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Reversible temperature-dependent Fermi-level movement for metal-GaAs(110) interfaces

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This paper describes how temperature regulates the movement of the surface Fermi level for lightly doped GaAs(110) onto which submonolayer amounts of Ti and Ag have been deposited. Synchrotron radiation photoemission spectra show that E_F can be moved from near the band edges to $\sim$600 meV into the gap for p- and n-type GaAs by changing temperature from 20 to 300 K. Band bending changes are shown to be reversible when there are no morphology changes (Ti), but are not completely reversible when clustering occurs during the thermal cycle (Ag). These results demonstrate that the existence of gap states is not sufficient in itself to induce full band bending because charge exchange with those states is needed. They are discussed in the context of our dynamic-coupling model which shows how surface-bulk coupling is controlled by the bulk dopant concentration and temperature.

Recent studies of surface Fermi level (E_F) movement in the band gap of GaAs(110) have shown strong dependences on the bulk dopant concentration and temperature in the low coverage regime, but much less sensitivity to the details of the adatom-induced states or the formation of disrupted surface regions.[1,2] At higher coverage, they have shown E_F movement into the gap when adatom-adatom interactions (metallization) facilitate delocalization of the adatom wave functions.[1-4] These same studies[1,2] showed remarkable symmetry in E_F movement for n- and p-type GaAs substrates having equal dopant concentrations, and the symmetry was particularly apparent for lightly doped samples. The inset of Fig. 1 shows this characteristic behavior for Ti/GaAs(110) interfaces formed at 60 K for samples doped at 1×10^{17} cm^{-3} (from Ref. 1).

This paper focuses on the temperature-dependent movement of E_F for n- and p-type GaAs(110) onto which submonolayer amounts of (reactive) Ti and (nonreactive) Ag atoms have been deposited. For Ti, E_F moves from near the band edges at 20 K to near midgap at 300 K for n- and p-type GaAs with the same bulk dopant concentration 1×10^{17} cm^{-3} but completely recovers upon cooling to 20 K. For Ag, warming from 20 to 300 K is accompanied by spontaneous Ag clustering, and this morphology change leads to less than completely reversible E_F movement. These temperature-related effects cannot be explained by the presence of static activated levels in the gap unless dynamic charge exchange is considered. They rule out the importance of any defect levels in the gap created by warming to 300 K.

The measurements used synchrotron radiation photoelectron spectroscopy to examine the chemical interaction, the associated formation of states in the gap, and the dynamic exchange of charge between the bulk and the surface as a function of temperature. Photoelectrons were collected with a double-pass cylindrical mirror analyzer. Core-level line shapes were analyzed with a least-squares minimization routine that made it possible to determine band bending changes with an accuracy better than 30 meV.[5] Samples were cleaved at 300 K at $\sim5\times10^{-11}$ Torr. The cleaved samples, and the Cu holders to which they were attached, were inserted into a specially designed Cu tank mounted on a closed-cycle He refrigerator. Intimate thermal contact between sample holder and tank was provided by *in situ* soldering with Ga; this soldering technique allowed rapid sample interchange without compromise of base temperature. A W filament heater

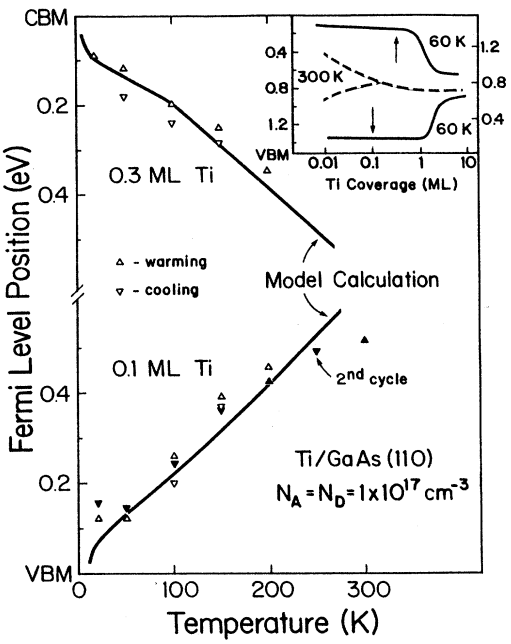

FIG. 1. Surface Fermi-level movement upon warming and cooling for Ti/n-type GaAs and Ti/p-type GaAs after submonolayer deposition at 20 K. E_F movement follows the prediction of the dynamic charge-exchange model (solid line). For p-type GaAs above 200 K, E_F saturates at a level determined by the adatom-induced states because coupling is not a limiting factor. The inset shows E_F movement as a function of coverage for Ti/GaAs(110) for 60 (Ref. 1) and 300 K (Ref. 15). Arrows indicate coverages used in the present study.

attached to the tank countered the cooling of the refrigerator so that stable temperatures of $20 \leq T \leq 350$ K could be maintained with the pressure $\leq 1\times10^{-10}$ Torr. Temperature was measured with a Au-Fe/Chromel thermocouple attached to the tank. Calibration measurements indicated no detectable temperature difference between sample and tank. To characterize the cleave quality, clean surface spectra were acquired at 300 K. Only cleaves with mirrorlike surfaces having E_F within 60 meV of the conduction-band minimum (CBM) or valence-band maximum (VBM) were retained. The n-type (p-type) samples were Si doped (Zn doped) at 1×10^{17} cm^{-3}. For a good cleave, temperature reduction to 20 K moved E_F by only 50–60 meV due to the temperature dependence of E_F relative to the band extrema in the bulk and the changing band gap. Greater movement indicated that E_F was partially pinned. For flat band cleaves, the difference in energy positions for the Ga or As core levels for n- and p-type GaAs was 1.42 ± 0.03 eV at 20 K compared to the band gap of 1.52 eV.

Adatoms were deposited from hot sources ~45 cm from the surface at pressures below 2×10^{-10} Torr. Surfaces were exposed to the metal vapor flux after stable evaporation rates of ~0.5 Å/min were established, as monitored by a quartz oscillator. There were no measurable changes in sample temperature during evaporation. While the precise amount of deposited metal was not crucial in these studies, coverages were selected to be substantially less than the coverage at which E_F moves toward midgap at low temperature [typically ~1–2 ML (monolayers), see Fig. 1 inset].[1–5] Metal coverages are expressed in monolayers referenced to the GaAs(110) surface density of 8.86×10^{14} atoms/cm^2. A complete set of core-level and valence-band spectra was taken at each temperature.

Figure 1 summarizes E_F variations with temperature for Ti adatoms on n- and p-type GaAs(110). The arrows in the inset denote the coverages for which the present measurements were undertaken. While the selection of lightly doped substrates and low metal coverages was made to emphasize temperature effects on band bending, the conclusions are quite general. As will be discussed, the solid lines of Fig. 1 are based on our model calculations.

The experiments involved the deposition of Ti at 20 K followed by warming and then recooling to 20 K (upward- and downward-pointing open triangles, respectively). A second cycle produced the solid triangles. Equivalent results would be obtained by depositing and starting the cycle at 300 K. As shown, the effects of temperature are completely reversible. In the 20–200 K range, band bending varies almost linearly with temperature. For p-type GaAs, however, the E_F position gradually saturates near 0.5 eV above the VBM at 300 K. This indicates convergence to an energy determined by the adatom-induced levels at this metal coverage, without constraint from temperature-controlled charge exchange. Throughout the cycling, there were no changes in the substrate core-level emission except for (reversible) phonon broadening, and we conclude that the surface morphology did not change. This is consistent with the fact that Ti is very reactive, that chemical changes occur upon deposition at any temperature, and that the adatoms are immobilized by reaction.[6] Equivalent disruption has been seen for n- and p-type GaAs. The reversibility in E_F demonstrates that warming does not create defects of the sort proposed to account for E_F pinning (Ref. 7); such defects could hardly be expected to disappear upon recooling.

Analogous experiments were undertaken for Ag/n-type GaAs(110) to investigate a system where morphology changes were expected. Ag atoms cluster spontaneously when deposited at 300 K, but the surface is more uniformly covered when adatoms are deposited at low temperature.[3,5] The results in the inset of Fig. 2 show that band bending increases until ~100 K, but that the rate of movement is accelerated at higher temperature. (The dashed line is a guide to the eye while the solid line is the predicted band bending.) At 300 K, E_F was 720 meV from the CBM, in excellent agreement with the 300-K results for this interface.[3,5] Cooling reduced the amount of band bending, but there was an offset in the warming and cooling results that amounted to ~140 meV at 20 K.

To correlate these changes in E_F movement with the distribution of Ag atoms on the surface, we examined the

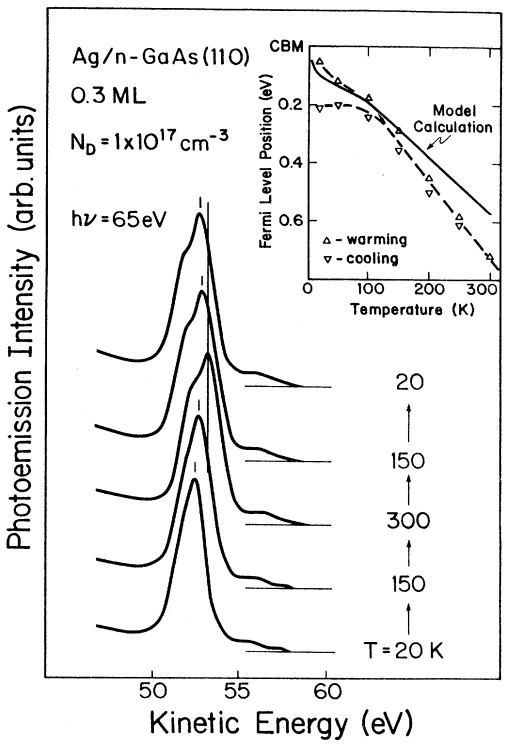

FIG. 2. Valence-band spectra for 0.3 ML Ag/n-type GaAs(110) as a function of temperature showing broadening and shifting toward higher kinetic energies of the Ag 4d feature. These changes correlate with partial clustering and metallization of the overlayer. Recooling to 20 K produces no change in the morphology but incomplete recovery in band bending. The inset summarizes E_F position vs temperature, as measured from the substrate core-level shifts. The solid line represents predictions of the dynamic-coupling model.

valence bands as a function of temperature. The results shown in Fig. 2 indicate Ag d-band broadening and a shift toward higher kinetic energy (lower binding energy) with increasing temperature from 20 to 300 K. The direction and magnitude of this shift followed the band bending (inset) and is related to cluster formation and surface electrostatics. This indicates that adatom-related states in the low coverage regime are referenced to intrinsic semiconductor energy levels rather than E_F.[8] Recooling to 20 K did not change the d-band broadening, and the Ag $4d$ features failed to return to their initial energy position. We believe that this reflects the formation of metallic states at the surface due to changes in overlayer morphology.[9,10] However, the morphology of interfaces formed at 20 K and annealed at 300 K was not identical to those formed by deposition at 300 K because of detailed differences in the adatom clustering process. This last observation is based on detailed core-level line-shape analysis and will be discussed elsewhere.

The reversible changes in E_F position can be understood in terms of a dynamic-coupling model (DCM)[1,2,8] developed to explain temperature- and dopant-concentration-dependent barrier formation for metal atoms deposited onto clean semiconductor surfaces. The existence of adatom-induced states in the gap is well known, and these states act as donors or acceptors on the surface to pin E_F. The occupation of these states by electrons (or holes) from the substrate produces a depletion region and band bending near the surface. This transfer of charge is required to achieve E_F continuity at the interface.

The temperature cycling results clearly indicate that the amount of charge residing on these levels is not fixed by the number of available adatom-induced states, since their number does not change. It is then the *partial occupancy* of these states which must change to yield the observed changes in the relative E_F position at the interface. A critical point of the DCM is that the variable band bending is a manifestation of the self-regulated coupling between surface and bulk states. The dynamic charge transfer across the depletion region is facilitated by increasing temperature, but enhanced transfer causes the depletion region to broaden and band bending to increase, thereby making electron exchange less probable. This self-limiting mechanism results in a distinct equilibrium E_F position for each combination of substrate temperature and doping. As explained in the following, the predictive power of the DCM then stems from the fact that the control mechanism strongly limits variations in the rate of charge exchange.

Although the detailed quantum mechanics of adatom-substrate coupling requires knowledge of electron capture and emission cross sections for adatom-induced states at the surface, the effective dynamic exchange of charge can be described via a current across a metal-semiconductor junction in equilibrium, as calculated by Crowell and Rideout.[11,12] Using the one-dimensional time-independent WKB approximation and a Maxwellian distribution of charge carriers in the conduction or valence band, this current can be written as

$$I = A^* T^2 \exp\left(\frac{-q\phi_s}{kT}\right)\left\{\frac{E_b}{kT}\int_0^1 \exp\left[\frac{-E_b}{kT}\left(\alpha+\frac{kT}{E_{00}}y(\alpha)\right)\right]d\alpha+\exp\left(\frac{-E_b}{kT}\right)\right\}. \quad (1)$$

A^* is the effective Richardson constant, T is temperature, k is the Boltzmann constant, $q\phi_s$ is the energy spacing in the bulk between E_F and the CBM, and E_b is the band bending across the depletion region. The Schottky barrier height is the sum of $q\phi_s$ and E_b. The first term in curly brackets describes tunneling, while the second gives the thermionic contribution. $y(\alpha)$ is part of the normalized transmission probability through the barrier and $\alpha = E/E_b$. $E_{00} = qh/4\pi(N/m^*\epsilon)^{1/2}$ where m^* is the majority carrier effective mass, ϵ is the dielectric constant, and N is the dopant concentration. For GaAs, the tunneling term dominates for $N \geq 10^{17}$ cm^{-3} and $T \leq 300$ K. Equation (1) can be used to predict the temperature-dependent barrier height for any dopant concentration. The current is then a constant determined by fitting to the observed band bending at different temperatures. The approximations involved in using Eq. (1) to describe the surface-bulk dynamic charge exchange neglect the specifics of the overlayer morphology and adatom-induced energy-level positions. Nevertheless, the body of experimental data indicates very similar E_F versus coverage results for diverse adatoms and encourages these assumptions. Indeed, these results necessitate a radically different way of considering E_F movement that incorporates T and N.

The predicted barrier heights as a function of temperature for n- and p-type GaAs doped at 1×10^{17} cm^{-3} are shown as solid lines in Figs. 1 and 2. For both n- and p-type GaAs, they predict almost linear band bending variations with temperature. The slight difference in slope for n- and p-type GaAs is due to the differences in the effective mass of majority carriers and dopant impurity energies. For p-type GaAs, the light holes have been assumed to play the dominant role in charge exchange. The effect of the dopant impurity energies (5.8 meV for Si in n-type GaAs vs 31 meV for Zn in p-type GaAs) is expected to be most profound at very low temperatures (<100 K), where the bulk E_F position $q\phi_s$ is located between these levels and the nearest band edge.[13] Careful inspection of the predicted curves in Fig. 1 does indeed reveal a slight change in slope at $\sim$100 K for n-type GaAs which is absent in p-type GaAs. These predicted curves represent upper bounds for the barrier height.

Excellent agreement between measured and predicted barriers for 0.3 ML Ti/n-type GaAs demonstrate that band bending is self-regulating. Saturation of the E_F position for Ti/p-type GaAs for $T \geq 200$ K indicates that the limiting parameter is the energy position of the adatom-induced states, not the exchange of charge. Pre-

liminary results for heavily doped GaAs emphasize the importance of the adatom-specific energy levels in the gap and their interplay with the dynamics of charge transport. The depletion region for heavily doped samples is sufficiently narrow to not inhibit charge exchange between surface and bulk states, even at 20 K, and E_F movement is not restricted by this effect.

The incomplete thermal reversibility for Ag/*n*-type GaAs leads to an interesting observation regarding the relation of interface morphology and the DCM. The accelerated rate of change in band bending for $T \geq 100$ K and the E_F hysteresis upon recooling are associated with partial clustering and overlayer metallization. As a result of clustering, E_F is affected by the delocalization of adatom states via adatom-adatom bonding.[10,14] Such delocalization facilitates coupling of the metallic states at the surface with the semiconductor, regardless of temperature. Consequently, different charge exchange equilibria and E_F positions are established. At high coverage full metallization is achieved, and the pinning positions are determined by the details of the adatom-induced states deep in the gap.

The results of this paper have shown that the exchange of charge is controlled by temperature in the low coverage regime, and E_F can be moved reversibly by $\sim$600 meV. The results require consideration of dynamic processes at semiconductor surfaces to describe E_F evolution.

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