^2)}+\frac{e^{-q|z+z_0|}}{\varepsilon_1}\right], \tag{7}$$

where

$$\kappa_1=(c+k_1^2+q^2)^{1/2}, \tag{8}$$

$$\kappa_2=(k_2^2+q^2)^{1/2}, \tag{9}$$

and

$$\varepsilon_1=1+k_1^2/c \tag{10}$$

is the static dielectric constant.

The indices M and V refer to semiconductor-metal and semiconductor-vacuum systems, respectively. Using the boundary conditions [Eqs. (3) and (4)], the coefficients $B^{M,V}$ are

$$B^M=\frac{2\pi Q}{q}\frac{[q/\kappa_2-1/\varepsilon_1+(q/\kappa_1)(1-1/\varepsilon_1)]e^{-qz_0}-2(q/\kappa_1)(1-1/\varepsilon_1)e^{-\kappa_1 z_0}}{2+1/\varepsilon_1+(q/\kappa_1)(1-1/\varepsilon_1)+q/\kappa_2}, \tag{11}$$

$$B^V=\frac{2\pi Q}{q}\left(1-\frac{1}{\varepsilon_1}\right)\frac{(1+q/\kappa_1)e^{-qz_0}-2(q/\kappa_1)e^{-\kappa_1 z_0}}{3+1/\varepsilon_1+(q/\kappa_1)(1-1/\varepsilon_1)}. \tag{12}$$

The electrostatic image potential $\phi_{1,\mathrm{im}}^{M,V}$ in the semiconductor region is the part corresponding to $B^{M,V}$:

$$\phi_{1,\mathrm{im}}^{M,V}(\rho,z)=\int\frac{d^2q}{(2\pi)^2}B^{M,V}\left[\frac{e^{qz}}{\varepsilon_1}+\frac{1}{2}\left(1-\frac{1}{\varepsilon_1}\right)\left(1+\frac{q}{\kappa_1}\right)e^{\kappa_1 z}\right]e^{iq\cdot\rho}. \tag{13}$$

The electrostatic image energy at the core hole is obtained by building up the charge Q from infinitesimal charges dQ:

$$W_{M,V}(0,-z_0)=\int_0^e dQ\,\phi_{1,\mathrm{im}}^{M,V}(0,-z_0). \tag{14}$$

In order to compare with the experiment, we also calculate the photoelectron distribution intensity according to

$$I_{M,V}(E)\sim\sum_i e^{-z_i/l}\frac{\gamma/2\pi}{[E-E_c-W_{M,V}(0,-z_i)]^2+(\gamma/2)^2}, \tag{15}$$

where E_c is the binding energy of the core level, z_i are the positions of the emitting atoms, l is the mean free path, and γ is the total broadening of the core level.

As a numerical example, we apply Eq. (15) to Ga($3d$) emission from a metallized GaAs(100) surface [3], in which case we imagine as a model a Ga-terminated surface touching a sharp metal interface. The distance from the first Ga layer to the image plane in the present model is therefore taken as $z_1=1.4$ Å. The screening length k_1^{-1} is a measure of the characteristic distance beyond which the core hole is completely screened. We believe that reasonable screening lengths for ionic semiconductors are ~2–5 Å. The core shifts are not very sensitive to screening lengths in this range, but will of course decrease with decreasing screening length (in this range of k_1^{-1} we obtain core shifts between 0.10 and 0.15 eV).

For the following calculations we used the screening lengths $k_1^{-1}=3.3$ Å and $k_2^{-1}=0.5$ Å for the semiconductor and the metal, respectively, and a bulk dielectric constant $\varepsilon_1=12.34$. The result for the (induced) potential in the semiconductor region is shown in Fig. 1. For the photoelectron distribution intensity, the total broadening γ is taken to be 0.7 eV. We did not include the Ga($3d$) spin-orbit splitting, since we only want to examine the size of the shift due to final-state screening. Figure 2 shows the result for $l=8$ Å, which is a typical probing depth in UV photoelectron spectroscopy. With

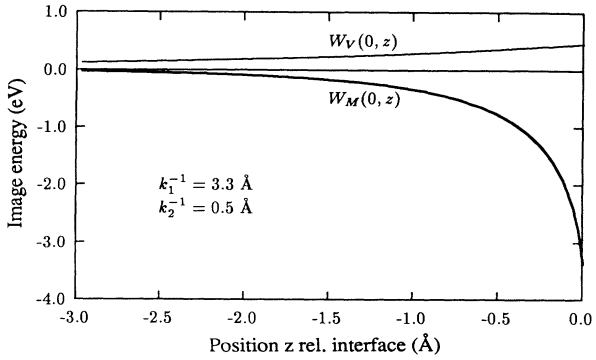

FIG. 1. The electrostatic image energy for semiconductor/vacuum (W_V) and semiconductor/metal (W_M) systems.

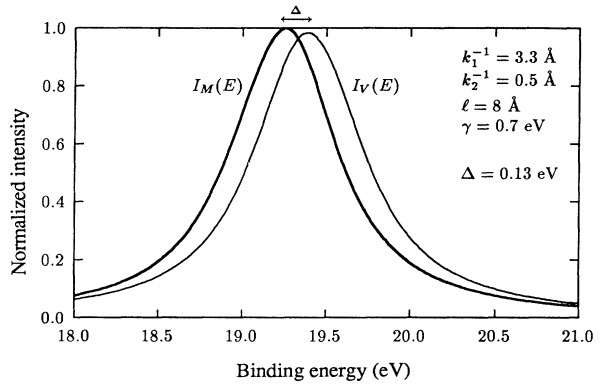

FIG. 2. The photoelectron energy distribution for the semiconductor/vacuum (I_V) and semiconductor/metal (I_M) systems.

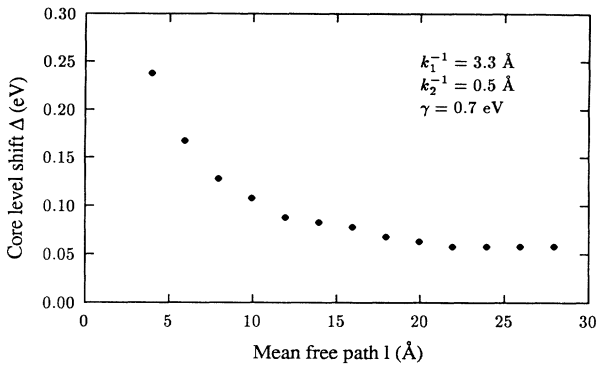

FIG. 3. The core-level shift Δ as a function of the mean free path l.

these parameters our calculation gives a shift (Δ) of 0.13 eV. To examine the effect of varying surface sensitivity we also calculate Δ as a function of l. The results are shown in Fig. 3. We notice that the shift increases with increasing surface sensitivity (small l). Clearly, the effect is by no means negligible for studies of the Schottky-barrier problem. As pointed out before, our model assumes that the local (on-site) screening is not perfect when the core hole is created. By "perfect" we mean that the screening charge (inside the atomic sphere) is less than one electron when the hole is created. The poor on-site screening of the core hole is due to lack of states for the screening charge. This effect has been seen in calculations on semiconducting CuO compounds [17] where the d band is nearly filled. When local empty states are available (e.g., in the case of Mn impurities) the core hole can actually be slightly overscreened [18]. The importance of on-site screening has also been investigated for adatoms on a metal (jellium) surface [19]. It was found that the screening is large only if the valence shell of the adatom can accommodate the extra charge supplied from the metal.

At this point we consider a couple of cases where we believe that the screening effects are actually observed. We have already mentioned the deviation between photoemission and electrical results on epitaxial Pb/Si(111) contacts. Leaving aside the problem of explaining the reported dependence of the Schottky-barrier height upon the interface geometry [8–10,20], we note that the barrier, as deduced from photoemission data, is larger than that obtained via I-V or C-V measurements. It has been suggested that this difference could be due to a structural modification at the interface when a thick metallic overlayer is formed [21]. However, there are indications that this is not the case [22]. An alternative explanation can be the above discussed metal-induced core-hole screening. The energy of the final state should be lowered by 0.1–0.2 eV. This would be observed via an increased kinetic energy of the photoelectron, implying a larger Schottky barrier.

One might suspect that details like the ones discussed here would only be distinguishable for ideal systems. However, in a series of studies of reacted rare-earth/GaAs(110) interfaces Prietsch *et al.* [4] could identify spectral features from the reacted overlayer as well as from the unreacted substrate. Following the development of the core-level binding energies with metal deposition, these authors observed distinct shifts accompanying the appearance of metallicity in the overlayer. It was found that all core-level energies were reduced in approximately the same manner, showing that the shifts are not of chemical nature. Two effects were considered which could explain the observed shifts, namely, final-state screening and MIG-state Fermi-level pinning. The screening mechanism was regarded as less likely, mainly because Schottky-barrier heights deduced from the photoemission data coincided with results from electrical measurements. In view of the above-mentioned discrepancies for more ideal interfaces, this criterion is rather dubious. On the contrary, assuming that the shifts are due to MIG states, we would expect a dipole associated with occupation of these states (noting that the rare-earth elements are strongly electropositive relative to Ga and As), and consequently, opposite core-level shifts in the substrate and in the overlayer.

Other types of experiments also indicate the importance of imperfect screening in ionic semiconductors. By combining photoemission and inverse photoemission it has been inferred [23] that the relatively poor screening in GaAs may increase the total energy (relative to a well screened system) by 0.4 eV.

The model calculation discussed above treats only one specific aspect of the photoemission process, namely, final-state screening of the core hole. A full description of the measured core-level shifts in principle has to be based on *ab initio* band-structure calculations. The initial state shifts can then be obtained from the difference between core-level eigenvalues for the semiconductor/

vacuum and semiconductor/metal systems. The effect of relaxation is given by total-energy calculations on systems with and without the core hole (ΔSCF). To our knowledge no such extensive calculations have been published so far.

We conclude that extreme care should be exercised when extracting information about Schottky barriers from core-level shifts in photoemission. Effects of final-state screening may be of the order of 0.1–0.2 eV according to the present model calculation.

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[14] More correctly, the real experimental situation should be modeled by two interfaces. However, as the fields decay very rapidly within the metal ($k_2^{-1} \sim 0.5$ Å), even a monatomic metallic overlayer is well represented by a semi-infinite system. The two-interface problem was treated in Ref. [13], where it was pointed out that the metal-layer thickness is irrelevant as long as the metal behaves as a perfect conductor.

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