Metallicity and Gap States in Tunneling to Fe Clusters on GaAs(110)

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We report the characteristics of tunneling to a GaAs(110) substrate with distinct, nanometer-size Fe clusters, as a function of distance from and size of the clusters. We show that Fe clusters of volumes ~ 150 Å^3, corresponding to $\simeq 13$ atoms, are observed to be nonmetallic with a gap at the Fermi level. Larger clusters with > 35 atoms begin to show metallic characteristics. We observe a continuum of cluster-induced gap states in tunneling to the GaAs substrate surrounding the metallic Fe clusters. The decay length of these states has a minimum decay of 3.4 Å at midgap and diverges at the valence- and conduction-band edges.

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Considerable interest lies in the electronic properties of small metal particles as a probe of the evolution of electronic structure toward that of the solid state. Small particles with $n = 10$–100 atoms span the regime where the electronic properties develop from atomiclike to metallic characteristics with increasing particle size.[1] In conventional electron tunneling experiments, small particles have been used to study the quantization of electron states[2] and single-electron tunneling effects due to the Coulomb interaction.[3] Recent tunneling measurements, emphasizing quantum size effects, have been made on fabricated and point-contact tunnel junctions,[4,5] but not on well-characterized single particles.

The study of metal clusters on semiconductor surfaces has also been of interest in understanding the fundamental electronic properties of metal-semiconductor interfaces.[6,7] Photoelectron measurements have inferred from linewidth trends that bulk electronic structure develops for clusters with $\simeq 100$ atoms.[8] Many of these studies, however, determine cluster sizes indirectly and average over a cluster size distribution. The determination of metallic characteristics in cluster systems by examining the Fermi-edge cutoff in photoelectron spectroscopy has been of recent controversy.[9] As shown below, metallic characteristics are quite evident when tunneling into a partially filled band of states at the Fermi level.

In this Letter, we report scanning tunneling microscopy (STM) experiments that determine the electron tunneling characteristics of *single* nanometer-size Fe clusters epitaxially grown on GaAs(110) substrates. We show that clusters with volumes of ~ 1000 Å^3 ($n \sim 85$ Fe atoms) display fully metallic characteristics with a finite differential conductance at zero applied bias, similar to thin Fe films. Clusters with volumes ~ 150 Å^3 ($n \sim 13$) are found to be nonmetallic, as evidenced by a finite tunneling gap at the Fermi level. We show further that a continuum of cluster-induced gap states is observed in the tunneling spectra obtained from regions of the semiconductor surrounding the metallic Fe clusters. The state density in the gap is found to decay exponentially with distance from the clusters. Specifically, we show that the decay length is dependent on the eigenstate energy within the band gap. The decay length has a minimum value of 3.4 Å at midgap and diverges at both the valence- and conduction-band edges. These observations represent the first measurements reflecting the dispersion of the *complex* solutions of the GaAs electronic band structure, which have been of central importance in theories of metal-semiconductor interfaces.[10–12]

Fe clusters and films were grown by molecular-beam-epitaxy techniques in an ultrahigh-vacuum system, as described in detail elsewhere.[13] Current-versus-voltage (I-V) characteristics were obtained by interrupting the STM feedback loop at each point in the topographic image. The tip-sample distance was decreased a fixed amount to increase the dynamic range of the I-V measurements in the region of the GaAs band gap.[14]

Figure 1 shows an STM image of the GaAs(110) surface with 0.1-Å coverage of Fe grown at 300 K. The GaAs substrate appears as rows of atoms along the $[1\bar{1}0]$ direction, which is at 45° with respect to the $+x$ direction. Only the substrate As atom locations are observed in the bare surface regions, since the image was obtained at negative sample bias. A variety of different size Fe clusters are observed in the image. STM contours show

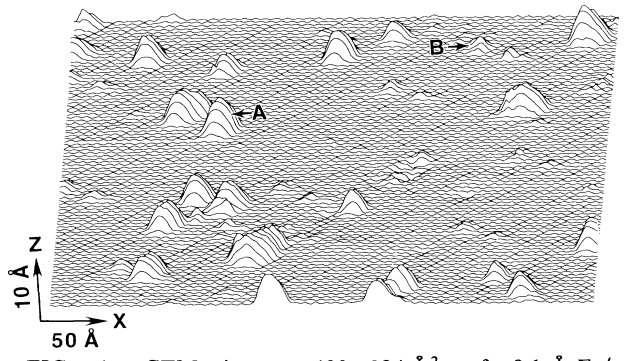

FIG. 1. STM image, 400×384 Å^2, of 0.1-Å-Fe/p-GaAs(110). The sample bias was -2.5 V. Arrow A indicates a cluster of volume 1180 Å^3 and arrow B points to a cluster of volume 160 Å^3.

several different cluster heights indicating 3D cluster growth.[13] LEED observations of coalesced clusters showed the bcc Fe diffraction pattern, consistent with previous work which determined the growth to be epitaxial.[15] Volume estimates of the clusters were achieved by integrating the STM height contours of the clusters, which we feel is a good estimate, since the charge-density contours of metals closely follow the positions of the metal atoms. The volumes of the clusters shown in Fig. 1 range from 100 to 1500 Å^3, corresponding to 9–127 atoms per cluster.

Figure 2(a) shows the tunneling characteristics as a function of cluster size, ranging from a 150-Å^3 cluster to a continuous 17-Å thin film. As a reference, curve *d* in Fig. 2(a) also shows the tunneling characteristics on the bare GaAs surface, 40 Å from the nearest cluster. In

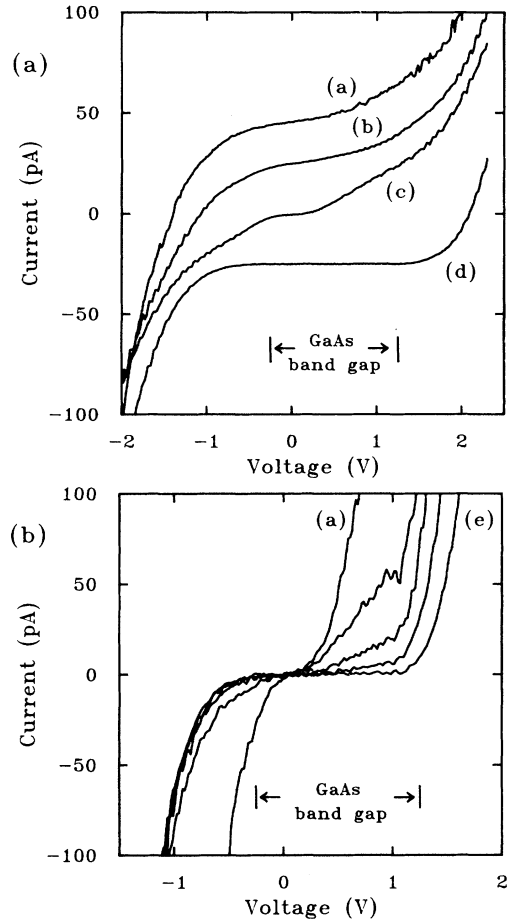

FIG. 2. (a) Top panel: Tunneling current vs voltage characteristics of Fe/*p*-GaAs(110). The four curves correspond to *a*, 17-Å Fe film; *b*, 1150-Å^3 cluster; *c*, 150-Å^3 cluster; and *d*, GaAs(110) surface, 40 Å from the nearest cluster. The curves have been shifted vertically for display. (b) Bottom panel: Tunneling current vs distance from the Fe cluster as indicated in Fig. 3(a). Curve *a* is on the cluster. Curves *b*–*e* correspond to distances from the cluster edge of *b*, 3.7 Å; *c*, 6.7 Å; *d*, 9.6 Å; and *e*, 14.3 Å.

curve *d*, we observe a band gap of 1.5 eV, which is close to the 1.4-eV band gap of GaAs, where no tunneling occurs since cleaved GaAs has no surface states in the band gap. In addition, the *I-V* characteristic in curve *d* shows the surface Fermi level pinned at 0.25 eV above the valence band. We found the pinning of the Fermi level to be homogeneous over the surface at the Fe coverages used in Fig. 2.

The *I-V* measurement on the thin Fe film in Fig. 2(a), curve *a*, shows current within the band-gap region. In particular, tunneling occurs with a finite differential conductance at zero bias (i.e., there is tunneling both at 0^+ and 0^- V), signifying metallic behavior with a partially filled band of states at the Fermi level. The *I-V* characteristic of the 1150-Å^3 cluster (curve *b*) displays metallic behavior similar to that of the thin film, with again a finite differential conductance at zero bias (note also the similarity in the overall characteristics). Deviation from metallic behavior is observed in particles with volumes of ~150–400 Å^3, as shown in Fig. 2(a), curve *c*, where a finite gap in the tunneling current is seen at zero bias. For the small clusters (e.g., curve *c*) gap widths ranging from 0.1 to 0.5 eV have been observed.

The size dependence of the tunneling characteristics in Fig. 2(a) shows that quantum size effects are appreciable for cluster volumes of ~150 Å^3. Such effects are expected when the spacing between energy levels is a few k_BT. The usual simple estimate for the level spacing is given by E_F/N, where E_F is the bulk Fermi energy and N is the number of valence electrons in the particle. This yields a spacing of 0.1 eV for an 11-atom Fe cluster. The cluster size where we observe a band gap of this magnitude corresponds to ~13 atoms, in agreement with the above estimate. The surprising result, perhaps, is not that the smaller particles are nonmetallic, but that metallic behavior begins to be observed in particles with volumes as small as 400 Å^3, corresponding to only ~35 atoms. In photoelectron measurements, bulk metallic behavior has been inferred for particle sizes on the order of 100 atoms.[8] These measurements use bandwidth trends to determine bulk behavior, which may not be a sensitive criterion for the onset of metallicity. Detection of the Fermi edge in photoelectron measurements may be more direct, but is hampered by low intensity and resolution problems.[9] Photoionization measurements, on beams of well-defined clusters, have found indications of band formation for Hg clusters with $n > 12$ atoms.[1] These measurements are consistent with the tunneling results shown here. We also note that detailed calculations for Fe clusters show level spacings of 0.1 eV near the Fermi level for 15-atom clusters,[16] and thus one might expect a transition to room-temperature metallic behavior in the range of 20–30 atoms. A direct comparison with the present results is not possible, since one has to take into consideration the binding of the Fe clusters to the GaAs surface.

The metallic states found on the clusters, which over-

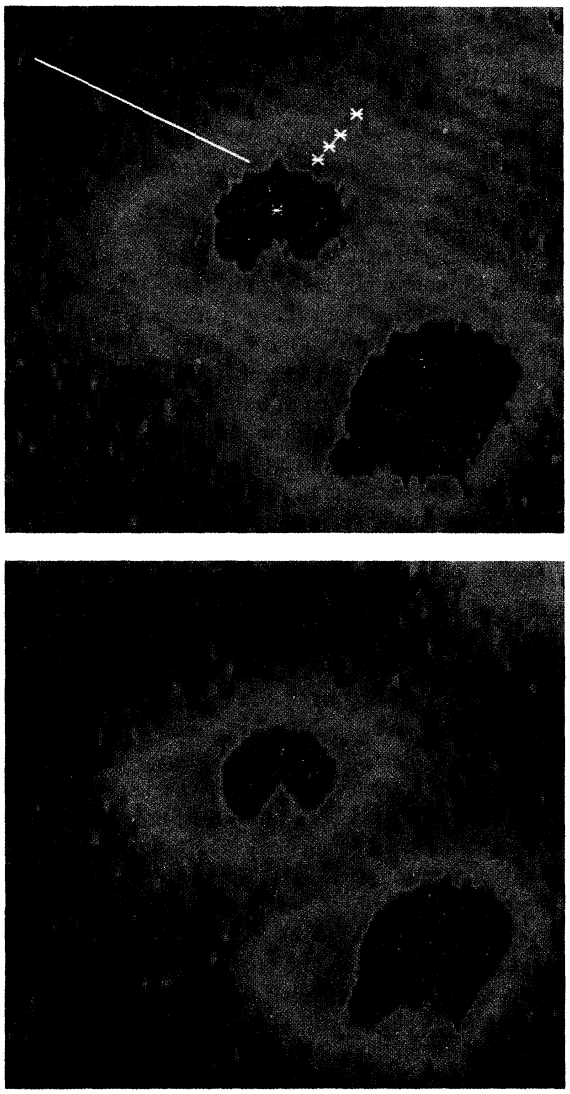

FIG. 3. Images of the logarithm of the differential conductance, $\log(dI/dV)$, obtained from the I-V characteristics of Fe/p-GaAs(110), recorded at each pixel in the normal topograhic image. The images in the top [(a)] and bottom [(b)] panels correspond to voltages 1.1 and 1.0 V, respectively (the observed conduction-band minimum is at 1.25 V). The images are shown with a black-red scale ranging from 0 to 300 pA/V. The blue regions denote areas of large current over the metallic clusters. The positions of the I-V curves, shown in Fig. 2(b), are indicated by the asterisks in (a). The solid line in (a) denotes the position of the [001] line profiles, shown in Fig. 4(a), while the line of asterisks shows the [1$\bar{1}$0] profile direction.

lap in energy the semiconductor band gap, are also observed on the semiconductor surface in the vicinity of the clusters, as shown in Fig. 2(b). Here, curve a displays metallic characteristics from a measurement on one of the Fe clusters shown in the image of Fig. 3(a). Curves b-e still show tunneling current in the GaAs band gap even though they are taken on the GaAs substrate, as indicated in Fig. 3(a). The tunneling current from states in the gap, observed in Fig. 2(b), is found to decrease exponentially with distance from the cluster.

To examine the spatial dependence of the gap states we have recorded I-V characteristics at each point in the topographic image. Images of the differential conductance dI/dV are obtained from the slope of the I-V measurements at voltage V, as shown in Fig. 3. The differential conductance is proportional to the surface density of states;[14] thus, images of dI/dV in the band gap show the spatial distribution of the gap states at an energy $E = eV$ with respect to the Fermi level at 0 V. In Fig. 3(a), we observe a finite conductance surrounding the Fe cluster at a voltage of 1.1 V, which is 0.15 eV below the experimentally observed conduction-band minimum. The contribution from the GaAs gap states is observed to have atomic corrugation with maxima on the Ga sites, as deduced from the phase relationship of the corrugation with that of the topograph. The gap-state amplitude at 1.1 V is found to decay spatially from the cluster with a decay length of 16.8 Å in Fig. 3(a). Figure 3(b) shows the differential conductance image at 1.0 V, just 0.1 eV below that of Fig. 3(a). The region of finite conductance is observed to encompass a smaller region surrounding the Fe cluster with a decay length of 11.4 Å, indicating the gap-state decay to be faster for energies deeper within the gap.

A quantitative examination of the spatial decay of the gap states is made from examining line profiles along the [001] and [1$\bar{1}$0] directions. The line scans along the [001] direction [indicated by the line in Fig. 3(a)] are shown in Fig. 4(a), corresponding to energies with respect to the top of the valence band of 0.95–1.55 eV, in increments of 0.05 eV. The differential conductance is observed to decay exponentially with a slope which increases with decreased energy approaching midgap. The decay length (inverse slope) obtained from a linear fit to these data is shown in Fig. 4(b). The decay length in Fig. 4, obtained on p-type samples from 0.7 to 1.6 eV, is observed to span a range of 3–200 Å, with the minimum corresponding to midgap, and a divergence at the bottom of the conduction band. Similar results are observed for the bottom portion of the gap (−0.15–0.65 eV), obtained on n-type samples, with a minimum decay length at midgap and a divergence at the valence-band edge.

The decay of the gap states in regions of the clean semiconductor, where initially no states exist, arises from matching the cluster wave functions to states in the semiconductor band gap. Within the gap, these wave functions will be evanescent waves determined by the complex solutions of the semiconductor band structure in the band gap.[11,17] At the band edges, the imaginary wave vectors go to zero and hence the decay lengths diverge as the evanescent solutions go over to plane waves. Deeper

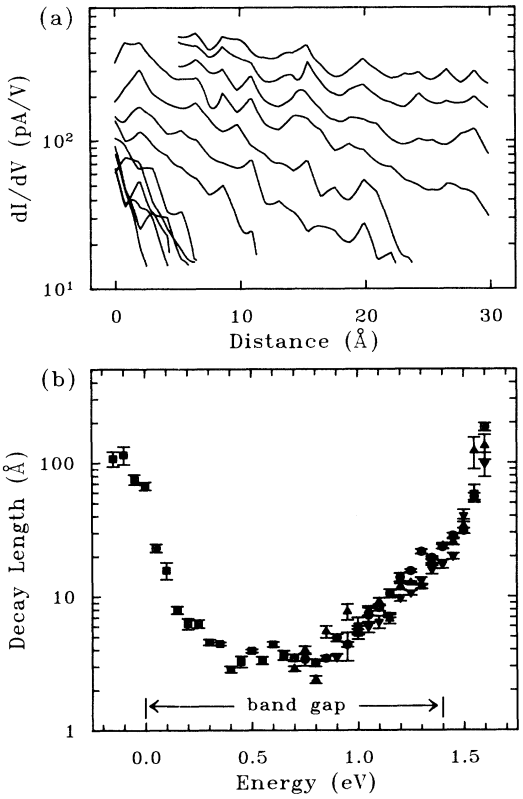

FIG. 4. (a) Line profiles along the [001] direction, indicated by the line in Fig. 3(a), for energies of 0.95–1.55 eV in increments of 0.05 eV. The slower decay corresponds to 1.55 eV. (b) Energy dependence of the decay length of the differential conductance obtained from the inverse slope of the dI/dV line profiles along the [001] (squares and circles) and [1$\bar{1}$0] (up and down triangles) directions. Data from p-type material are shown by the circles and triangles, and from n-type by squares. The tip-sample separation was decreased by 1.0 (circles and up triangles from the data in Fig. 3) and 2.0 Å (squares and down triangles) relative to that used for topographic imaging. The energy scales have been shifted to give zero energy at the valence-band maximum.

in the gap the imaginary wave vectors reach a maximum between the two corresponding bands, usually near midgap, resulting in a loop in complex reciprocal space. The charge-density decay at midgap is $\sim$3 Å for GaAs.[11] The data in Fig. 4 display a decay length at midgap of 3.4 Å and also a divergence at the valence- and conduction-band edges, in agreement with expectations from the complex band structure of GaAs. We attribute the finite decay of the evanescent states in the lower 0.2 eV of the conduction band to the availability of the larger density of states near the L minimum which is at 1.7 eV above the valence-band edge.

In conclusion, we have shown that single nanometer-size Fe clusters, with volumes of 150 Å^3, corresponding to $n \simeq 13$ atoms, are nonmetallic with a gap at the Fermi level. Larger clusters with $n > 35$ atoms show metallic characteristics with a partially filled band at the Fermi level. We attribute this onset of metallicity to the decreasing influence of quantum size effects with increasing cluster size. We have provided a measurement of the spatial characteristics of the semiconductor gap states by showing that the cluster-induced states lying within the semiconductor band gap decay exponentially with distance along the surface. The decay constant is 3.4 Å at midgap and diverges at the valence- and conduction-band edges, reflecting the evanescent character of the complex solutions of the GaAs band structure.

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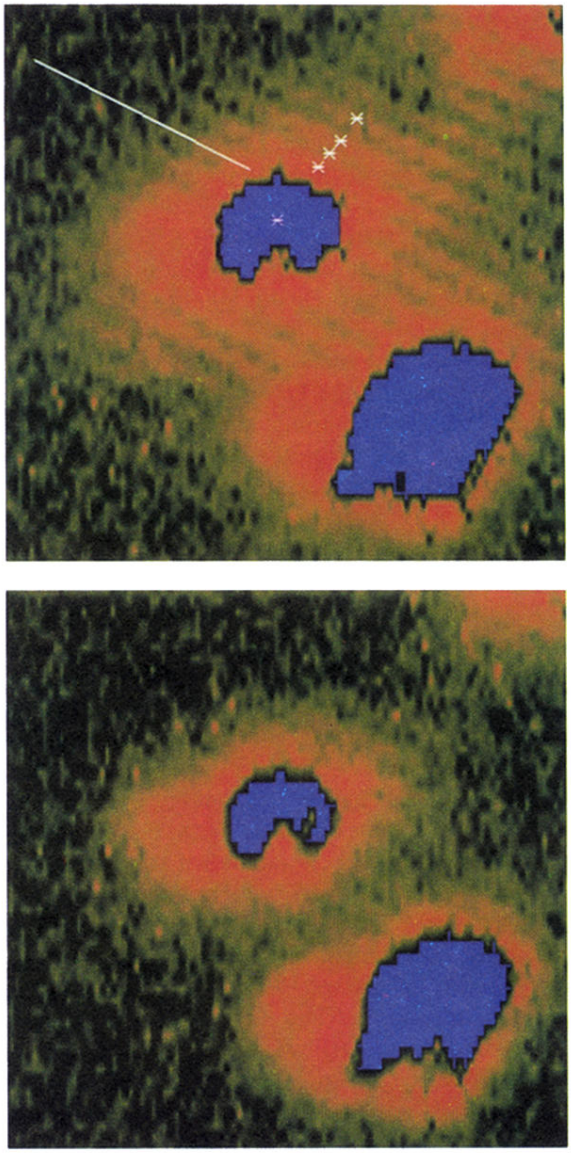

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