Semiconductor-to-Metal Transition in an Ultrathin Interface: Cs/GaAs(110)

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Electronic excitation spectra ($0 \le \hbar\omega < 4$ eV) of an ultrathin Cs/GaAs(110) interface have been measured at various stages of development with electron-energy-loss spectroscopy. Spectral features which appear as a function of Cs coverage clearly identify the semiconductor-to-metal transition. The semiconducting interface observed up to one Cs layer is characterized as a highly correlated electronic system—a two-dimensional Mott insulator. Interfacial metallization upon Cs multilayer growth is identified by a metallic-excitation continuum and a collective excitation related to the Cs surface plasmon.

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Metal-semiconductor interfaces have been the subject of intense investigation.[1] Metal-induced electronic states in the band gap,[2] the relation of local electronic and geometric structure,[3] and Fermi-level movement as a function of metal coverage[4,5] are key issues for understanding Schottky-barrier formation. Previous electron-energy-loss-spectroscopy (EELS) measurements of metal-semiconductor interfaces have focused on broadening of the quasielastic peak at the onset of metallization,[6,7] and a theoretical formalism has been developed to relate the quasielastic peak width to conductivity.[8] However, few high-resolution measurements of the electronic excitation spectra—the dielectric response—of metal-semiconductor interfaces through the band-gap region have been reported.[9] Metallization is distinguished from semiconducting behavior by the appearance of a metallic-excitation continuum. EELS exhibits high surface sensitivity and can easily measure the interfacial dielectric response in the infrared and visible spectral regions.

In this Letter, we report EELS measurements of the dielectric response of the Cs/GaAs(110) interface passing through the semiconductor-to-metal transition. The semiconducting Cs/GaAs(110) interface behaves as a novel two-dimensional, highly correlated electronic system; i.e., a single-particle picture is inappropriate to describe the excitation spectra. For multilayer Cs growth, the appearance of both a metallic-loss continuum and a loss related to the Cs surface plasmon signifies interfacial metallization.

Cs/GaAs(110) has been chosen as a model metal-semiconductor system since Cs atoms do not intermix with or diffuse into the substrate.[10] For Cs coverages, Θ, below ~0.5 ML at $T \approx 300$ K,[11] Cs rows with a *local Cs density of 0.5 ML* have been observed by scanning tunneling microscopy (STM).[12] A *compressional phase* begins to develop above ~0.5 ML. Saturation coverage at $T \approx 300$ K is 0.9 Cs atom per GaAs unit cell,[13] which corresponds to a close-packed two-dimensional Cs layer with a surface density approximately equal to that of Cs(110). We note that the density of bulk metallic Cs is near the Mott limit.[14] Under low-temperature growth conditions, Cs multilayers form. In the development of the second Cs layer, electronic states are observed at the Fermi level (E_F) by photoemission spectroscopy[10] (PES) signifying interfacial metallization.

The EELS measurements were performed with a Leybold-Heraeus ELS-22 spectrometer operated at ~30-meV resolution. The azimuthal orientation of the sample was set with components of both principal axes in the scattering plane. The work-function change ($\Delta\phi$) was determined by the retarding-field method using the LEED gun. For EELS measurements, the sample bias was adjusted to compensate $\Delta\phi$. The surface of the n-type GaAs(110) wafer (Si doped, $n_{Si} \approx 10^{18}$ cm^{-3}) was prepared by cycles of neon-ion bombardment at 1 keV for ~30 min and annealing at $T \approx 520\,°C$ for ~10 min. This procedure resulted in excellent (1×1) LEED patterns and EELS spectra consistent with previous work.[15] Cs depositions were made with a SAES Getters alkali source. Cs coverages were determined from a previous calibration of $\Delta\phi$ vs Θ.[13,16]

EELS spectra for sequential Cs exposures at $T \approx 300$ K using a specular scattering geometry are presented in Fig. 1. The elastic peak intensities are normalized. The clean surface exhibits the expected band-gap onset at ~1.40 eV.[15] For $\Theta < 0.5$ ML, the interfacial band gap narrows somewhat and the intensity of transitions above the gap is increased with respect to the clean surface. Above 0.5 ML, two losses appear at 0.42 and 1.04 eV (FWHM ≈ 0.27 eV). These losses do not shift in energy up to saturation coverage. The correlated increase of the intensities of these losses suggests a common origin. This observation coupled with thermal desorption measurements[16] suggests that the compressional phase is a mixed phase until saturation coverage is reached. Off-

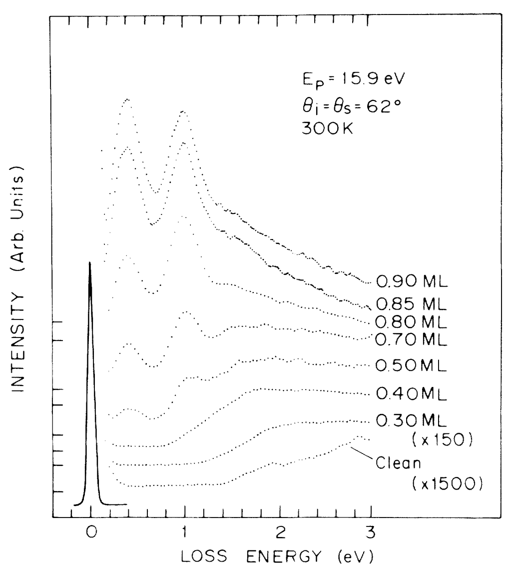

FIG. 1. This series of EELS spectra shows the coverage dependence of electronic losses for sequential room-temperature exposures of Cs on GaAs(110) up to saturation coverage (0.9 ML).

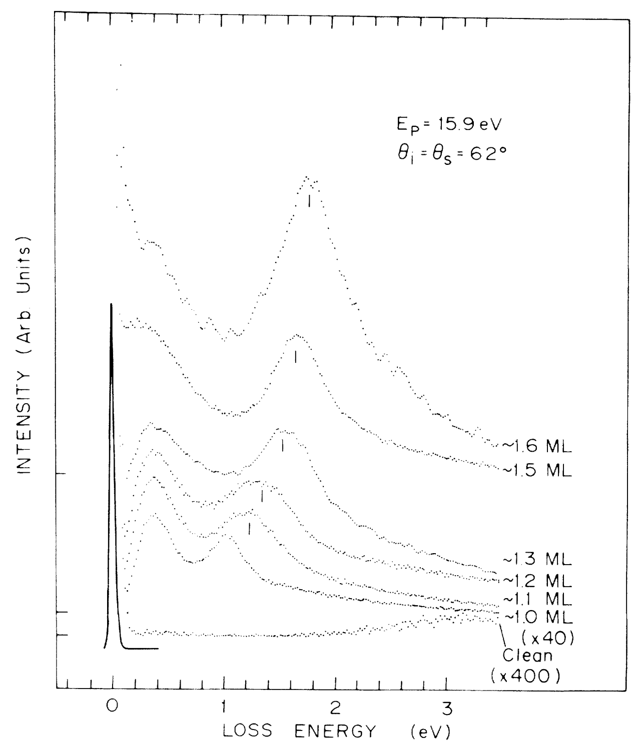

FIG. 2. This series of EELS spectra shows the coverage dependence of the electronic losses for exposures of Cs at a temperature of ~150 K atop a saturated Cs layer formed at room temperature.

specular scattering indicates a dipole excitation mechanism and shows no measurable momentum dispersion, suggesting that the excitations are localized. We dismiss isolated defects as the origin of these features since we assume that defect-related electronic states would form in the initial stages of adsorption and not abruptly at finite coverage. *The EELS spectra identify the interface as semiconducting up to saturation coverage at room temperature.*

The semiconductor-to-metal transition is observed in the series of EELS spectra in Fig. 2. For this series, the surface was first saturated with a Cs layer at room temperature and then additional Cs exposures were made at $T \approx 150$ K to form subsequent layer(s). As the Cs coverage increases above 1 ML, a new loss at 1.14 eV appears distinct from the 1.04-eV feature (see 1.1 ML), and an excitation continuum begins to fill in the band gap (see, e.g., 1.5 ML). The loss shifts upwards in energy with increasing coverage (tick marks) approaching ~1.95 eV, the energy of the surface plasmon for bulk Cs. The 1.04-eV loss of the first Cs layer attenuates upon growth of a multilayer, while the 0.42-eV loss is more persistent, eventually becoming buried in the metallic tail. *Upon growth of a second Cs layer, the EELS spectra show that the interface becomes metallic.*

These experiments clearly demonstrate the high sensitivity of EELS to the evolution of the interfacial dielectric response through the semiconductor-to-metal transition. Three coverage regimes are distinguished—(I) $\Theta < 0.5$ ML, with a featureless energy gap; (II) 0.5 ML $< \Theta < 0.9$ ML, exhibiting sub-band-gap excitations; and (III) multilayer regime, with a metallic-loss continuum. *The submonolayer interface (regimes I and II) has a particular physical significance. We propose that this semiconducting interface represents a highly correlated two-dimensional electronic system, i.e., a Mott insulator.*[17] Regimes I and II represent *two* such insulating systems with different areal densities.

We first consider Cs structures and their respective unit cells for (I) $\Theta \leq 0.5$ (local density of 0.5 Cs atom per unit cell) and (II) the compressed phase (local density ~0.9 Cs atom per unit cell) mixed with the half-monolayer structure as shown in Fig. 3. Only structures for $\Theta < 0.3$ ML have been experimentally determined.[12] Adsorption and desorption kinetics suggest that the 0.5-ML structure, representing coalesced doubly periodic Cs rows along $[1\bar{1}0]$, is the most stable configuration.[16] The compressional phase is less stable. The Cs structures shown contain an unpaired electron per surface unit cell which would create a metallic interface *in a single-particle picture.* At first glance, the EELS spectra *for* $\Theta > 0.5$ *ML* indeed suggest the presence of electronic state(s) in the band gap. In a local bonding picture, we consider a Cs-Ga complex formed by admixture of the Cs(6*s*) orbital and the unoccupied Ga orbital. Molecular-orbital diagrams for two such complexes are sketched in Fig. 3. The singly occupied state defines E_F, and the unoccupied state is presumably a resonance state near to or overlapping the conduction band (CB). A singly occupied state ~0.4 eV above the valence-band

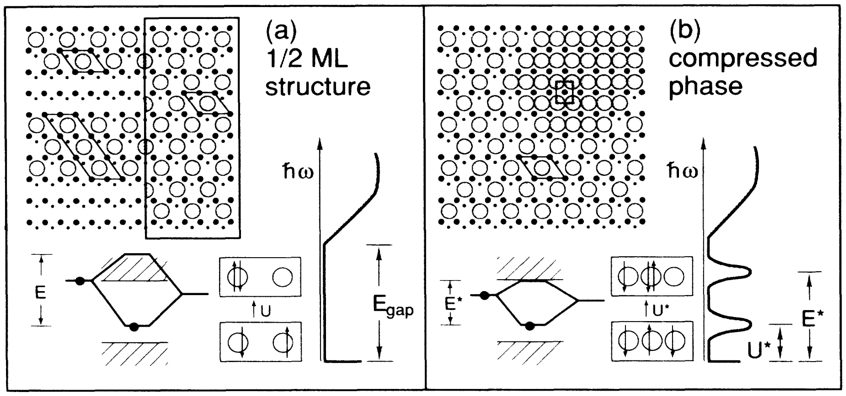

FIG. 3. (a) Overlayer structures [two row and three row (Ref. 12); 0.5 ML] and unit cells for regime I—local coverage of 0.5 ML with schematic molecular-orbital scheme, CT excitation scheme, and excitation spectrum. E is the single-particle excitation energy, and U is the Coulomb repulsion energy. (b) Same as (a) for regime II (here, the compressed phase mixed with 0.5-ML phase) with $U \rightarrow U^*$ and $E \rightarrow E^*$.

maximum[16] (VBM) could produce excitation onsets at ~ 0.4 and ~ 1.0 eV. *However, all other spectroscopic observations contradict this single-particle picture.* In particular, (1) no state at E_F is observed with PES [10] or inverse photoemission spectroscopy[18] (IPS) for submonolayer coverages; (2) for $\Theta < 0.5$ ML, the single-particle picture predicts sub-band-gap excitations which are not observed by EELS; and (3) a metallic excitation continuum is not observed in EELS up to saturation coverage at room temperature. Regarding point (1), it has been suggested that photoemission lacks the sensitivity to observe alkali electron emission at E_F due to the low photon excitation cross section of s electronic states. However, the photoexcitation cross section for Cs multilayers has been carefully extrapolated to the submonolayer regime,[10] and the detection of alkali states in the gap is well within experimental sensitivity.

In order to explain our experimental results, *we go beyond the single-particle description and introduce a many-electron model invoking electron correlation effects in the interface. This discussion depends upon electron counting and does not depend on a quantitative structural analysis.* Electron localization and correlation effects have previously been considered theoretically for metal-semiconductor systems[19] and have been invoked in the STM analysis of localized electronic states of the Au/GaAs(110) system.[3] Local Cs coverages of 0.5 ML form structures with one electron per Cs site [Fig. 3(a)] and a Cs-Cs nearest-neighbor distance of 6.9 Å. *We propose that the singlet ground state of this system represents a Mott insulator.* Although the singly occupied state sits at E_F, a charge-transfer (CT) excitation between adjacent Cs atoms, localizing *two* electrons at one site, costs a Coulomb repulsion energy U of order 1.4 eV.[19] Furthermore, the single-particle transition between the two levels of the Cs-Ga complex are separated by $E > 1.4$ eV. *For such assumed values of U and E, the excitation spectrum of Fig. 3(a) exhibits a generally featureless band gap.* Possible single-particle transitions between the E_F state and CB states may account for the observed energy-gap narrowing. The increased spectral intensity beyond the band gap, then, results from these excitations which are likely broadened due to reduced lifetimes.

For $\Theta > 0.5$ ML, patches of Cs in the higher density compressional phase coexist with the 0.5-ML structure until saturation. We propose that the Coulomb repulsion is reduced to $U^* \approx 0.4$ eV; i.e., the interface is still a Mott insulator with reduced electron localization as depicted in Fig. 3(b). In addition, since the compressed phase is less stable than the $\Theta = 0.5$ ML phase, the separation between the levels of the Cs-Ga complex is reduced to $E^* < E$. The excitation spectrum for this case is sketched in Fig. 3(b), where the CT excitation is ~ 0.4 eV and the electronic transition of the complex corresponds to $E^* \approx 1.0$ eV. *This scheme produces a spectrum with the experimentally observed sub-band-gap excitations.* Other excitations between the state at E_F and the substrate valence band (VB) and CB may comprise the observed underlying background.

The absence of states at E_F observed by PES and IPS is also explained by this picture. In PES, a lack of screening of a *localized* ion final state shifts emission from the level at E_F into the VB. With E_F at ~ 0.4 eV above the VBM,[16] a shift of ≥ 0.4 eV to higher binding energy, analogous to a core-level shakeup[20] is reasonable. In IPS, Cs-induced peaks at $\sim(E_F + 1.2$ eV) and at $\sim(E_F + 0.7$ eV) have been observed[18] for exposures which we relate to regimes I and II, respectively. These peaks can be assigned to negative-ion final states of the respective regimes.

Since questions regarding the structure of the interface remain, consideration of the observed excitations in a single-particle picture should be raised. Buckling or dimerization in the Cs overlayer could result in a semiconducting surface, or reaction-induced bond breaking could generate electronic states in the band gap. The intensity of luminescence features at 0.2 and 0.8 eV for metal/GaAs systems, assigned to reaction-induced acceptor levels in the gap[21,22] correlates with the density of active sites from steps or defects. Since Cs reacts weakly with GaAs(110), this defect-related mechanism is probably not applicable to the present study. It should be emphasized that the problem correlating photoemission and EELS in a single-particle picture still exists.

The appearance of a metallic continuum in the excitation spectrum for low-temperature Cs growth clearly signifies interfacial metallization in regime III. The 0.42-eV peak attenuates slowly, initially merging with the continuum tail, while the 1.04-eV peak attenuates more rapidly. Although these features grow in a coupled fashion, they decay differently during multilayer Cs growth. Based upon the correspondence of a multilayer Cs film with the surface plasmon energy of Cs metal, we assign this loss as a collective excitation of the developing metallic interface, an *interface plasmon.* It is difficult to identify the mechanisms for the attenuation of the features of the first Cs layer or for the upward energy shift of the plasmon since the morphology of the second Cs layer is not yet known. The detailed structural aspects of the Cs/GaAs(110) interface in the entire range of coverages are among the important remaining questions yet to be resolved.

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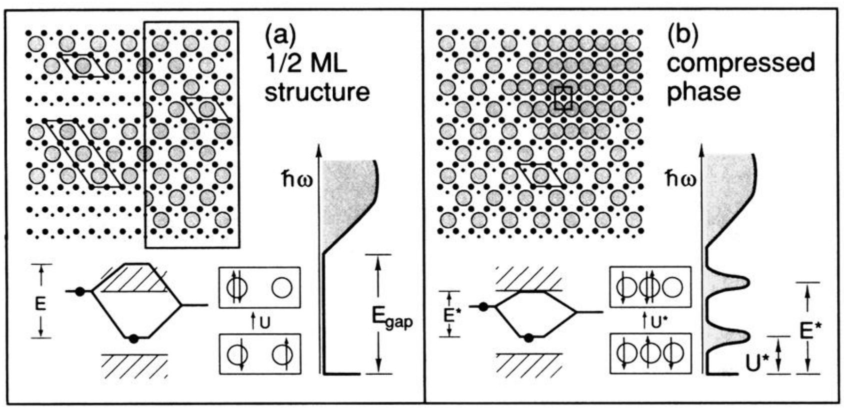

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