

Cluster Assembly of Interfaces: Nanoscale Engineering

J. H. WEAVER AND G. D. WADDILL

Overlayer structures can be formed on surfaces by the deposition of clusters containing hundreds or thousands of atoms. Cluster assembly alters the reaction pathway at the surface so that novel structures with unique chemical and physical properties can be stabilized. This article discusses the process of cluster assembly. Cluster-assembled interfaces are compared to those obtained by conventional techniques, and examples are given for metal-semiconductor and semiconductor-high temperature superconductor systems.

THE IMPORTANCE OF INTERFACES IN AN EXPANDING NUMBER of disciplines has resulted in a proliferation of research, both experimental and theoretical, that focuses on their novel properties (1). Interfaces, defined as the spatial regions between two dissimilar materials, are vital to the production of electronic devices, the incorporation of materials such as the high-temperature superconductors (HTSs) into multicomponent systems, the development of better catalysts, the synthesis of composites, and the creation of materials based on interface-governed structures. Examples of solid-solid interfaces include metal overlayers grown on semiconductors and contacts formed on HTSs. Overlayers on semiconductors produce electrical properties that control the operation of electronic devices and solar cells. Contacts to HTSs tend to induce interface reaction and substrate degradation (2). Interfaces involving liquids are important in biological and electrochemical processes, and solid-gas and solid-liquid interfaces are the basis for catalysis.

The properties of solid boundary regions are often complex, differing from those of the bulk materials on either side and dependent on the processes of formation (1). Their dependence on growth conditions reflects the fact that the atoms are not, or need not be, distributed in equilibrium configurations. Hence, the role of kinetics is extremely important when stability issues are considered. Phenomena involving the transport of mass, charge, or energy across an interface are dependent on the chemical constituents and stoichiometry, the degree of order and homogeneity, and the spatial extent of the boundary region. Phenomena related to adhesion, wetting, and mechanical strength are directly affected by the microscopic configuration of the interface.

Interface research encompasses experimental and theoretical efforts in materials science, physics, chemistry, and engineering. Often it is driven by the need to synthesize a product with very specific properties. The characterization of the rich and varied nature of solid interfaces presents a formidable challenge, particularly for

intermixed systems for which local bonding is far from homogeneous. For the experimentalist, analytical techniques include photoemission and inverse photoemission (to probe the occupied and empty electronic states and to examine bonding configurations), low-energy electron diffraction and surface-extended x-ray absorption fine-structure spectroscopy (to provide structural and geometric information), and scanning and transmission electron microscopy (to gain structural information). Most recently, scanning tunneling microscopy (STM) has been used to image the surface with atomic-scale spatial resolution and to probe the overlayer electronic states (3). For the theorist, issues associated with surface bonding and overlayer structure are challenging because of the lack of periodicity. Simulations such as molecular dynamics, as recently described by Landman *et al.* (4), offer promise for predicting the behavior of interacting atoms in a dynamic system, with the force of interaction being derived from increasingly reliable interatomic potential energy surfaces (5).

Interface Formation by Atom Deposition

Most methods for the formation of solid-solid interfaces begin with the condensation of single atoms of the overlayer material onto a prepared substrate (6). Typically, these atoms are produced by evaporation from hot sources, by sputtering, or by gas-phase reactions, and they arrive with kinetic energies that are determined by the source. Condensation releases additional energy because the adatoms have become part of a new solid surface and bonding has occurred. The adatoms are effectively isolated when their number is very small. The interaction of isolated species with a wide variety of substrates has been the subject of intensive research in surface science (7). As such, it serves as the foundation for modeling overlayer growth. As the number of adatoms increases, interesting growth structures develop that depend on the detailed interactions of adatoms with the substrate atoms and with one another.

As an example of overlayer growth morphologies, we show in Fig. 1 a series of STM images (8) of cleaved GaAs(110) onto which Ag atoms have been deposited at 300 K. The images were acquired with a tip biased positive relative to the sample so that tunneling was from surface As atoms and the lines running diagonally define the [110] direction. Ga atoms can be imaged by negative biasing (3). These images were obtained in the constant-tunneling-current mode. They are displayed in a manner that simulates illumination from the upper right. Figure 1A shows Ag clusters dispersed on the surface formed after the deposition of 4×10^{14} atoms cm^{-2} (scale, 220 Å by 220 Å). For reference, the surface atom density of GaAs(110) is 8.85×10^{14} atoms cm^{-2} . The existence of clusters demonstrates that Ag atoms are highly mobile on GaAs(110) because of weak substrate bonding. Nucleation of Ag clusters occurs because of the relatively strong Ag-Ag bonding. There is no evidence for surface disruption induced by the condensation of Ag

The authors are with the Materials Science and Chemical Engineering Department at the University of Minnesota, Minneapolis, MN 55455.

atoms. Unfortunately, individual atoms within the nanoscale clusters cannot be resolved.

Figure 1B shows the result of depositing 1.4×10^{15} atoms cm^{-2} . In this case also, the surface $[1\bar{1}0]$ direction runs diagonally, but the substrate is much less visible for this 320 \AA by 320 \AA area. Several relatively large clusters have grown, but smaller clusters are also visible. In this coverage regime, overlayer growth proceeds by surface migration of Ag atoms until they bond to existing clusters or until they nucleate to form new clusters. Ag atoms, deposited onto the tops of clusters, enhance three-dimensional growth.

Figure 1C shows the surface morphology after 4×10^{15} atoms cm^{-2} of Ag had been deposited (scale, 425 \AA by 425 \AA). Distinct nanocrystallites with typical lateral dimensions of 40 to 50 \AA are clearly evident. Faceting is also apparent as the crystallites seek to minimize their surface energy. The result is a very irregular surface that bears little resemblance to the layer-by-layer growth often envisioned for thin films. Figure 1D (scale, 425 \AA by 425 \AA) for 8×10^{15} atoms cm^{-2} shows the formation of beautiful Ag structures with (111) facets that are not parallel to the substrate, single-atom-height steps, terraces, and regions of less long-range order. Further deposition ultimately reduces the surface roughness as the nanocrystallites grow and merge.

The images in Fig. 1 show that islands nucleate directly atop the substrate for Ag/GaAs(110). Other modes for nonintermixing systems involve layer-by-layer growth and the formation of clusters atop an initial monolayer that wets the surface for nonintermixing systems (6). The tendency to form one structure or the other is determined by the surface free energy (surface tension) of the two

materials. The specifics of the overlayer morphology are, however, intimately related to the system parameters during the growth process. For example, the size of the Ag crystals in Fig. 1 would depend on the deposition rate and the substrate temperature during growth. Because electron transport in the film and the ability of the overlayer to passivate the substrate vary with the density of crystallite grain boundaries, the properties of an interface will depend on growth conditions.

Thus far, we have considered interfaces for which there is no intermixing of overlayer and substrate atoms. These are the exception rather than the rule, and most interfaces exhibit intermixing over many atomic layers. As a result, complex local bonding configurations are established. Surface disruption that leads to intermixing can be triggered by the condensation of the adatom itself (an exothermic process) or by the growth of two-dimensional or three-dimensional aggregates on the surface (9). Intermixing produces configurations that resemble solid solutions when there is little chemical preference for bonding between the different atomic species. Compounds derived from the substrate and overlayer atoms can also form, subject to kinetic limitations on atom redistribution. At high temperature, mass transport is enhanced and the extent of mixing increases. These nonequilibrium systems have unique properties related to their structural, chemical, and kinetic constraints, with a rich literature that is beyond the scope of this article (1). We will, however, return to some of the issues to compare cluster-assembled interfaces to those grown by atom deposition.

Cluster Assembly

In studies of the growth of one material on another, it is important to vary the growth parameters so as to understand the physics and chemistry at the interface and to control the product. For metal overlayers on semiconductors, for example, attempts have been made to alter the complexities of interfaces by controlling substrate temperature (1, 10), by using neutral atoms and ions in the growth process (1, 11), and by making judicious choice of overlayer-substrate systems (12). In each case, overlayer growth is initiated when individual adatoms come into contact with the substrate surface. For metal-semiconductor interfaces, substrate disruption accompanied by intermixing of substrate and overlayer atoms generally occurs, even at low temperature, although the kinetics of intermixing are temperature-dependent (1). These processes are dictated by atom-substrate reactivity.

We recently undertook the creation of an abrupt, defect-free interface by forming overlayers as gently as possible. To do this, we sought to reduce the kinetic energy of the incoming species, and we wanted to minimize or eliminate direct atom-substrate interactions. We speculated that the best way to do this would involve the formation of clusters composed of hundreds or thousands of atoms so that their deposition onto the surface would resemble the contacting of two solids, or at least two large objects. In this way constraints related to solid-solid rather than atom-solid interactions could be investigated, and we assumed that very different final states could be reached at the interface. As with most interfaces, these would be metastable, but the reaction pathway would be altered. The trick, of course, was to create large, clean clusters and to condense them with no kinetic energy onto a pristine surface. The process we developed was simple, and it is flexible enough to allow investigations into new forms of composites, with applications in electronics, magnetism, catalysis, and adhesion. It has direct relevance to the physics of forces between clusters and surfaces (13) and to phenomena associated with surface wetting and cluster sintering (6).

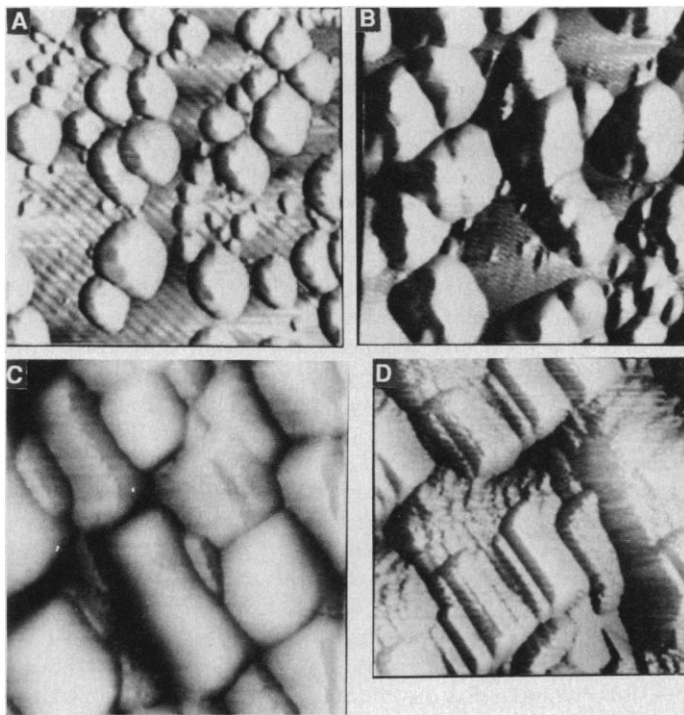


Fig. 1. STM images of Ag overlayer growth by conventional atom deposition onto GaAs(110) at 300 K. Ag clustering, apparent from (A) and (B), reflects weak substrate interactions and high surface mobility. The irregular agglomerates form nanocrystallites, even at very low deposition, as shown in (C) and (D). Image (D) shows Ag(111) facets that are not parallel to the substrate surface, single-layer steps, and terraces, as well as regions with less long-range order. Faceting is also apparent in images at lower coverage. The scales correspond to (A) 220 \AA by 220 \AA , (B) 320 \AA by 320 \AA , (C) 425 \AA by 425 \AA , and (D) 425 \AA by 425 \AA ; the number of atoms deposited corresponds to 0.5, 1.5, 5, and 10 monolayer equivalents of the GaAs(110) surface where one monolayer equals 8.85×10^{14} atoms cm^{-2} .

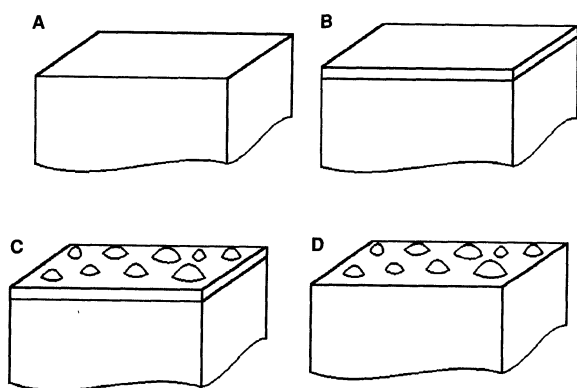


Fig. 2. Schematic of the cluster-assembly process showing (A) the clean surface, (B) the condensation of a rare gas buffer layer on the surface, (C) the deposition of adatoms from a hot source and the formation of clusters on the buffer layer, and (D) the desorption of the buffer layer and the assembly of clusters on the pristine substrate. This form of deposition replaces atom-substrate interactions with cluster-substrate interactions, which impose novel constraints on reaction.

Our approach to cluster assembly is as follows (Fig. 2). First, multilayers of Xe are condensed by sample exposure to partial pressures of 10^{-6} torr at temperatures of ~ 50 K. We have found that thicknesses of ~ 30 Å adequately buffer the substrate while being thin enough to avoid charging during photoemission characterization of cluster growth on the Xe. Rare gas solids are ideal buffer layers because they do not modify the substrate, and they can be easily desorbed. After restoration of 10^{-11} torr conditions, the rare gas layer is exposed to a flux of atoms evaporated from a thermal source in a conventional manner. To date, all adatoms deposited onto the Xe layers have been sufficiently mobile, even at 50 K, to form clusters (14, 15). This tendency reflects their weak interaction with Xe. Cluster formation on the buffer layer is still an exothermic process, but the energy is dissipated by the rare gas solid without substrate disruption. The adatoms are brought into contact with the pristine substrate by warming above ~ 90 K and desorbing the Xe layer.

The clusters are attracted to the substrate by relatively long-range dispersion or van der Waals forces. Although the details of the attraction depend on the cluster geometry (13), the dispersion forces vary with the distance of separation approximately as r^{-n} , where n is between 2 and 4. Indeed, one of the intriguing aspects of cluster assembly is that as a result of the use of this process insight into the forces between clusters and the surface can be gained. Preliminary measurements for Ag clusters grown on Xe layers on GaAs(110) show time-dependent movement of the clusters toward the GaAs surface due to the dispersion forces.

Cluster assembly has now been used to form novel overlayers on semiconductors (14, 15) and on HTSs (16, 17). Each cluster is composed of hundreds of atoms, and the extent of surface reaction is markedly less than when overlayers are grown atom by atom. For most metallic and nonmetallic overlayers grown in this way on semiconductor substrates, disruptive reaction has been entirely frustrated, and novel Fermi level (E_F) pinning positions independent of overlayer material and coverage have been observed. For HTS overlayers, cluster assembly at low temperature produces a contact for which the substrate has been modified only minimally by the overlayer—it does not produce the highly disrupted, O-depleted insulating surface region known to form upon atom deposition.

Insight into the structure of cluster-assembled overlayers can be derived from electron microscopy and STM. Figure 3 shows scanning electron microscopy and transmission electron microscopy (TEM) images obtained after Au clusters had been assembled on

GaAs(110). The total amount of Au deposited corresponds to 7 Å, but the morphology is very irregular (Fig. 3A). This overlayer structure was produced by a single deposition process. Interconnected clusters are clearly evident over the surface. These clusters are metallic. The cross-sectional image for this interface (Fig. 3B) reveals clusters with lateral dimensions of ~ 150 Å and heights of ~ 50 Å. Figure 3C shows a high-resolution lattice image for a single Au cluster on GaAs(110). The (111) lattice planes of two differently oriented Au crystallites can be identified by the array of parallel lines, separated by a less well-ordered region. From this image, it is apparent that cluster coalescence has occurred during assembly on the Xe or at the substrate and that ordered nanocrystallites have formed. Moreover, the Au/GaAs(110) interface is abrupt.

We have used synchrotron radiation photoemission to investigate GaAs- and InP-based interfaces produced by cluster assembly with surface coverages between ~ 1 and $\sim 90\%$. At low coverage, the clusters are widely dispersed across the surface, and they are smaller than the composite islands shown in Fig. 3. In this case, the individual clusters are likely to be isolated on the Xe before deposition, and coalescence during the desorption process is unlikely. This idea is supported by TEM studies for Cu cluster assembly on silica surfaces. However, cluster coalescence becomes more likely as the amount of material deposited onto the Xe is increased. Although we have not done so, we assume that the growth of thick layers on Xe would fully cover the substrate upon deposition. The morphology of such a structure is likely to be complex, but insight into wetting could come from such studies.

Metal clusters on semiconductors. Our first application of cluster assembly, which focused on metal-semiconductor interfaces, was motivated by an interest in creating an interface as gently as possible to simulate an ideal interface free of defects. Those results showed that the deposition of metal atoms onto the Xe buffer produced clusters with electronic structures indistinguishable by photoemission from those of the bulk metal.

We have investigated the onset of metallic character for cluster-assembled overlayers by studying the valence band evolution for amounts of overlayer material corresponding to nominal depositions between 0.05 and 50 Å. In Fig. 4, we show representative photoemission energy distribution curves (EDCs) for Ag clusters deposited onto GaAs(110) at ~ 90 K. For direct comparison, we also show results for atom deposition from a thermal source onto GaAs(110) at 60 K. We acquired these spectra with synchrotron radiation, using a photon energy of 65 eV. In both cases, the bottommost EDC is for the clean cleaved *p*-type GaAs(110) surface with 0.1 Å of Ag deposited onto it. Both spectra are dominated by emission from the Ag 4*d*-derived states ~ 5 eV below E_F . This is due to the fact that the photoionization cross section for Ag is so much greater than for GaAs at these photon energies. Features from GaAs are evident, however, at a binding energy of ~ 2.5 eV. For atom deposition at 60 K, film growth occurs in a more layer-by-layer fashion than discussed above for 300 K because of reduced Ag mobility. Indeed, the photoemission results show that the Ag *d* bands are incompletely developed for depositions between 0.5 and 2 Å. It is not until ~ 5 Å that the bulk-like *d* bands have formed, and a step at E_F representing a thermally broadened Fermi-Dirac function has developed (the step is hard to see in this figure because it is small compared to the *d* bands).

Cluster deposition of Ag produces metallic particles on the surface at relatively low nominal coverages. Indeed, photoemission from these clusters indicates that the Ag *d* bands are fully developed by 1 Å deposition, and enlargement of the spectra near E_F reveals the sharp cutoff at E_F characteristic of metals (Fig. 4). For cluster assembly, the persistence of emission from the GaAs substrate at ~ 2.5 eV below E_F demonstrates that the substrate is only partially

covered by clusters (compare to EDC for atom deposition). With increased cluster deposition, the fraction of exposed substrate is diminished.

The nature of the contact between the cluster and the semiconductor surface is of particular interest. Core-level photoemission is the technique of choice to investigate chemical changes associated with reaction at the contact even though the clusters quickly become thick enough to prevent the escape of photoelectrons from the substrate. In Fig. 5 we show representative As 3*d* core-level spectra taken at $h\nu = 90$ eV (photoelectron mean free path, ~ 4 Å) for Co cluster deposition (right) and atom deposition at 60 K (left). For the clean GaAs(110) surface, the As (and Ga) 3*d* EDCs include contri-

butions from atoms at the relaxed surface (labeled 2) and in the bulk (labeled 1). These two components are observed at different binding energies because surface atoms relax into positions that are not bulk-like and the surface charge distribution differs from that in the bulk. The ratio of the intensities of components 1 and 2 is an indication of the surface sensitivity of the measuring technique. The deposition of overlayer material is often accompanied by line shape changes in the EDCs. These changes reflect differences in the chemical environments of Ga and As atoms, and they are an indication of substrate disruption and atomic intermixing.

For Co cluster deposition on GaAs(110), the only line shape changes from those of spectra collected from the clean surface correspond to a slight increase in the Gaussian width of the spectra and a decrease in the emission intensity from surface-shifted atoms (component 2) relative to that from bulk atoms (component 1) as coverage increases. The increased Gaussian width is due to the fact that the measurements for the clean surface were done at 60 K whereas those after cluster deposition were done at ~ 300 K, that is, thermal broadening. As will be discussed shortly, the relative intensity changes are important in understanding the electrical properties of the interface. No adsorbate-induced features are required to fit the core-level spectra. This conclusion for Co(clusters) on GaAs(110) is also valid for a wide range of different metal cluster overlayers on GaAs(110) (14, 15).

In contrast to the cluster assembly results, examination of the As 3*d* core-level spectra after Co atom deposition shows dramatic line shape changes (Fig. 5). The two components that dominate the spectra for depositions above ~ 2 Å are due to As atoms released from the substrate (1). In this case, the released As atoms tend to segregate to the surface region of the thickening Co overlayer, as indicated by the persistence of emission for thick metal coverages. Component 3 can be identified with As atoms at the surface, and component 4 arises from As atoms within the Co matrix near the surface. The redistribution of the released atoms depends on wheth-

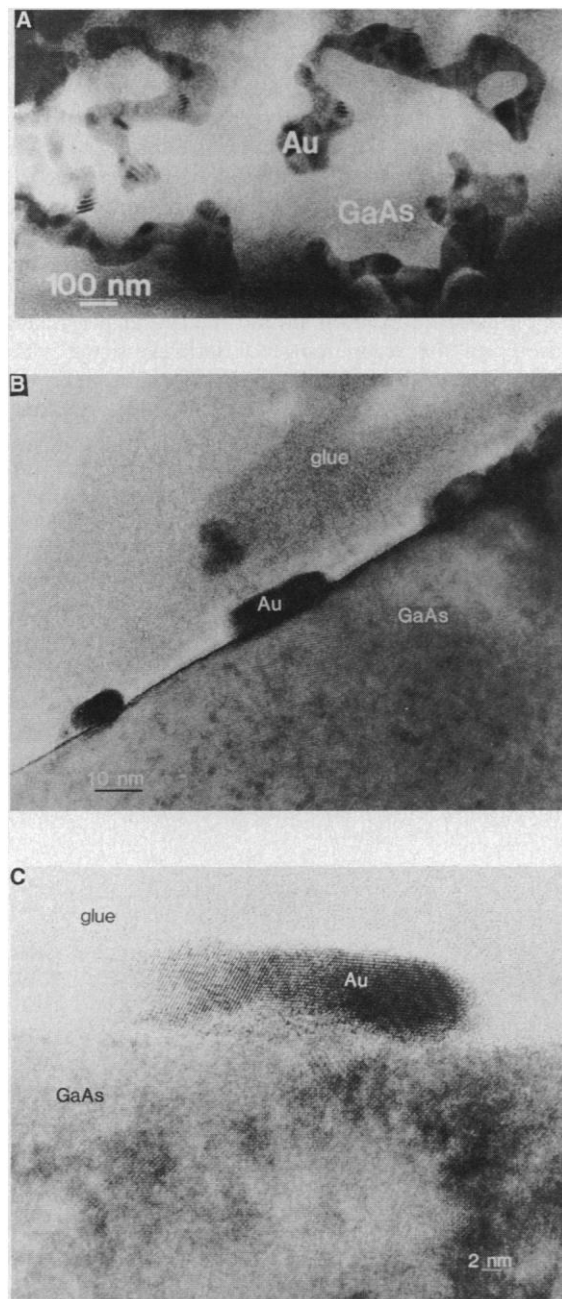


Fig. 3. Electron micrographs for 7 Å of Au deposited onto GaAs(110) by cluster assembly. Interconnected Au clusters are evident from the plan view (A). The cross-sectional image in (B) shows single clusters on the surface, and the high-resolution image (C) shows parallel lines in a single cluster that reflect two differently oriented crystallites of Au. [Adapted from (15), reprinted with permission of the American Physical Society, copyright 1990]

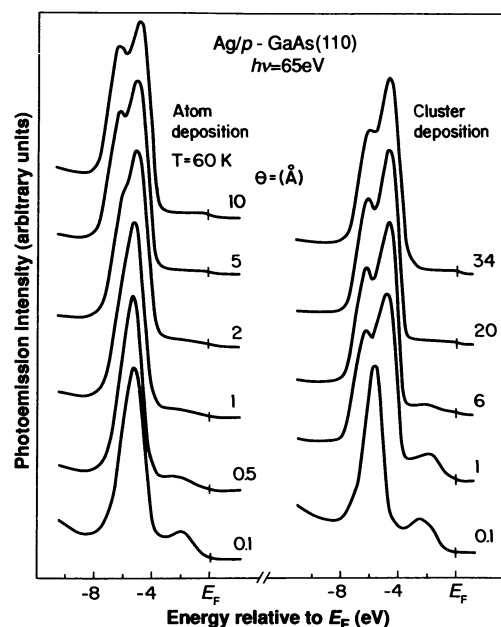


Fig. 4. Photoemission valence band spectra for Ag atom deposition at 60 K (left) and cluster assembly (right). These spectra demonstrate that cluster assembly produces metallic agglomerates even at very low coverage. This is reflected by the development of the metal-like 4*d*-derived states ~ 5 eV below E_F . For atom deposition at 60 K, the Ag layer grows in a layer-by-layer fashion and does not exhibit bulk-like metallic character until ~ 5 Å deposition. [Adapted from (15), reprinted with permission of the American Physical Society, copyright 1990]

er alloy- or compound-like structures can be formed and the solubility of the atoms in the overlayer, with nonequilibrium distributions for growth at 300 K, and even more nonequilibrium distributions for low-temperature growth. These processes are common at interfaces grown by conventional atom deposition (1). What is remarkable is that they are not observed at interfaces grown by cluster deposition.

For the clean GaAs(110) surface, there are no surface states within the band gap and E_F is located very near the valence band maximum (VBM) or conduction band minimum (CBM), depending on doping types. In particular, Ga and As 4*p* states that would be in the gap for the ideal surface are swept out of the gap by surface relaxation. Thus, there is no band bending at the surface. However, when a metal overlayer is formed, a potential energy barrier develops as a result of the creation of gap states near the semiconductor surface and a redistribution of charge in the region. This Schottky barrier produces the rectifying properties of these junctions (12). Despite years of study, the precise nature of these states remains controversial (1, 12).

For metal overlayers grown by conventional atom deposition methods, the position of E_F at the surface depends on coverage, with gradual movement into the semiconductor band gap after deposition of a few monolayers. The final E_F position and the coverage at which it is reached depend somewhat on the metal overlayer itself. In contrast, cluster deposition produces a barrier height that is nearly independent of coverage and overlayer metal.

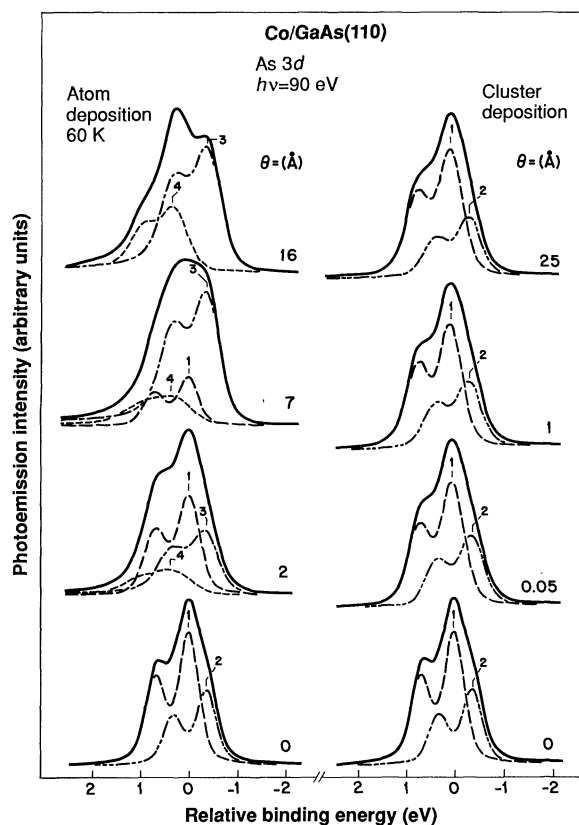


Fig. 5. Examples of As 3*d* core level photoemission spectra for Co atom deposition at 60 K and cluster assembly. Line shape analysis for the clean surface spectra shows emission from atoms that are part of the surface layer (labeled 2) and atoms that are part of the bulk (labeled 1). Cluster assembly introduces no new features but leads to a faster than expected loss of the surface component. Atom deposition produces surface disruption, and two new As bonding configurations (labeled 3 and 4) are readily apparent. [Adapted from (15), reprinted with permission of the American Physical Society, copyright 1990]

This can be seen from Fig. 6, where we show the E_F position relative to the CBM as a function of cluster deposition of Ag, Al, Au, Co, Ga, and Ti on *n*-GaAs(110). For the cleaved surface, E_F is within 60 meV of the CBM, but it moves to ~260 meV below the CBM for depositions as low as 0.02 Å. Thereafter, it moves only gradually to a position ~320 meV below the CBM. For 35 Å deposition, ~90% of the substrate has been covered by clusters and it seems unlikely that E_F will move much farther. For these same metals, the final E_F position for atom deposition varies from 0.6 eV below the CBM for Ga to 0.9 eV below the CBM for Au. It is therefore quite surprising to observe a pinning position for cluster deposition that is so high in the band gap, that exhibits so little coverage dependence, and that has so little metal specificity. Indeed, these results cannot be reconciled with existing models of Schottky barrier formation (12, 14, 15).

One can understand the results of Fig. 6, however, by recalling that the only change in core-level line shape observed after cluster deposition was due to a decrease in emission from the surface atoms relative to the bulk atoms (for example, Fig. 5 for Co). The existence of the emission feature from surface-shifted atoms is due to differences in charge occupation of the surface dangling bonds relative to the bulk bonds and to the surface relaxation. Thus, the change in the relative intensity of emission from the surface-shifted and bulk substrate atoms at the cluster-assembled interface is probably due to a loss of the surface relaxation around the cluster perimeters. This would result in the reappearance of intrinsic states within the semiconductor gap that would pin E_F , in agreement with the experimental results. In fact, such states have been predicted for an unrelaxed surface (18).

The E_F movements of Fig. 6 are due to energetic processes involved in cluster assembly rather than simply to the cluster morphology at the interface. For example, we showed above that large clusters are formed when Ag is deposited on GaAs(110) at 300 K in an atom-by-atom method. Although cluster deposition gives the same structure, the final E_F positions are quite different for both Ag (clusters)/GaAs structures (14, 15). The fact that energy is dissipated by the GaAs substrate for atom deposition but is dissipated by the Xe film for cluster deposition indicates that such

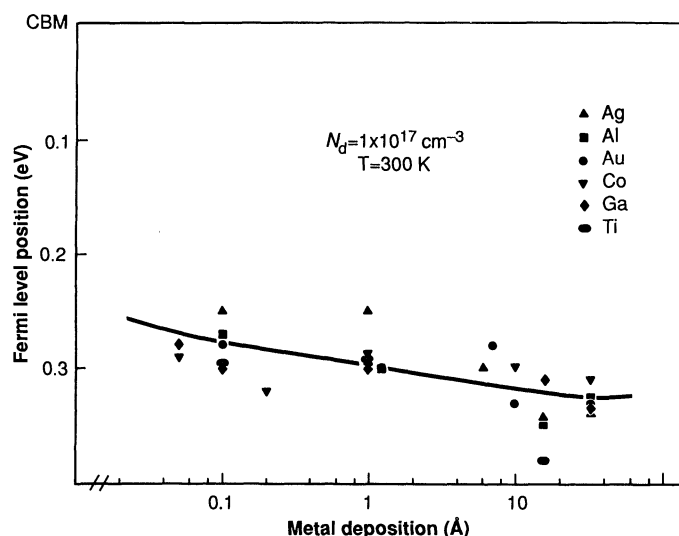


Fig. 6. Summary of results for the cluster assembly of a wide variety of metals onto *n*-type GaAs(110), showing the location of the surface E_F relative to the conduction band minimum as a function of deposition. All of the results fall on a smooth line, and none agree with results obtained for atom deposition and conventional Schottky barrier formation (N_d , doping concentration). [Adapted from (15), reprinted with permission of the American Physical Society, copyright 1990]

energies play a critical role in the properties of the interface.

In concluding this discussion of metal-semiconductor interfaces, we should make three cautionary observations. First, not all such interfaces formed by cluster deposition are as abrupt and free of disruption as those formed by Ag, Al, Au, Co, Ga, and Ge on the GaAs(110) surface. For cluster deposition on InP(110), for example, there is evidence for substrate disruption. Nevertheless, it is substantially less in every case than observed for atom deposition of the same overlayer. Second, most interfaces formed by cluster deposition appear to be stable in the sense that no chemical or E_F changes that reflect surface modification are observed upon warming to 300 K. The Ti/GaAs interface is a noteworthy exception, and this is believed to be due to the high reactivity of Ti with GaAs. In that case, the thermodynamic tendency to react is simply too great to be prevented. Third, cluster assembly produces a polycrystalline overlayer, and such a morphology may influence the electrical properties of a junction.

HTS-based interfaces. The prospects of forming abrupt or nearly abrupt interfaces are not limited to semiconductor-based systems, nor are these the only systems for which such interfaces are desirable.

Indeed, cluster assembly can be more generally applied to any system. One of the most stringent tests of the technique involves the assembly of clusters on the HTSs where there are strong driving forces for intermixing. In this case, the opportunity to create a boundary by solid-solid assembly is particularly attractive because the loss of superconductivity is associated with substrate disruption.

For the HTS materials, it has been established that atom assembly of all but a few overlayers results in disruption of the superconductor surface region (2). This involves the depletion of O from Cu–O bonds of the HTS in favor of overlayer oxide formation, processes that can be understood qualitatively from the relatively low heats of formation for Cu–O compared to most other oxides. The loss of O renders the crystal structure of the HTS unstable, and complex bonding configurations are formed that differ from those of the HTS. This O-depleted region exhibits a loss of states near E_F due to conversion from a superconducting to an insulating layer. Photoemission experiments place a lower limit of 50 Å for the extent of disruption. This layer complicates the use of these HTS materials as electronic devices, and its existence has frustrated fundamental studies that would reveal the magnitude of the superconducting gap. It was postulated, therefore, that constraints associated with solid-solid reactions might make it possible to form more ideal interfaces.

Investigations of cluster assembly of HTS interfaces to date (16, 17) have focused on Ge, Cr, and Au. They have involved photoemission characterization of cluster-HTS contacts for clean single-crystal surfaces prepared by the cleaving of $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_{8+y}$ (BSCCO) and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO). Of these HTS materials, BSCCO is the more stable as far as its surface characteristics are concerned, probably because of the self-passivating Bi–O layers of the (100) surface. The overlayer materials were chosen because they are representative of semiconductors, reactive metals, and nonreactive metals.

In Fig. 7A we show O, Bi, Cu, and Ge core-level photoemission spectra for Ge atom deposition on BSCCO. The clean surface spectra were obtained at 300 K after a single crystal was cleaved in ultrahigh vacuum. They show that Cu atoms are bonded to O in formally 2+ states, as characterized by the main line at ~933 eV and the broad feature at higher energy. The latter is a satellite associated with coupling of the Cu 2p core hole to the electrons in the 3d⁹ shell; eight multiplet features are contained within the satellite. The O atoms in BSCCO are bound to Bi, Sr, Ca, and Cu, depending on the site in the lattice. Inequivalent bonding configurations are expected and have been observed (2), although the O 1s feature in Fig. 7 does not resolve them. For Bi, the 4f doublet is sharp and well-defined. After atom-by-atom deposition of 1 Å of Ge, the Ge 2p_{3/2} core level appears at 1219 eV and there is a new O 1s component at 530.5 eV. These energies suggest the formation of GeO₂-like bonding configurations. The appearance of a new dou-

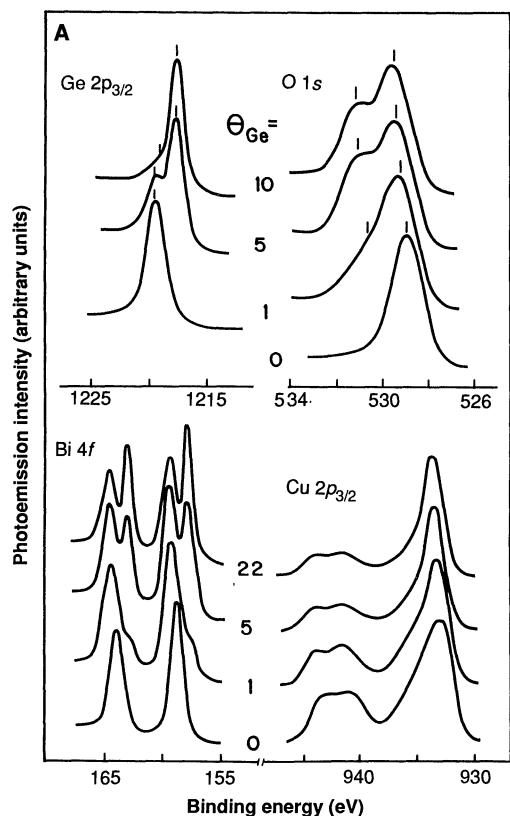
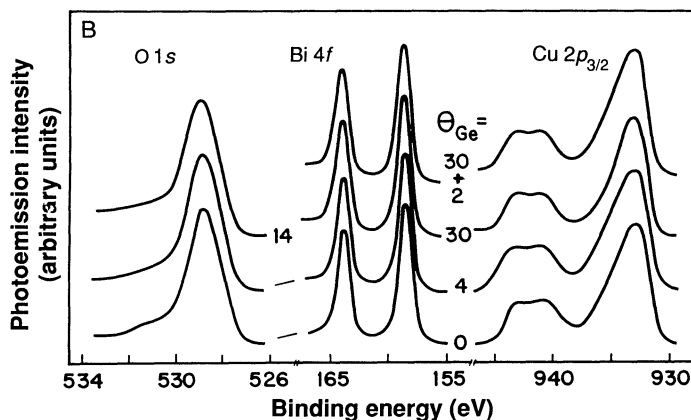


Fig. 7. (A) Core-level photoemission results for Ge atom deposition onto cleaved single-crystal BSCCO(100) at 300 K, showing that the adatoms induce chemical changes for each of the substrate components. Moreover, the Ge atoms appear in GeO₂-like bonding configurations during the early stages of overlayer growth. This results in the leaching of oxygen from the HTS substrate to form an overlayer oxide and produce a disrupted HTS surface region. Ultimately, reaction is kinetically limited and elemental Ge starts to form. [Adapted from (17), reprinted with permission of the American Institute of Physics, copyright 1990] **(B)** Core level photoemission results for Ge cluster assembly on BSCCO(100), showing that the changes induced by the presence of the Ge clusters are negligible. For these measurements, multiple cycles of 2 or 5 Å Ge depositions onto Xe followed by Xe desorption were used to produce an overlayer of nominal thickness 30 Å. The deposition of 2 Å of Ge by atom deposition onto this overlayer produced no changes, indicating complete coverage of the substrate. [Adapted from (17), reprinted with permission of the American Institute of Physics, copyright 1990]



blet in the Bi 4f emission indicates that Bi atoms have been released by the disruption of Bi–O planes, and the decrease of the intensity of the Cu 2p_{3/2} satellite relative to the main-line emission indicates disruption of Cu–O planes as well. With increased Ge deposition, these disruptive processes continue, at least until the transport of O to continue the GeO₂-like reaction becomes kinetically curtailed. This is evident in the photoemission results in the stabilization of the line shapes of Bi and Cu and the appearance of a Ge component at 1217.5 eV that reflects Ge growth atop the Ge oxide on the disrupted HTS layer. Ultimately, the overlayer becomes Ge-like with a small number of Bi atoms that segregate to the surface. The result is a highly complex interface. The extent of HTS modification is much smaller for BSCCO than for YBCO where all evidence of Cu²⁺ bonding is lost during the early stages of overlayer growth as Cu atoms within at least 50 Å of the surface are reduced from 2+ to 1+ valence.

In Fig. 7B we show results for Ge cluster deposition on BSCCO obtained after cleaving BSCCO in situ to expose a (100) surface and depositing Ge overlayers by the cluster-assembly method. To assure a maximum sensitivity for changes in substrate core-level spectra, we deposited relatively small amounts of material but repeated the deposition process many times, namely, growth by 2 Å increments to 20 Å total, then in 5 Å increments to a total of 30 Å. It is important to note that the longer photoelectron mean free path for these x-ray photoelectron spectroscopy measurements and the relatively small size of the clusters assured that the region beneath the clusters could be inspected. The measurements were carried out at 20 K, and the sample temperature was always below ~100 K during the assembly cycles.

The most important message from the Ge cluster-assembly experiments on BSCCO is that there were no significant changes in the Bi 4f, Cu 2p_{3/2}, or O 1s emission. Moreover, there was no evidence for oxidation of Ge. Indeed, the Ge spectra did not change with coverage, consistent with observations made above that these clusters contain enough atoms to be bulk-like. We conclude that the Ge(cluster)/BSCCO interface is abrupt and free of substrate disruption, with the tendency to form a Ge oxide frustrated by cluster–solid reaction constraints.

For cluster assembly, there is the possibility that the surface is not completely covered by the deposited layers. Photoemission results give information about the attenuation of the substrate signal, but partial exposure cannot be completely ruled out for irregular surfaces. To test this, we deposited 2 Å of Ge by conventional atom deposition onto the 30 Å Ge(cluster)/BSCCO interface. As shown in Fig. 7B, there was no discernible change. This titration of the surface indicates that the cluster-assembled overlayer is effectively complete (any uncovered substrate would be modified by the additional Ge and there would be spectral line shape changes). Finally, to examine the stability of the Ge(cluster)/BSCCO interface, we warmed the system to 300 K. No changes were observed, and we conclude that the interface is stable in this temperature range. Of course, heating to higher temperature would allow the system to seek a lower energy configuration, but that configuration is not known and has not been investigated.

Although the results for Ge cluster assembly are promising, it would be incorrect to assume that all overlayers on HTS materials are nonreactive when formed by cluster assembly, just as it was incorrect to assume that all metal-semiconductor interfaces remain completely unreacted. This can be understood in terms of the heats of formation of the oxides. This caveat notwithstanding, interfacial reactions for the more reactive metal overlayers such as Cr are dramatically reduced from those associated with atom deposition.

A final issue to be addressed for cluster assembly involves effects associated with heating to well above the growth temperature. In

this case, one must consider the relative surface free energy of the overlayer and the substrate, together with the interface energy. We have investigated cluster stability for Au(clusters)/BSCCO. In this case, the overlayer was grown by repetitive cycles of Xe condensation with the deposition of 2 Å of Au per cycle to a total amount of 20 Å. For growth at temperatures below ~100 K, the photoemission results indicated complete coverage of the BSCCO surface. When warmed to 300 K, however, there was evidence of delamination from the surface and additional roughening of the Au layer. Although intriguing, the structure of this metastable overlayer is not yet well characterized.

Conclusions

We have shown that it is possible to eliminate certain processes that occur during conventional methods of interface growth simply by eliminating contact between the two materials until bulk-like properties are developed for both. The gentle joining associated with cluster assembly circumvents the dissipation of energy derived from processes such as adatom impact, bonding, and coalescence directly into the substrate. In principle, these interfaces are more suitable for theoretical modeling of processes and properties, and their properties are substantially different from those of conventional interfaces.

It should be emphasized that investigations into controlling and altering interface properties in this manner are very recent, and the understanding of these interfaces is still in its infancy. As far as future studies are concerned, it is expected that cluster assembly will make it possible to address a number of issues concerning surface magnetism, catalysis, and compound growth. It should be possible to produce isolated magnetic clusters so that the fundamental properties of these systems and their interactions can be investigated. Cluster-assembled interfaces can also be used as model catalysts, and the properties of molecular chemisorbed species on these clusters can be probed. Intriguing issues concerning surface wetting and cluster sintering can be addressed by growth of clusters and nanostructures. Finally, it should be possible to address the transition from atomic-like materials to bulk solids by studying the properties of different sized clusters, synthesized by variations on the techniques described. Many of these studies are, of course, under way, and substantial progress is expected in the near future.

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Cadherin Cell Adhesion Receptors as a Morphogenetic Regulator

MASATOSHI TAKEICHI

Cadherins are a family of cell adhesion receptors that are crucial for the mutual association of vertebrate cells. Through their homophilic binding interactions, cadherins play a role in cell-sorting mechanisms, conferring adhesion specificities on cells. The regulated expression of cadherins also controls cell polarity and tissue morphology. Cadherins are thus considered to be important regulators of morphogenesis. Moreover, pathological examinations suggest that the down-regulation of cadherin expression is associated with the invasiveness of tumor cells.

AMONG VARIOUS ASPECTS OF ADHESION-MEDIATED control of cell behaviors, the adhesion selectivity is especially important in regulating morphogenesis. Selective cell adhesion or cell sorting is observed in a wide variety of developmental and pathological events where specific cells are connected only to particular cell types (for example, egg-sperm interactions, neuronal connections, and lymphocyte homing). Essentially all types of animal cells appear to have such adhesive properties, as suggested by classical findings that cells derived from any one particular tissue can be sorted from those of other tissues when mixed (1). It is thus likely that cell adhesion selectivity is a general property of cells and participates in the entire process of morphogenesis.

Cell-sorting behaviors *in vitro* were often theoretically explained by various models such as the differential adhesion hypothesis (2). With the recent progress in identification of cell adhesion receptors, we are now unraveling the molecular basis of the selectivity of cell adhesion. The receptors required for cell adhesion are classified into several groups, of which two major groups are the immunoglobulin (Ig) superfamily and the integrin superfamily. Many members of the Ig superfamily specifically bind to other molecules identical to themselves (3). This phenomenon is called homophilic binding, and it suggests that the members of the Ig superfamily may be involved in specific cell-cell interactions. Some members of the integrin superfamily bind to particular members of the Ig superfamily

expressed on the surface of certain cell types and thus act as mediators for specific cell-cell binding interactions, especially in the immune system (4). In addition to these molecular families, selectins are also crucial for specific lymphocyte adhesions (4). The *Drosophila* molecules fasciclin I and III also show homophilic cell binding specificities (5).

Although these classes of molecules participate in events that occur in particular cell systems, they may not be involved in the general phenomenon of cell adhesion specificity. Cadherins are another protein family of cell-cell adhesion receptors (6). All cell types that form solid tissues express some members of this molecular family, and each member displays a homophilic binding specificity. Therefore, cadherins could define adhesion specificities for the majority of cell types. Moreover, cadherins may take part in other cell-cell interaction phenomena, such as the formation of a junctional complex, cell polarization, or tumor invasion. In this article, the properties of cadherins are summarized, and the mechanisms by which this molecular family regulates morphogenetic and neoplastic cell behaviors are discussed.

Basic Properties of Cadherins

Cadherins are Ca^{2+} -dependent cell-cell adhesion receptors that have been identified in vertebrates. They bind cells by means of homophilic interactions. As expected from the importance of Ca^{2+} in cell-cell adhesion, cadherins are important for establishing and maintaining intercellular connections. Generally, cells with fewer cadherin molecules are less adhesive. However, when cadherin-deficient cells are transfected with complementary DNA (cDNA) that codes for cadherins, they acquire the Ca^{2+} -dependent, cadherin-mediated adhesive activity (6). In addition, cell morphology is generally altered, for example, from the fibroblastic cell type to the epithelial cell type, which reflects increases in the cell's adhesiveness. Treatment of cell layers that express cadherins with antibodies to these cadherins induces dispersion of cells (6). As long as cadherins are functioning, inactivation of other adhesion systems has little effect on cell-cell adhesion (7). Cadherins are therefore the cell-cell adhesion receptors that are most important for the formation of physical cell-cell associations.

Cadherins are divided into subclasses, all of which share a common basic structure (Fig. 1). Four subclasses are well charac-

The author is in the Department of Biophysics, Faculty of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606, Japan.