Microscopic Metal Clusters and Schottky-Barrier Formation

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A simple interpretation is given of the observed logarithmic dependence of the surface Fermi level on coverage of GaAs(110) in the range 10^{-4}–10^{-1} monolayer in terms of the charging energy of microscopic metal clusters formed during the deposition process. New data taken on films formed at low temperature suggest that the clustering process is strongly temperature dependent.

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The formation of a Schottky barrier at a metal-semiconductor interface appears to involve a number of factors including intrinsic surface defects[1] and the nature of the weak metal-atom–semiconductor bonding.[2] In this paper we will be concerned with the very early stages of barrier formation for metal coverages on the scale of 10^{-3}–10^{-1} monolayer (ML).

The measurements of Ludeke, Chiang, and Miller[3] and more recently of Chin *et al.*[4] and Daniels, Zhao, and Margaritondo[5] have shown that the band bending observed at low coverages on the above scale corresponds to the transfer of only a small fraction (on the scale of a few percent) of an electron per adsorbed metal atom to the semiconductor valence band (in the case of *p*-type carriers) or from the conduction band (in the case of *n*-type carriers). Furthermore, the observed coverage dependence corresponds more to a barrier height proportional to the logarithm of the coverage than to the parabolic law which would be expected from a simple surface-defect picture.

In this paper we suggest that a new physical mechanism resulting from the formation of microscopic metal clusters dominates the coverage dependence of the Schottky-barrier height at ultralow coverage. We also present new data leading to the conclusion that the cluster size is a strong function of the substrate temperature.

The formation of noble-metal clusters on Si substrates at high coverage has been well established by direct observation with use of scanning electron microscopy.[6] Savage and Lagally[7] and Bonapace *et al.*[7] have reported evidence for the formation of clusters of In on the scale of 30 Å (a few hundred atoms) on a GaAs(110) substrate at submonolayer coverage. The fact that uniform overlayers of metals with electronegativity differences as large as 0.4 eV (Ag and Al) produce the same surface Fermi level (within a certainty of about 0.1 eV) at high coverage is convincing evidence for the existence of metal-associated intrinsic interface states[1,2] which lead to pinning of the Fermi level. We now argue that, at very low coverage, before a uniform metal overlayer can be established, the screening of these interface states will be dependent on the size of the metal cluster with which they are associated.

Consider a metal cluster on the scale of 30 Å in diameter. For the sake of definitiveness, we focus on the metal-induced gap states[2] as a pinning mechanism, though our argument does not require specification of the precise nature of the interface states. Transfer of electrons to the interface states (*n*-type substrate) or from them (*p*-type substrate) will induce a polarization of the metal cluster (Fig. 1). Since the pinning states are within angstroms of the cluster, the transferred charge will tend to be screened out by the metal (producing a local dipole) leaving the excess charge to be distributed over the surface of the metal cluster. This will cause the total Coulomb energy of the cluster-interface state complex to rise, thus inhibiting the transfer of many charges to the complex.

This mechanism may be quantified by a simple semiclassical model. Since the interface states are closely coupled to the metal cluster, the net effective capacitance of the complex will be controlled by the self-capacitance of the metal cluster with respect to carriers deep inside the semiconductor. The Coulomb energy of the complex of the cluster and associated interface states will increase as the square of the transferred change with a coefficient which depends on the size of the effective cluster capacitance. This model thus represents the way in which

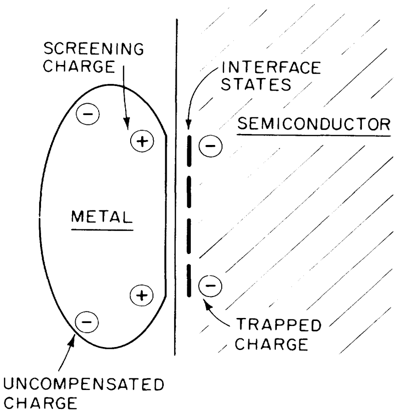

FIG. 1. Screening effects for a metal cluster on the semiconductor surface.

charging will limit electron transfer to or from the interface states and reduce the amount of band bending per adsorbed metal atom.

We represent the dependence of the total energy of a given metal cluster and associated interface states on the total charge transferred, ne, as

$$E_c(n) = n\varepsilon_{F,c} + n^2e^2/2C(N). \tag{1}$$

Here $\varepsilon_{F,c}$ is the Fermi level of the complex. In general this is N dependent, particularly for very small clusters. For large N, $\varepsilon_{F,c}$ will tend to the surface Fermi level in the presence of a uniform metal overlayer. Here we approximate $\varepsilon_{F,c}$ by an N-independent constant. n denotes the excess number of electrons relative to the number required to neutralize the complex. n may be positive (excess electrons) or negative (excess holes, or charge depletion). $C(N)$ denotes the effective self-capacitance of the complex. We make a basic assumption that C scales as the linear dimension of the cluster and hence as a power of N:

$$C(N) = C_1 N^{1/\nu}. \tag{2}$$

Here ν lies somewhere between 2 (2D clusters) and 3 (3D clusters). The chemical potential of the complex, $\mu = \partial E_c/\partial n$ is given by

$$\begin{aligned} \mu_e &= \varepsilon_{F,c} + n_e e^2/C(N) \text{ for electrons,} \\ \mu_h &= \varepsilon_{F,c} - n_h e^2/C(N) \text{ for holes.} \end{aligned} \tag{3}$$

In equilibrium we take $\mu_c(\text{complex}) = \mu_s(\text{semiconductor surface})$, where

$$\mu_s = \varepsilon_{F,s} + e\phi_B, \tag{4}$$

$\varepsilon_{F,s}$ represents the bulk semiconductor chemical potential, and ϕ_B the band-bending potential at the semiconductor surface.

It is convenient to define a surface density of atoms N_{sat} such that if each metal atom were to donate exactly one electron, the resulting band bending would bring the semiconductor Fermi level up to the cluster Fermi level (for p-type substrate) [or down to it (for n-type substrate)]:

$$\varepsilon_{F,c} - \varepsilon_{F,s} = e^2 N_{\text{sat}}^2 / 2\varepsilon_0 \varepsilon_s n_{D(A)}. \tag{5}$$

Here ε_s is the semiconductor dielectric constant, while $n_{D(A)}$ is the donor (acceptor) density in the semiconductor.

With the definition of mean surface cluster density as N_c clusters per square centimeter, so that the total surface coverage is

$$\theta = N N_c / N_{\text{ML}}, \tag{6}$$

where N is the mean number of atoms per cluster, and N_{ML} is the semiconductor's monolayer-surface atom density, the equation for equilibrium then becomes (for p-type)

$$\begin{aligned} &\varepsilon_{F,c} - n_h e^2/C(N) \\ &\quad = e\phi_B + \varepsilon_{F,s} = n_h^2 (N_c/N_{\text{sat}})^2 (\varepsilon_{F,c} - \varepsilon_{F,s}) + \varepsilon_{F,s}. \end{aligned} \tag{7}$$

This simple quadratic equation may be solved in terms of the parameters $\alpha = (e^2/C_1)/(\varepsilon_{F,c} - \varepsilon_{F,s})$ and $\beta = (N_c/N_{\text{sat}})^2$. In terms of this solution, the surface Fermi level is given by use of Eq. (3).

The predicted behavior of the Schottky barrier at ultralow coverage now depends on the density of metallic clusters and its dependence on coverage. We make the simple assumption that the cluster density is determined by a surface density of nucleation sites: When the metal atoms are deposited, they diffuse along the surface until they encounter a nucleation site or cluster, and then stick. In this model, after an initial nucleation stage, N_c is taken to be independent of coverage, while N grows linearly as the coverage θ increases.

Fits of the solution of Eq. (7) to the surface Fermi level of GaAs(110) with submonolayer coverages of Ag (n-type substrate) and Al (p-type substrate) deposited at room temperature (RT) are shown in Fig. 2. The position of the cluster Fermi level, $\varepsilon_{F,c}$, was set equal to 0.6 eV above the valence-band maximum (VBM) for the Al data and slightly higher (0.7 eV) for the Ag data. In fitting the n-type data, we took account of data for a freshly cleaved surface showing a surface Fermi level of 1.31 eV (still somewhat below the conduction-band minimum at 1.42 eV) by including a simulated data point at 10^{-5}-ML coverage. The resulting fit put the bulk semiconductor Fermi level at 1.33 eV.

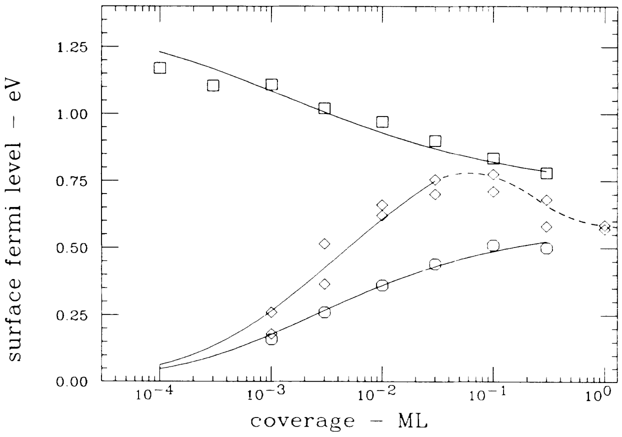

FIG. 2. Solid lines are fits to data for the surface Fermi level of GaAs(110) for submonolayer films of Ag deposited on an n-type substrate at RT (squares), Al deposited on p-type substrate at RT (lozenges), and Al deposited at LT (octagons). The dashed line is hand drawn to indicate a crossover in electronic properties for ultrasmall clusters (four to six atoms) to those for larger clusters (tens of atoms).

It was found numerically that the fits determine a functional relationship between the parameters α and β which may be represented approximately by the analytic form $\beta = \beta_0^{\alpha^{3.3}}$. The quality of the fit does not change markedly over a fairly wide range of values $0.2 \lesssim \alpha \lesssim 2$. It is also relatively insensitive to the cluster-size exponent ν, in the range $2.5 \lesssim \nu \lesssim 3$. Since the value of β [defined following Eq. (7)] determines the cluster size at given coverage, we see that while the fits to the data do not determine the absolute scale of the cluster size, they do determine the relative scales. We find from the fits that the Ag clusters are about a factor of 5 larger than the Al clusters, assuming the same charging parameter U for both metals.

An assumption that the Ag clusters contain about 1000 atoms at $\frac{1}{3}$ ML (consistent with the observations[7] for In) leads to a value of $U \cong 0.2$ eV. For the corresponding Al clusters, nucleation would occur at 1.7×10^{-3} ML. Since N_{sat} is fairly low for the samples of GaAs used in the experiments (2×10^{-3} ML for the n-type and 5×10^{-3} ML for the p-type substrate), the data at 10^{-3} ML already reveal a reduction in electrons transferred per adsorbed metal atom, and hence significant clustering. The neglect of fluctuations in cluster size is clearly a limitation of our simple model at these low coverages.

In order to further elucidate the nature of Schottky-barrier formation at ultralow coverage, the dependence of the surface Fermi level was studied for Al deposited on GaAs(110) at low temperature (LT) (−90°C). These data, and the room-temperature data reported above, were taken in experiments performed at the Stanford Synchrotron Radiation Laboratory, by use of soft-x-ray core-level photoelectron spectroscopy.

The photon energies used were 80 and 100 eV, which excited the most-surface-sensitive electrons, for Ga-3d and As-3d core-level electrons. A standard ulrahigh-vacuum chamber (base pressure, 10^{-11}-Torr scale) equipped with a double-pass cylindrical-mirror analyzer was used. As we expected to observe some interesting features in the LT band-bending process in the low-coverage regime, special care was taken in evaporating Al with a submonolayer coverage.

A newly designed ultralow-coverage metal evaporator[8] was used, which could reproducibly evaporate various metals at a coverage as low as 10^{-4} ML and significantly reduce the heating effect of the sample surface. For higher coverages we used a conventional Al evaporator, the heating effect of which was expected to be negligible at such coverages. In each study of the band-bending process, the spectra were taken with the sample kept at the same temperature as when it was cleaved and when undergoing the Al evaporation. Other experimental details will be published elsewhere.

As may be seen in Fig. 2 the band bending for the LT data saturates much faster and reaches a maximum by about 3×10^{-2} ML, i.e., for 10 times less Al than for the room-temperature data, but still slower than would be expected for one donor state per Al atom deposited. Fits of the charging model to these LT data show a striking difference from those for the room-temperature data: The effective Fermi energy $\varepsilon_{\text{F},c}$ of the cluster-interface state complex is found to be about 1.12 eV above the VBM compared to 0.6 eV for the RT data. At coverages above 3×10^{-2} ML the surface Fermi energy is then seen to decrease towards the bulk value, indicating a subsequent decrease of $\varepsilon_{\text{F},c}$.

A possible explanation of these results lies in the cluster size which in turn depends on the nature of the cluster-formation process. At low deposition temperature, surface imperfections with small binding energy for metal atoms will be effective as nucleation sites, while at room temperature there will be fewer effective binding sites. Consequently in Eq. (6) the mean cluster size at given θ will be expected to be larger for deposition at room temperature than at low temperature. If we make the assumption that the cluster size at LT is a factor 3 to 5 times smaller than at RT, so that at the saturation coverage (0.03 ML) the clusters contain an average of four to six atoms, the fits yield a charging parameter in the region of $U = 1.3$ eV. We are thus led to the conclusion that both the Fermi level and the charging parameter of very small complexes on the scale of a few atoms differ markedly from those of the larger clusters which may be forming in the RT deposition process.

We can only speculate about the origin of this dependence of electronic properties on cluster size. One possibility could lie in the quantum mechanics of interface-state formation. As the linear dimension of the metal cluster becomes smaller than the mean extent of the interface-state wave function, the energy of the interface states will rise towards the Fermi level set by the cluster atoms themselves. As the transferred charge becomes more localized in the metal, as opposed to the interface states, it is plausible that the effective Coulomb-energy-scale parameter, U, will also increase. In this picture the crossover observed in the data for the low-temperature–deposited film above 0.03 ML towards the high-coverage Fermi level is consistent with the setting in of the interface states as the cluster diameter increases beyond a critical value in the range of 5–7 Å. An alternative possibility is that the formation of defects at the metal-semiconductor interface is reduced for very small clusters on the scale of a few atoms.

Data for ultralow coverage of Al deposited on GaAs(110) at low temperature (not shown) exhibited a lack of band bending up to coverages on the scale of 0.3 ML. This fits in qualitatively with the idea that $\varepsilon_{\text{F},c}$ is in the region of the CBM for very small clusters, though further work is needed to check consistency with the p-type data.

Once the metal overlayer starts to coalesce into a two-dimensional sheet, the surface Fermi level [Eq. (7)] will be expected to approach the same value for n- and *p*-type substrates in a manner depending on the density of interface states. The coverage at which this occurs will depend on details of the cluster statistics and shape. Percolating aggregates will be expected to occur when the mean cluster spacing is about $\sqrt{2}$ cluster diameters. Thus the simple isolated-cluster model should not be expected to work in the saturation regime which will set in as the coverage approaches a monolayer.

In conclusion, the RT data for both Al on *p*-type GaAs and noble metals on *n*-type GaAs are consistent with a model in which the effects of charging of metal clusters on the screening of interface states associated with the metal dominates the observed coverage dependence of the surface Fermi level at ultralow coverages. The data on low-temperature–deposited surface layers suggest that the electronic properties of very small clusters on the scale of a few atoms differ significantly for those of clusters on the scale of tens to hundreds of atoms. It would be interesting to see if such differences could be correlated with other physical measurements or calculations.[9]

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[1] W. E. Spicer, I. Lindau, P. Skeath, C. Y. Su, and P. Chye, Phys. Rev. Lett. **44**, 420 (180), and J. Vac. Sci Technol. **16**, 1422 (1979).

[2] V. Heine, Phys. Rev. A **138**, 1689 (1965); S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B **15**, 2154 (1977); J. Tersoff, Phys. Rev. Lett. **52**, 465 (1984); S. B. Zhang, M. L. Cohen, and S. G. Louie, Phys. Rev. B **34**, 767 (1986).

[3] R. Ludeke, T.-C. Chiang, and T. Miller, J. Vac. Sci. Technol. B **1**, 581 (1983).

[4] K. K. Chin, R. Cao, K. Miyano, C. E. Cants, I. Lindau, and W. E. Spicer, Mater. Res. Soc. Symp. Proc. **54**, 341 (1986).

[5] R. R. Daniels, Te-Xiu Zhao, and G. Margaritondo, J. Vac. Sci. Technol. A **2**, 831 (1984).

[6] J. A. Venables, J. Derrien, and A. P. Jansen, Surf. Sci. **95**, 441 (1980).

[7] D. E. Savage and M. G. Lagally, Phys. Rev. Lett. **55**, 959 (1985); C. R. Bonapace, D. W. Tiu, K. Li, and A. Kahn, J. Vac. Sci. Technol. B **3**, 1099 (1985).

[8] K. K. Chin, P. MacKernan, and I. Lindau, J. Vac. Sci. Technol. A **4**, 1949 (1986).

[9] W. A. Saunders, K. Clemenger, W. A. de Heer, and W. D. Knight, Phys. Rev. B **32**, 1366 (1985); M. Manninen, R. M. Nieminen, and M. J. Puska, Phys. Rev. B **33**, 4289 (1986). Note that the dielectric screening due to the semiconductor substrate would substantially reduce the charging energy of the clusters.