PHYSICAL REVIEW B VOLUME 38, NUMBER 18 15 DECEMBER 1988-II

Interface dipoles, surface work functions, and Schottky-barrier formation at Au/ZnSe(100) interfaces

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(Received 25 April 1988)

Ultraviolet-photoemission studies for Au–*n*-type ZnSe(100) interfaces show parallel changes in substrate band bending and the surface work function as a function of Au coverage. For the Zn-rich reconstructed $c(2\times2)$ ZnSe(100) surface, the electron affinity is 0.55 eV less than that for the cleaved (110) surface, suggesting the existence of a positive surface dipole. This surface dipole is gradually reduced by 0.19 eV by the deposition of ~2 Å of Au. The deposition of Au results in exponential decay of the Zn 3*d* core-level emission, but no changes in line shape that would indicate chemical interaction. The final position of the Fermi level is 1.25 ± 0.10 eV above the valence-band maximum of ZnSe, but changes are very slow. There is a clear correlation of band bending with the surface work function as Au adatoms evolve from a dispersed state to a metallic film, indicating the validity of the original Schottky model for this system.

The physical mechanism behind the formation of a rectifying Schottky barrier has been a central issue of the studies of metal-semiconductor interfaces.[1] For some systems, it has been suggested that the heights of these barriers are essentially determined by the intrinsic properties of the substrate semiconductors, including surface states and defects. For others, the barrier formation depends on the properties of the overlayer materials, including work function and electronegativity. Many of the group III-V compound semiconductors and Si and Ge belong to the former category—the limiting case of the Bardeen model.[2] Many of the more ionic group II-VI compound semiconductors seem to be classified in the latter category—the limiting case of the Schottky model.[3]

A great many experimental results have been reported for metal-semiconductor contacts, especially for systems based on Si, Ge, GaAs, and InP.[1] Likewise, many theoretical models have been developed, including the unified defect model, the metal-induced gap states model, and the effective work-function model.[4–6] Less attention has been paid to metal contacts to group II-VI compound semiconductors.[7]

In this Brief Report we report a photoemission study of the room-temperature evolution of the Au/ZnSe(100) interface. The goal of this study was to correlate the interface dipole, the surface work function, and the formation of the Schottky barrier so as to test the original Schottky model for an ionic group II-VI semiconductor where chemical interactions could be minimized. Our interest was also stimulated by the growing number of applications of ZnSe in optoelectronic devices.

In this study, the Zn 3*d* core-emission line shape and the secondary electron onset were followed systematically as a function of Au coverage. Photoelectron spectra were recorded with a double-pass cylindrical-mirror analyzer (pass energy 10 eV, $h\nu=21.2$ eV). Data acquisition was facilitated with an on-line Tektronix computer, and analysis was performed with an IBM PC AT. The base pressure in the photoelectron spectrometer was 8×10^{-11} torr, and it rose to 1.5×10^{-9} torr during He lamp operation. Gold was evaporated from a resistively heated tungsten basket, and the amount of material deposited was monitored with an Inficon crystal oscillator. The evaporation rate was typically 0.2 Å/min. We use units of angstroms for the Au coverage where 1 Å Au would correspond to 0.94 monolayers of ZnSe(100) (surface atom density 6.27×10^{14} atoms/cm^2) or 0.48 monolayers of Au(100) (surface density 1.22×10^{15} atoms/cm^2).

Undoped *n*-type ZnSe(100) samples ~2 μm thick were grown on GaAs(100) substrates using molecular-beam epitaxy techniques.[8] Surfaces were prepared for study in the measurement chamber by Ar$^+$ sputtering at 600 V for 30 min, and their cleanliness was verified with Auger-electron spectroscopy. Annealing at 400 °C for 20 min produced a Zn-rich $c(2\times2)$ reconstruction, as determined with low-energy electron diffraction. Throughout the experiments, the possibility of charging and surface voltaic effects was checked by varying the photon flux and by darkening the chamber. No appreciable shifts of the photoemission features were observed (≤0.04 eV). We therefore regard subsequent spectral changes as induced entirely by the metal overlayer.

To measure the electron affinity χ and to follow changes in the surface work function during interface formation, we negatively biased our sample relative to the spectrometer and systematically measured the secondary-photoelectron onset energy E_{SO}. The electron affinity is given by

$$\chi=h\nu-(E_{\mathrm{VBM}}-E_{\mathrm{SO}})-E_g$$

and the work function ϕ by

$$\phi = h\nu - (E_F - E_{SO}) ,$$

where $h\nu$ is the photon energy (21.2 eV), $E_{\rm VBM}$ is the energy of the valence-band maximum, E_g is the band gap, and E_F is the Fermi energy. E_F was determined directly by measuring the high-energy cutoff after the deposition of a thick metal layer.

In Fig. 1 we show Zn 3*d* energy-distribution curves (EDC's) for representative Au depositions onto ZnSe(100). These EDC's have been background subtracted and normalized to a constant height to emphasize line-shape changes. The bottommost EDC is for the clean ZnSe(100) surface; the dominant feature reflects bulk contributions and the shoulder at 0.9 eV higher binding energy is due to the Zn atoms terminating the polar $c(2\times2)$ surface. This surface-shifted component is not observed for a cleaved nonpolar ZnSe(110) surface. To quantitatively assess changes in the Zn 3*d* line shape caused by Au deposition, we decomposed these EDC's using a standard computer fitting program.[9] Our results show no change in Zn 3*d* peak shape except for the shift of the binding-energy position due to band bending. The surface component decreases rapidly with Au deposition and is absent by ~2 Å. Further, the Zn 3*d* core-emission intensity decays nearly exponentially with deposition, indicative of layer-by-layer growth. Studies of the valence-band emission show that the shape of the Au 5*d* band changes gradually from one typical of dispersed Au to that of bulk Au. This evolution is typical for systems where there is no substrate disruption and there are no semiconductor atoms in the Au matrix. We conclude that Au grows nondisruptively on the surface. At the same time, low-energy electron diffraction (LEED) studies show that there is no long-range order at the surface.

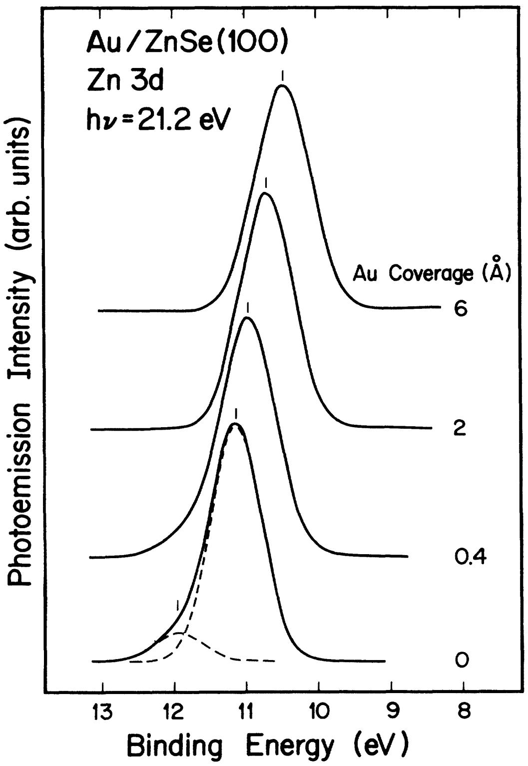

FIG. 1. Zn 3*d* energy-distribution curves for representative Au depositions onto $c(2\times2)$ ZnSe(100). The spectra are background subtracted and normalized to the same height. The binding energies are referenced to the known Fermi level of the spectrometer.

The changes in peak position in the Zn 3*d* core-level EDC's thus reflect substrate band bending caused by charge redistribution at the metal-semiconductor junction. In order to show these changes, we plot the Fermi-level pinning position versus Au coverage in Fig. 2. It is interesting to note that the Fermi-level position is not fully established until ~14 Å of Au have been deposited. At this point, E_F lies 1.25 ± 0.10 eV above the valence-band maximum of ZnSe. This slow band-bending evolution suggests that the Schottky-barrier height is not determined by interface states which should be established at low coverage. Instead, the physical mechanism should be sought from changes in the overlayer properties.

The changes in work function were measured as a function of metal coverage. These results are summarized through the triangles in Fig. 2, referenced to the scale at the right. After ~2 Å of Au deposition, the surface work-function changes are parallel to those observed for substrate band bending (circles, left axis). This observation strongly supports the original Schottky mechanism for the formation of a rectifying barrier. In that model, the barrier height was predicted to be the difference between the metal work function and the semiconductor electron affinity. However, at high metal coverage there exists a constant offset between the measured Schottky-barrier height $\phi_{\rm SB} = E_g - (E_F - E_{\rm VBM})$ and $\phi - \chi_0$, where E_g is the energy band gap of ZnSe (2.7 eV), $E_F - E_{\rm VBM}$ is the measured Fermi-level position relative to the valence-band maximum, ϕ is the surface work function, and χ_0 is the measured electron affinity for the polar ZnSe(100) surface. This difference may result from the formation of an interface dipole which systematically offsets the electron affinity of the semiconductor, as we will discuss.

The parallel changes of the surface work function and

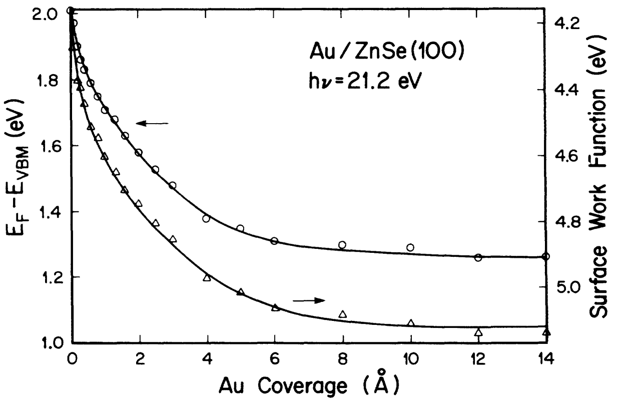

FIG. 2. Fermi-level pinning position relative to the valence-band maximum (left axis) and the surface work function (right axis) as a function of the Au coverage.

the substrate band bending for coverages ≥2 Å indicate that interface evolution can be characterized in two stages. For coverages below 2 Å, a thin dipole layer dominates but, thereafter, the developing overlayer surface work function dominates. As shown from the energy-level picture of Fig. 3, the interface dipole ρ can be calculated as $\rho = \chi + E_g - (E_F - E_{\mathrm{VBM}}) - \phi$, where χ is the electron affinity for the nonpolar (110) ZnSe surface. Such dipole variations, presented in Fig. 4, show that the increase in the work function $\Delta\phi$ is larger than the band bending during the early stages of interface formation. This suggests a gradual buildup of a negative interface dipole relative to the clean surface.

The electron affinity $\chi_0 = 3.51 \pm 0.10$ eV for our sputter-annealed (100)-$c(2\times2)$ surface was 0.55 eV less than the value measured for vacuum-cleaved ZnSe(110), namely $\chi = 4.06$ eV. It is known that the $c(2\times2)$ reconstructed surface is Zn rich,[8] and the reduction in the electron affinity unambiguously indicates the existence of a positive surface dipole ρ_0. Upon Au deposition, an interface dipole starts to form at low coverages due to charge transfer from highly electronegative Au atoms to the underlying Zn atoms. This charge transfer reduces the original Zn-Se surface dipole by forming a thin Au-Zn dipole layer with opposite sign. Since Au grows uniformly on the ZnSe(100) substrate, this thin interface dipole layer is completed at low coverages, as indicated by the results of Fig. 4. Second and third layers of Au adatoms are not in direct contact with the ZnSe substrate and, as they converge to a more bulklike film, their changes are of rapidly diminishing importance as far as the interface dipoles are concerned.

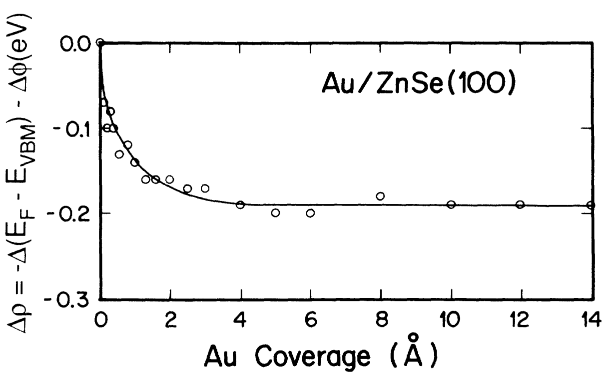

FIG. 4. The change in the interface dipole as measured from changes in the substrate band bending and changes in the surface work function during the evolution of the interface. Note that the original ZnSe(100) surface had a positive dipole of 0.55 eV and the deposition of Au reduced this dipole.

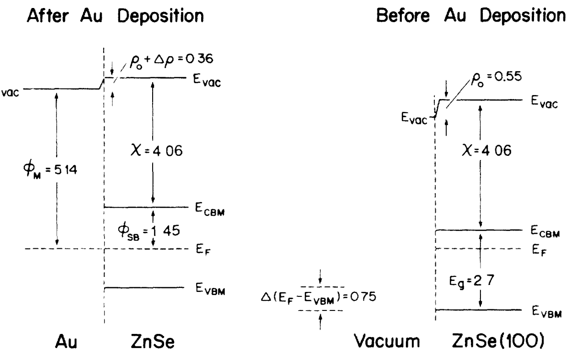

FIG. 3. Energy levels near the surface (a few atomic layers) of ZnSe before and after the deposition of Au. All energies are given in eV. Band bending (not shown in this figure) will change the energy levels over distances of the order 1000 Å.

The value of the Schottky-barrier height found by these measurements is

$$\phi_{\mathrm{SB}} = E_g - (E_F - E_{\mathrm{VBM}}) = 1.45 \text{ eV}$$

and is slightly larger than the experimental value of 1.36 eV obtained from electrical measurements.[10] The real problem is that this value is at odds with the value of $\phi_{\mathrm{SB}} = \phi - \chi_0 = 5.14 - 3.51 = 1.63$ eV, predicted by the Schottky model, and the measured values of work function and electron affinity of our sputter-annealed surface. The difference between the experimental result and the value obtained from the Schottky formula can be interpreted in terms of a change of the dipole layer on the polar (100) surface. The existence of a surface dipole on the (100) surface is consistent with the observed difference in electron affinities for the (110) and (100) surfaces of ZnSe. The magnitude of this dipole may be inferred from the difference in electron affinities of the (110) and (100) surfaces, namely

$$\rho = \chi - \chi_0 = 4.06 - 3.51 = 0.55 \text{ eV} .$$

However, this dipole is too large. The dipole must be reduced by 0.19 eV, but this is consistent with the large electronegativity of Au.

A different dipole-plus-work-function model was introduced by Brillson to explain their photovoltage measurements for reactive metal-semiconductor interfaces.[11,12] In their studies, they assumed that the surface dipole layer was formed at ~0.5 Å of metal coverage (usually Al) and that the dipole layer remained constant despite further metal disposition.[12] However, for most reactive systems the interface reaction continues well beyond ~0.5 Å deposition and interface reaction and segregation of semiconductor constituents to the surface can significantly alter both the existing interface dipole and the overlayer surface work function. Indeed, we found no apparent correlation between the surface work function and substrate band bending for the reactive Pd/ZnSe interface.[13] If this simple model is retained for that system, then it implies that changes in the interface dipole would extend for many monolayers.[12] We suggest that the general application of this simple model to the reactive systems should be viewed with caution.

In conclusion, we have demonstrated that the changes in band bending exceed the changes in work function for the first monolayer of Au deposited. This is attributed to changes in the surface dipole. Thereafter, work-function and band-bending changes are parallel for the abrupt Au/ZnSe(100) interface. Schottky-barrier formation can be successfully modeled by the original Schottky mechanism, provided that changes in electron affinity for the semiconductor due to dipole formation are appropriately taken into account.

We gratefully acknowledge stimulating discussions with S. G. Anderson and C. M. Aldao. The work at the University of Minnesota was supported by the National Science Foundation under DMR 86-10837. The work at 3M Company was supported in part by the Defense Advanced Research Projects Agency under Office of Naval Research Contract No. N00014-85-C-0052.

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