Deposition of Ag ions and neutral atoms on ZnSe(100): Influence of interface morphology on Schottky-barrier formation

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Ag overlayers were grown on ZnSe(100) by thermal evaporation and by a new approach using partially ionized beams. For the latter, $\sim 4\%$ of the atoms were ionized and accelerated to an energy of 300-400 eV, thus making it possible to vary the amount of surface disruption. Interface evolution was monitored with photoemission and low-energy electron diffraction. No disruption of the ZnSe surface was found for thermal evaporation, and three-dimensional growth was observed. For ion deposition, three-dimensional growth was again observed, but there was clear evidence of substrate disruption. Parallel measurements of band-bending changes show that the barrier height is the same to within 100 meV for neutral-atom and ion deposition, despite differences in interface morphology.

Despite major efforts to understand the alignment of the Fermi level at a metal-semiconductor interface, the physics of Schottky-barrier formation is still much in debate.¹ Many of the models that deal with this phenomena, such as the original Schottky model² and the metalinduced gap-state model,³ try to relate the barrier height with intrinsic properties of the metal and semiconductor. Others describe the Schottky-barrier formation in terms of specific properties of the interface, such as defects generated during metal deposition⁴ or the formation of a chemically reacted layer.⁵

A number of studies have recently sought to control the morphology of the interface and to clarify the driving forces for E_F alignment. Some have examined interfaces formed at low temperature.^{6,7} They have shown that Fermi-level movement is intriguingly different at low temperature and at room temperature, but the barrier height at thick metal coverage is usually not too different from that formed at room temperature. In a different approach, metal clusters have been grown on condensed Xe buffer layers, the Xe layers have been evaporated, and the effect of cluster deposition has been studied.⁸ This replaced interactions between atoms and the surface with interaction between metal clusters and the surface. Interestingly, band bending for interfaces formed in this way were very different from that observed for conventional atom deposition.

These low-temperature-deposition and the clusterdeposition experiments sought to minimize the disruptive interaction at the surface. In this paper, we describe a new approach to increase that interaction by deposition using low-energy ionized atom beams. The goal was to establish a relationship between Schottky-barrier height and interface morphology at the extremes of disruptive and nondisruptive interfaces.⁹ The ions were accelerated to 300-400 eV to overcome kinetic barriers that prevent reaction and defect formation [the energy required to form a Zn or Se vacancy is ~3 eV, and that for an antisite defect is ~8 eV (Ref. 10)]. These energies are small enough to ensure that the ions are confined to a region near the interface [~ 4 Å average range of 400-eV Ag ions in ZnSe (Ref. 11)]. Similar ion sources have been used to incorporate dopants during growth of Si (Ref. 12) and the deposition of oriented films.¹³

Undoped *n*-type ZnSe(100) samples were grown on GaAs(100) substrates using molecular beam epitaxy (MBE).¹⁴ Clean surfaces were prepared in the measurement chamber by Ar⁺ sputtering at 500 eV, followed by annealing at 400 °C for 20 min. The base pressure of the chamber was 8×10^{-11} Torr. The surface structure was determined with low-energy electron diffraction (LEED), and Auger-electron spectroscopy was used to confirm the cleanliness of the sample. The reconstructed $c(2 \times 2)$ structure found with LEED corresponds to a Znterminated surface.^{9,14} Ultraviolet photoemission spectra (hv=21.2 eV) were taken using a cylindrical mirror analyzer operated at a pass energy of 10 eV. The overall resolution was ~ 0.15 eV. For the conventional deposition experiments, Ag was evaporated from thoroughly degassed Ta boats. The amount of metal deposited was monitored with a crystal oscillator close to the sample. The evaporation rate was typically ~ 0.5 Å/min.

The partially ionized beam was created using the ion source shown schematically in Fig. 1. In this ion source, silver was heated in an alumina crucible, and a cylindrical stainless-steel anode was placed above the source. A W filament within the anode was biased $\sim 50 \text{ eV}$ relative to the anode. When the vapor pressure of the Ag atoms within the anode was high enough, a plasma was formed and the filament emission current increased from \sim 70 to 330 mA. The ion source floats at the acceleration voltage of 300-400 eV. The fraction of Ag atoms that was ionized was determined by comparing the amount of Ag deposited, as measured with a crystal thickness monitor, and the ion current, measured with a Faraday cup. The sample was placed 25 cm away from the ion source, and current densities of 100 nA/cm² were obtained. The crystal thickness monitor measured a growth rate of





FIG. 1. Schematic of the ion source. The Ag-bearing alumina crucible (1) is heated by a W coil, and evaporated atoms pass through the cylindrical anode (2). The biased W filament (3) provides electrons that establish a contained plasma, and the grid connected to ground (4) extracts the ions from the source. Approximately 4% of the flux reaching the sample is ionized.

1.5-2 Å/min for these ion source conditions, corresponding to ionization of $\sim 4\%$ of the Ag flux.

In Fig. 2 we show the Zn 3d core-level emission as a function of Ag deposition. All spectra were background subtracted and normalized to equal height. These corelevel spectra were analyzed using a nonlinear-leastsquares minimization routine, as described in detail elsewhere.¹⁵ Spectral features were fitted by simultaneously varying a cubic polynomial background function. The spin-orbit splitting was 0.36 eV, and broadening was represented by the convolution of a Gaussian and a Lorentzian (a Voigt function).^{9,15} During interface formation by Ag-atom deposition (right panel), the emission from the substrate shifts to lower binding energy and is attenuated slowly. The only change in line shape is the gradual disappearance of the surface-shifted component; no broadening of the spectra is observed. The spectra for deposition using a partially ionized beam are shown in the left panel. Inspection shows that the Zn 3d emission broadens asymmetrically to lower binding energy, and a clear shoulder is observed for the Ag coverages exceeding 16 A. These ion-deposition spectra can be fitted with a component that corresponds to the substrate and another that is shifted by 0.60 eV. From studies of numerous metal overlayers on ZnSe(100),⁹ the second component is clear indication of Zn dissolved in the metal overlayer. We conclude that the effect of the partially ionized Ag beam is to break ZnSe bonds in such a way that Zn atoms are released and dissolved in the Ag overlayer. As a consequence, the interface morphology is more complex for ion deposition than for thermal deposition. From the intensity ratio between the reacted and the bulk component, the amount of disruption can be estimated to be ~ 1 ML. Examination of the Ag 4d valence-band emission shows very similar evolution for ion and atom deposition, and we conclude that the shape of the Ag valence band is not very sensitive to the presence of small amounts of Zn in solution. Moreover, ion deposition does not yield different d-band character or evolution.

Quantitative assessment of the attenuation rate of substrate Zn 3d emission shows very similar behavior for ionized- and neutral-Ag deposition. Here, the kinetic energy of the Zn photoelectrons is ~10 eV relative to the Fermi level, and the photoelectron mean free path is ~16 Å. ¹⁶ For both forms of deposition, the substrate attenuation is slower than this value (16% of the original intensity persists at 32 Å compared to 9% expected for layer-



FIG. 2. Photoemission spectra showing the Zn 3d evolution as a function of Ag-atom deposition (right) and Ag-ion deposition (left). A surface-shifted component appears on the highbinding-energy side of the clean-surface substrate peak. For neutral-Ag deposition, the surface component is reduced, but there is no indication of Ag-induced disruption. The energy shift corresponds to band bending. For ion deposition, the development of the shoulder at lower binding energy indicates disruption.

by-layer growth in our geometry at an angle of 30° between detector and surface normal), and the substrate emission decay rate is even slower at higher coverage. For a nonreacted, nondisrupted interface, this indicates that three-dimensional island growth is occurring. This is not surprising for Ag since spontaneous clustering is generally observed on semiconductor surfaces. However, the fact that the attenuation is the same for ion deposition is surprising. In particular, Ag ions create defects at the ZnSe surface. This increases the density of Ag nucleation sites, and a more uniform coverage would be expected. The fact that this is not observed indicates that the Ag nucleation density is not very dependent on the perfection of the ZnSe(100) surface.

For Ag-atom deposition, the quality of the LEED pattern deteriorated gradually, and the reconstructed spots were too weak to be detected by 2 Å. Although spots of primary lattice were visible to ~ 16 Å, they were weak and broadened. This is consistent with Ag-cluster formation and the continued exposure of the clean surface to the electron beam. For ion deposition, the reconstructed spots were not visible after 1 Å, and no LEED spots could be observed above 8 Å. Hence, LEED indicates island formation for both forms of deposition, but the long-range order of the ZnSe surface degraded faster when part of the Ag beam was ionized.

To correlate these surface structural changes with band bending, we measured the changes in Zn 3d core-level energies as a function of Ag deposition, as summarized in Fig. 3. The accuracy in measuring the changes is ± 30 meV and the run-to-run reproducibility is 0.1 eV. As a measure of this reproducibility for ZnSe(100) wafers, we note that the high-coverage band bending observed here is 80 meV smaller than we reported previously.⁹ In part, this reflects variations in the quality of sputter-annealed surfaces. For Ag-ion deposition, we now see that band bending is 60-100 meV larger at any given coverage than for neutral-Ag deposition. The final position of E_F [1.65] eV above the valence-band maximum (VBM), as noted at the right of Fig. 3] is effectively identical to the value for evaporated Ag reported in Ref. 9, namely 1.64 eV. We conclude that the effect of the disruption induced by ion deposition is not more than 100 meV. This is a conservative upper bound since an even smaller magnitude would have been deduced from the runs of Ref. 9.

A recent systematic investigation of metals on ZnSe(100) showed a wide range of Fermi-level pinning positions, as summarized on the right axis of Fig. 3 for Ce, Al, Ti, Co, Ag, Cu, Au, and Pd.⁹ As can be seen, the metal-to-metal spread is larger than 1 eV. A clear correlation was found between metal work function and the observed barrier height, in a way similar to the Schottky model.² At the same time, there was also a correlation between barrier height and reactivity of the metal overlayer⁵ because metals with low work functions are usually more reactive. Hence, there was concern that the observed relationship between Schottky-barrier height and metal work function might have been accidental, and the true driving force might involve the chemistry at the interface. In that context, the results presented here are particularly important because the surface chemistry



FIG. 3. Band bending induced by deposition of neutral- and ionized-Ag atoms on ZnSe(100). The \leq 100-meV difference in band bending between ion and atom deposition is comparable to the reproducibility of the experiment. Comparison to the final Fermi-level positions for a variety of metals (right axis, from Ref. 9) shows much greater sensitivity of barrier height to choice of metal than surface character.

could be modified with energetic ion deposition. Significantly, the Schottky barrier varied less than 100 meV, a value which is much less than the variation among different metals. We conclude that the properties of the metal overlayer, rather than details of the interface morphology, determine the Schottky-barrier height for ZnSe(100).

Comparison of the present results with the predictions of the defect model,^{4,9} where there would be similar pinning position for all metals, shows that the model does not provide an accurate description of Schottky-barrier formation for ZnSe. One might argue that the formation of defects by metal deposition is suppressed for ZnSe compared to GaAs because the cohesive energy of ZnSe is much larger [-163 versus -71.1 kJ/mole (Ref. 17)] and simple condensation cannot create defects. However, the present results show that ions deposited with 300-400 eV are able to create defects at and near the surface. Even for partially ionized beams, the number of defects should be more than sufficient to pin E_F . The absence of significant differences in Schottky-barrier height between atom and ion deposition argues that defects do not play an important role in pinning for ZnSe.

The ability to directly compare the effects of neutralatom and ionized-atom deposition on clean semiconductor surfaces makes it possible to determine changes in band bending while altering the chemistry and morphology of the surface. For Ag/ZnSe(100), we have shown that band bending is remarkably insensitive to the structural properties. If this is the case for other systems, then a very important generalization can be established. Systematic studies are currently underway.

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