

Metal-semiconductor interfaces

The mixing of atoms at boundaries produces regions with distinctive properties; the resulting combinations have a wide variety of uses—from smaller microelectronic devices to new, exotic composite materials.

John H. Weaver

In my view of the evolution of solid-state physics, the 1970s were the decade of bulk phenomena. We made enormous strides in understanding crystals—we mapped their energy bands, developed clever computational schemes and became experimentally and theoretically adept at characterizing solid crystals. At the same time, we developed the tools to study surfaces, and we continue to make amazing progress in this area, as Shuk Y. Tong explained in a recent article (*PHYSICS TODAY*, August 1984, page 50).

Today, the drive to develop ever-smaller microelectronic devices, exotic multicomponent composites, complex catalysts and biological implants is increasing the need to understand interfaces. It seems to me that the 1980s, and possibly the 1990s as well, will be viewed as the decade when we brought boundary regions under microscopic scrutiny.

If the study of interfaces is indeed the next step in solid-state physics, it is a step made possible by all we have learned about bulk and surface phenomena and by the fancy new tools developed to investigate solids and

surfaces. The excellent work done with crystalline materials and their surfaces makes it possible, for example, to consider interfaces where the atoms are not uniformly distributed; with such interfaces we may be able to create unique atomic structures stabilized by the surrounding material. Furthermore, supercomputers and elegant computational schemes allow quantitative modeling of increasingly complex systems. In light of the wide range of experimental and theoretical tools at our disposal, it appears that the next few years hold great promise for major breakthroughs in our understanding and control of the properties of interfaces.

The interfacial zone

An interfacial zone is a transition region between two different materials. It might be the boundary formed when a metal is deposited onto gallium arsenide in the modulation-doped field-effect transistor diagrammed in figure 1, or the boundary between NiSi_2 and silicon in a buried metallic layer of a three-dimensional integrated circuit.

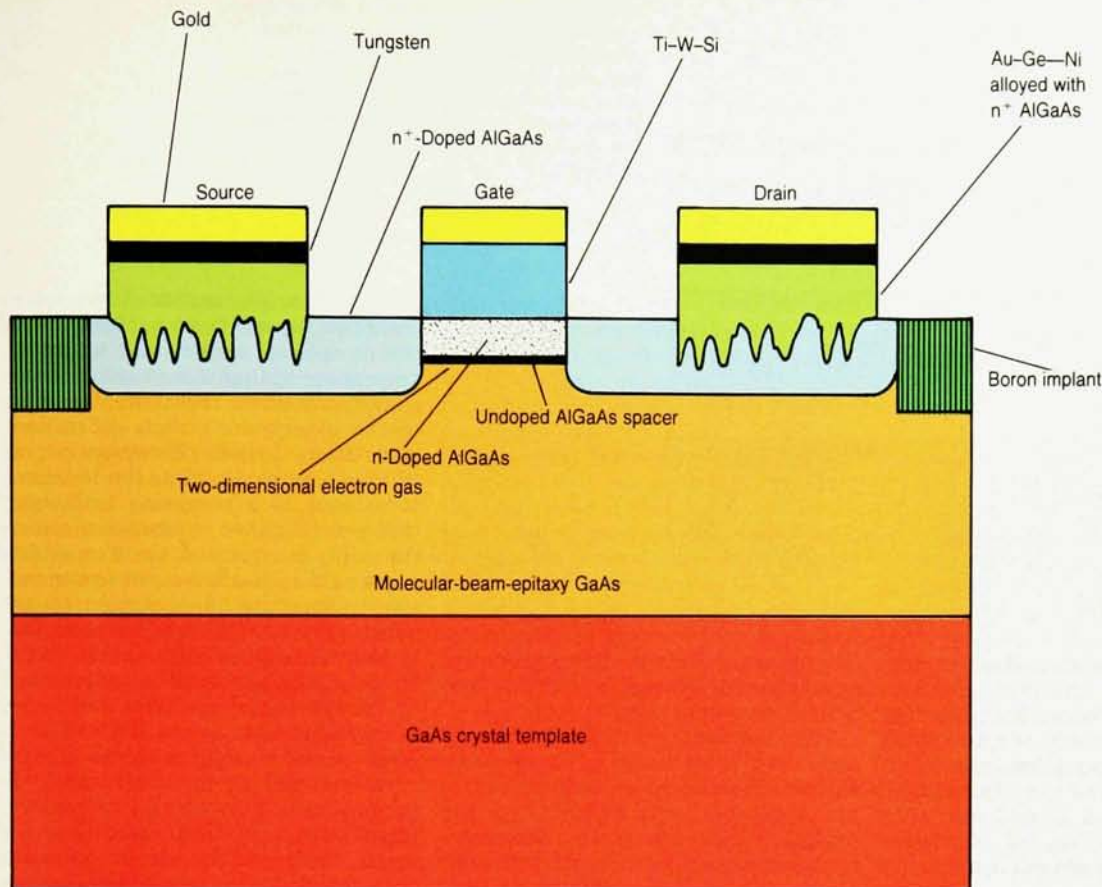
Interface research focuses on the unique properties of such boundary regions. It seeks to understand how the properties of boundary regions differ from those of the bulk solids on either side and how these regions influence

the behavior of the composite. The interface zone can be atomic in scale for abrupt interfaces, or it can extend for tens or hundreds of angstroms for interfaces where the two materials react chemically. The properties of the interface region are influenced by, for example, dimensional constraints (quantum effects), disorder, defects, the formation of compounds, heterogeneity and kinetics. Boundaries are therefore fascinating regions, rich in both scientific challenge and technological importance.^{1,2}

Interface research is inherently interdisciplinary, blending experimental and theoretical work in physics, chemistry, materials science and engineering. Many of the issues are so complex that teams of researchers join forces to address them. Not surprisingly, the scientific and technological relevance of interface research have prompted significant cooperation among academic, government and industrial laboratories.

Solid-state physicists are showing increasing interest in a subclass of interface phenomena, namely those at metal-semiconductor interfaces. One indication of this interest is the growing number of meetings and conferences³ on the subject. One finds wide-ranging discussions of interface phenomena at conferences sponsored by

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Interfaces. This schematic diagram of a modulation-doped field-effect transistor shows a variety of interfaces encountered in microelectronic devices. The two-dimensional electron gas is a result of the GaAs/AlGaAs heterojunction. The gate is composed of a titanium-tungsten-silicon composite, which creates a Schottky barrier on the doped AlGaAs, and a gold overlayer, which serves as the connector. Contacts to the n⁺-doped AlGaAs regions are made by reacting them with a gold-germanium mixture to which nickel is added to form an ohmic contact. The tungsten layer serves as a diffusion barrier that isolates the ohmic contact from the gold layer.

Figure 1

organizations such as the American Vacuum Society, the Materials Research Society and The American Physical Society, and there are numerous specialty symposia, workshops and meetings on the subject.

This article focuses on the formation of metal-semiconductor interfaces. After an overview of interfaces in microelectronic devices, we consider interface morphologies and the experimental probes used to study them. We then discuss the vanadium-germanium system to see how reactive junctions evolve, to show the implications of local chemical bonding and to illustrate the applicability of bulk concepts. We consider the nickel-silicon system to show how one can characterize abrupt interfaces, and we conclude with discussions of modified surface reactivities and diffusion barriers.

Microelectronic devices

Interfaces play a central role in

device performance and indeed their importance has prompted major corporations that fabricate microelectronic materials to invest significantly in studies of either interface properties or device properties that are influenced by interfaces. As a device shrinks, boundary regions represent a greater and greater fraction of its volume, and may ultimately determine its electronic characteristics and stability.

In the modulation-doped field-effect transistor sketched in figure 1, we find a complex, multicomponent system with a great many interfaces. The AlGaAs/GaAs boundary itself is the core of the device and produces⁴ a confinement region for the electron gas. Contact to the device is made through ohmic metal-semiconductor interfaces that serve as the source and drain. Schottky-type interfaces form when one deposits a Ti-W-Si overlayer on the n-doped AlGaAs. One introduces diffusion barriers to minimize

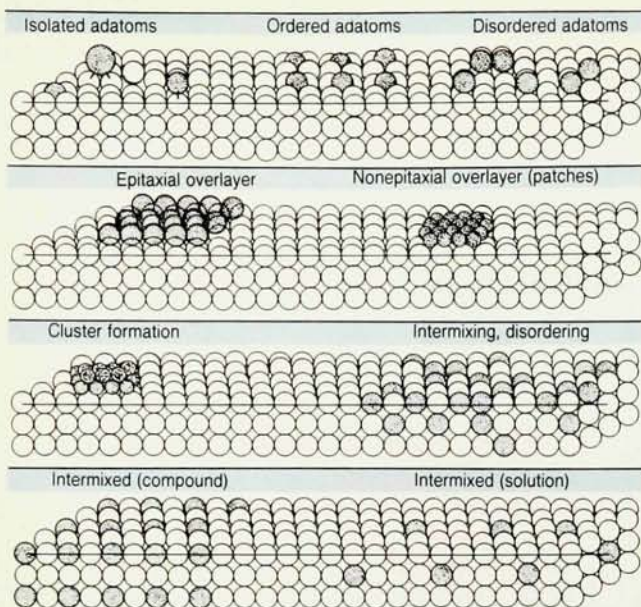
atomic intermixing of the gold metallization layer and other layers. During lithographic processing of the device, polymer interfaces play important roles. Bonding the fabricated chip to its package introduces even more interfaces.

It should be clear from figure 1 that a modern microelectronic device such as the MODFET contains many different materials. As devices become increasingly complex, greater and greater demands are placed on materials stability. When one is designing and optimizing a multilayer device, the challenge is to determine which elements, compounds or alloys are most suitable in particular applications, to investigate the properties those materials have when they form interfaces, to identify the extent of intermixing and to assess the stability of the interfaces during processing and operation.

Interface growth morphologies

Figure 2 shows the morphologies of an interface at several stages of evolution. Although the drawings are highly simplified compared with the actual situation in a device such as the MODFET described in figure 1, they allow us to identify many issues of concern in interface research.⁵

The top drawing in the figure depicts the adsorption of foreign atoms on a



Evolution of an interface. In this pictorial description the development of an interface begins with isolated adatoms on a surface and proceeds through an intermixed boundary layer. The text focuses on the situation in the bottom two panels, which depict cluster formation and intermixing for compounds and solutions. (From reference 5.)

Figure 2

surface, the precursor stage to the formation of an interface. Surface science has long been interested in chemisorption and physisorption, and has discovered a great deal about surface bonding, surface reconstruction and the formation of ordered and disordered monolayers. Such information is very important for modeling overlayer growth.

The second drawing in figure 2 shows the formation of a monolayer of adatoms. Epitaxial growth of perfect overlayers in crystallographic registry with the substrate is most likely when the lattice parameters of the overlayer closely match those of the substrate and when the tendency for intermixing is not strong. Nonepitaxial growth is more likely when there is a large lattice mismatch.⁶

Layer-by-layer growth represents only one of the common growth modes. Other modes include the formation of three-dimensional clusters over the first monolayer or directly over the substrate, as illustrated in the third diagram in figure 2.

These growth schemes are most applicable when there is minimal atomic intermixing and when convergence to bulk properties is rapid on both sides of the sharp boundary. Our focus here, however, is on intermixing, depicted by the bottom two pictures in figure 2. For a single-phase bulk system in equilibrium, we expect intermixing to produce either a solid solution or a compound. The former is favored when the interactions of atom A with atom B are chemically equivalent to those of A with A or B with B; the driving force for mixing is then entropic, not chemical. The right side of the third diagram shows the outcome. On the other hand, if a compound forms, the chemical

environments for the different atoms should be well defined, as shown in the bottom diagram.

This description of the interface in terms of the formation of compounds assumes that the system is in equilibrium and that bulk thermodynamics applies to ultrathin layers. Interface research generally deals with metastable or nonequilibrium materials systems that have novel properties stabilized by interfacial or diffusion constraints. We will return to these systems when we discuss models of reactive interfaces and compare thin overlayers formed at room temperature with fully reacted, thick interfaces.

Experimental probes

The experimental techniques used to examine evolving interfaces include those developed for surface studies as well as those that can probe deeper into the solid. Figure 3 depicts several techniques and the means by which they probe an interface, which is shown evolving from an ordered overlayer (left) to an unreacted cluster (center) to a heterogeneous intermixed system (right).

Ultraviolet, x-ray or synchrotron-radiation photoemission techniques (see the article by Franz Himpsel and Neville Smith, *PHYSICS TODAY*, December, page 60) are sensitive to the chemical state of atoms in the overlayer as well as to their distribution, and can therefore detect changes in bonding and charge distribution. (The cover of this issue shows a photograph of a small-spot high-resolution x-ray photoemission spectrometer.) Low-energy electron diffraction reveals whether there is ordering on the surface and gives structural information.

Auger and angle-resolved Auger spectroscopies use electrons to identify the atomic species present and to determine their spatial distribution; these spectroscopies also reveal the structure of the overlayer through diffraction modulation. Inverse photoemission, in which electrons stimulate the emission of photons, is a promising technique that gives detailed information about the empty electronic states in an evolving interface. Surface EXAFS (extended x-ray absorption fine structure), in which photons stimulate the emission of electrons, gives information about bond lengths and surface geometries. The scattering of medium- and high-energy ions (energies in the keV and MeV ranges) is useful in studies of thin overlayers and thick films, respectively. Ion milling, in which ions remove target atoms, is used extensively to obtain profiles of the atomic composition of thick reacted overlayers. Transmission and scanning electron microscopies give images that show the morphology of the interface. To get the best picture of a complex interface such as that sketched in figure 3, one uses information from a variety of these techniques.

Cluster-induced reactions

Understanding the transition from a system composed of isolated free atoms far from a solid surface to one in which those atoms are intermixed with the solid is critical for treating interface reaction phenomena. To describe the process we must know the details of the adatom-substrate and adatom-adatom chemical bonding. Systematic studies in which one changes the chemical parameters (such as the atoms themselves, their electronic configuration and their bonding) or the physical parameters (temperature and defect density, for example) make it possible to assess and control the onset of reaction.

Several recent experimental studies of ultrathin metal overlayers on semiconductors have shown⁷ that there are systems in which no reaction occurs below a threshold coverage. Although it is difficult to calculate the reaction energetics from first principles, a promising idea involving the clustering of adatoms at low coverage has been advanced⁸ to describe these delayed

reactions. In this model it is energy provided by the disruption, or breaking up, of the clusters that initiates intermixing. The model has intriguing implications: We must assume that adatoms on the surface are weakly bound to the substrate. Disruption of the substrate is then related to the delicate balance of the growing clusters, the strained boundary layer between the cluster and the substrate, the heat of formation of the reacted phase and the largely unknown influence of surface defects and temperature.

This cluster-induced-reaction model has been tested⁷ by photoemission studies of several metal-semiconductor interfaces. These show that cluster disruption occurs at an average coverage of $4\text{--}15 \times 10^{14}$ atoms/cm² for Ce/Si(111), V/Ge(111), Sm/GaAs(110) and Al/GaAs(110). Medium-energy ion-scattering results also suggest⁹ nickel clustering on the (111) surface of silicon prior to the onset of reaction. I should note that if reaction starts in this way, through cluster formation, the subsequent surface will be highly heterogeneous, with reacted regions and regions of free substrate.

Reactive intermixing

It is crucial to determine the properties and spatial extent of the species that form once intermixing begins. The greatest single challenge has been, and will continue to be, characterizing a thin, inherently multiphase region

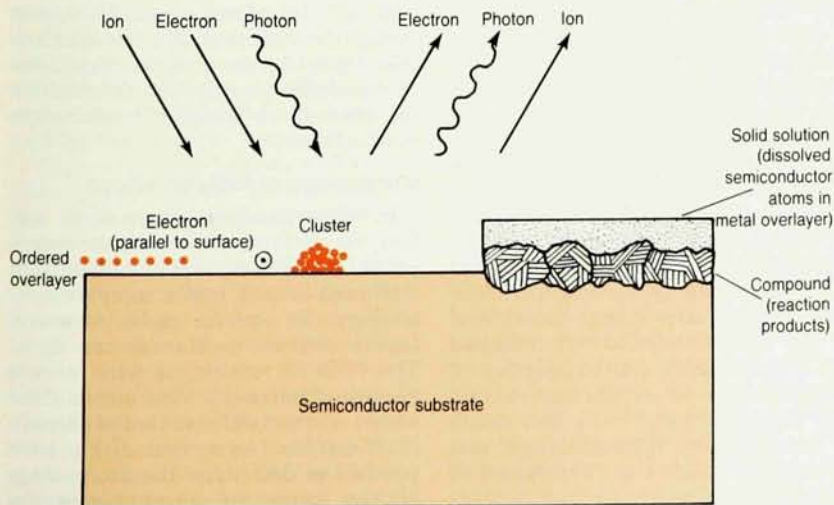
that may be subject to change with temperature and operating conditions. Nevertheless, recent work¹⁰ with models has shown significant success in describing evolving junctions and establishing similarities and differences between thin layers and bulk systems. A look at one of our own experiments at the University of Minnesota will allow me to describe the model in detail and to examine several important issues.

The reactive junction V/Ge(111) exhibits¹⁰ intriguing properties related to intermixing. Figure 4 shows photoelectron-energy-distribution curves for vanadium deposited onto the cleaved (111) surface of germanium at 300 K. To obtain these results, we used highly monochromatic synchrotron radiation to excite 3d core photoelectrons in germanium. The binding energies of these electrons change as the charge distribution around the germanium atom is modified. This sensitivity to the chemical environment of the germanium atom is evident from the way the appearance of the emission from the germanium 3d core level changes as a function of vanadium coverage. For coverages below about 2 monolayers, or about 1.5×10^{15} atoms/cm², the changes are subtle because the vanadium adatoms cluster, as discussed above. When reaction is induced, the spectra show modifications as two new, well-defined chemical environments are established. As the number of deposited vanadium atoms in-

creases, the energy-distribution curves show that the amount of the reacted species labeled 2 grows, but that at high coverage it is supplanted by the one labeled 3.

If we return to figure 3, we can form a qualitative picture of the evolving interface. At the lowest coverage, there is clustering and little change in the line shape of the core emission; then intermixing sets in and the first feature in the spectrum characteristic of reacted material appears; finally, the interface becomes rich in the overlayer material, with some substrate atoms in solution, and the final spectral feature appears. In light of this picture the spectral observations of figure 4 are very important because they show that the boundary region of the vanadium-germanium system supports distinct chemical configurations, or phases, rather than random distributions of atoms.

To give a quantitative description of an evolving interface, we need to know the amount of each phase present in the probed region at each stage. To do this in our vanadium-germanium system, we decomposed the experimental results of figure 4 into spin-orbit doublets, as shown on the right side of that figure, and determined the relative amounts of each component. By normalizing these amounts to the total germanium 3d emission for the clean surface, we obtained the curves of growth versus attenuation shown in



Techniques used to examine evolving interfaces. Indicated here are photoemission (photons in, electrons out), Auger spectroscopy (electrons in, electrons out), inverse photoemission spectroscopy (electrons in, photons out), low-energy electron diffraction (electrons in, diffracted electrons out), ion scattering (ions in, ions out), scanning electron microscopy (electrons in, electrons out) and transmission electron microscopy (electrons in parallel to surface, electrons out for lattice imaging).

Figure 3

Photoemission energies and line-shape decompositions. The photoemission energy-distribution curves (left) reveal chemical changes through the evolving line shape of the germanium 3d core emission. The colored curves on the right are line-shape decompositions of a few of the energy-distribution curves. They show the presence of three distinct phases: substrate germanium (1), V_2Ge_3 (2) and a solid solution of germanium dissolved in vanadium (3). Figure 4

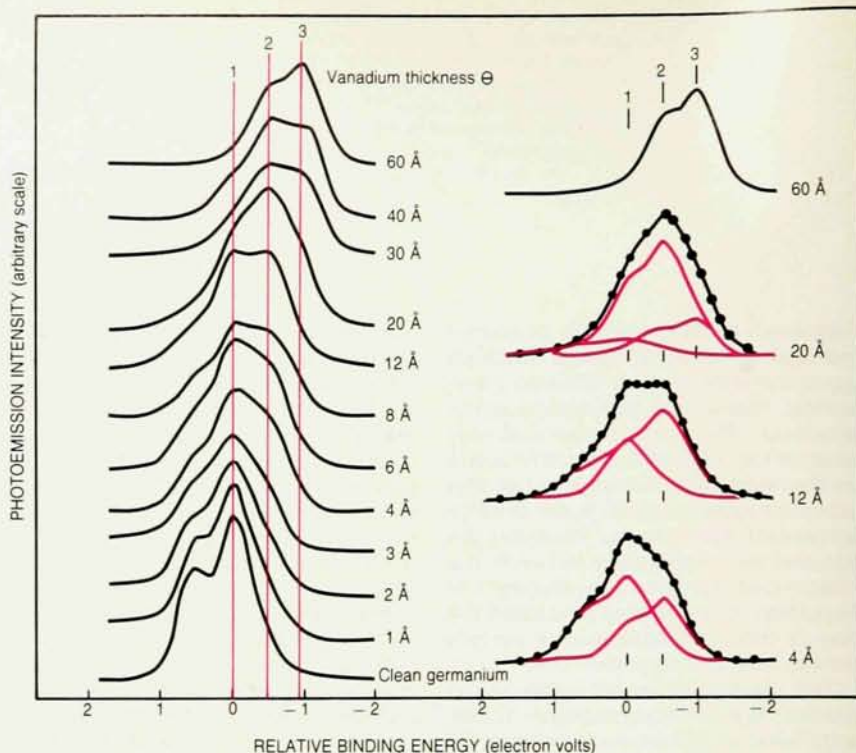


figure 5. These curves show that the first reacted species appears at a coverage near 2 Å, that it grows to dominance by 12 Å and that the final germanium configuration becomes clear at coverages above 20 Å. There is little attenuation of this final component for vanadium depositions from about 40 to 80 Å, but it diminishes rapidly above about 80 Å.

To make the most effective use of these photoemission results for quantitative modeling, we must make some important assumptions about the reacted layer. First, we must assume that because the experimental results show that distinct phases form, we can write suitable chemical equations to describe the formation of those phases. For these reactions to proceed, there must be sources of vanadium and germanium atoms—an evaporator and substrate, respectively. The number of germanium atoms present in the reaction region is controlled by outdiffusion from the substrate through the reacting layer, or possibly by conversion of one phase into another.

Second, we must somehow describe the partitioning of the adatoms between the reacted phases and take account of how this partitioning changes.

We can describe the growth of two competing phases in a mixed-phase regime by the lever rule of thermodynamics, according to which the amount of each phase depends on its composition and the overall mole fractions of the constituents. To apply this rule to reacting interfaces means assuming, of

course, that thermodynamic concepts are applicable to ultrathin layers.

It is only the ability of the model to fit experimental results that indicates that the above three assumptions are reasonable.

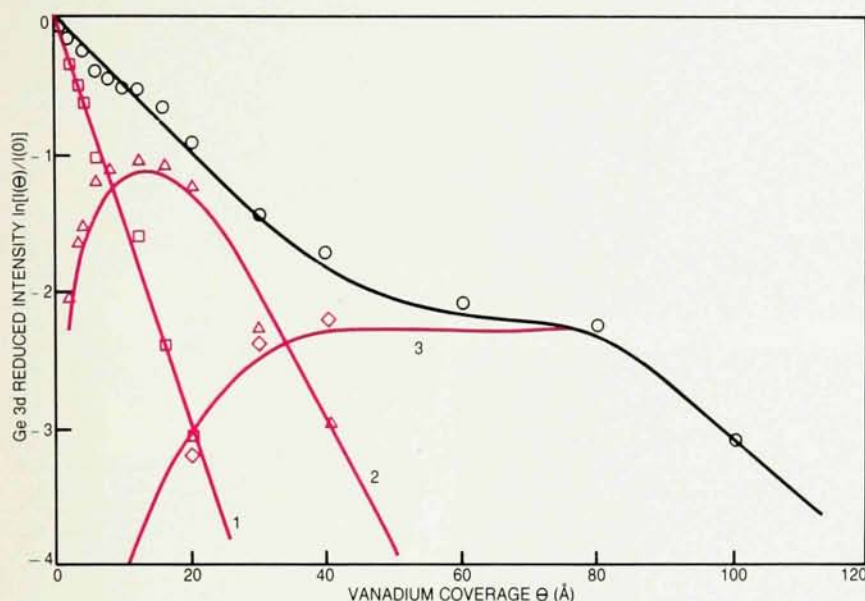
The model then describes the excitation of germanium 3d electrons in the reacted medium and the propagation of those electrons to the surface. By taking into account the intrinsic properties and the diffusion-limited growth of the reaction products, it is possible to model the growth-attenuation curves of figure 5. The fit of the colored curves to the experimental data in the figure indicates that the model succeeds in describing the experimental results for the vanadium-germanium system and allows quantitative discussion of this evolving interface—and of other intermixed systems as well. In particular we can conclude that the range over which the first reacted species forms is 0–34 Å and that its composition is V_2Ge_3 . The second phase does not form at the expense of the first—they grow simultaneously and in competition—so the first phase that forms on the semiconductor persists unless thermally modified. The second phase is present at much lower coverages than experimental sensitivity allows us to detect, and its low germanium content indicates that it is probably a solid solution of germanium in polycrystalline vanadium. The pure metal overlayer starts to form at very high coverage, and then only because the outdiffusion of germanium is restricted.

We now see that the interfacial zone is highly heterogeneous, with both vertical and lateral variation in properties. To make matters more complicated, the morphology also varies with temperature because of changes in the transport of germanium from the substrate. Indeed, studies involving temperature variations demonstrate that one can sustain the first reacted phase up to coverages of at least 100 Å by moderate heating and that one can control the relative amounts of the two phases.

We can apply the same technique to other reacting systems and obtain results analogous to those for the vanadium-germanium system, as long as the reaction products have sufficiently large chemical shifts in their photoemission spectra. Such characterization of interfaces should become straightforward with the new synchrotron light sources, and we should see increasingly quantitative information for even more complex multicomponent systems.

Morphology of $NiSi_2$ on silicon

In the vanadium-germanium system, we were considering a heterogeneous boundary layer that evolves from disrupted islands into a complex morphology. In special cases, however, highly ordered overlayers can form. The $NiSi_2/Si$ system is such a case because of the nearly ideal match of the nickel silicide lattice to that of silicon's (111) surface. As a result it has been possible to determine the morphology of the transition layer better for



Growth versus attenuation. These curves, derived from those in figure 4, show the relative amounts of the phases (labeled 1, 2 and 3) present in the probed V/Ge interfacial region as a function of vanadium coverage. The first reacted phase starts to form at a coverage near 2 Å. It is dominant near 12 Å and is ultimately replaced by the final component. It is not until about 80-Å coverage that a pure vanadium film starts to form. Modeling based on the assumptions discussed in the text produces the colored lines and provides quantitative information about the evolving interface. Figure 5

NiSi₂/Si than for any other system.

When one deposits¹ thick layers of nickel onto the (111) surface of silicon, the first reaction product is a metal-rich silicide, Ni₂Si. Heating the interface converts the metal-rich silicide into NiSi and, ultimately, into NiSi₂, the most thermodynamically stable phase. This final reaction product has important properties, including an excellent lattice match with silicon, a simple CaF₂ crystal structure and a metallic character. The lattice match raises the intriguing possibility of growing a three-layer structure of the form silicon-silicide-silicon. Indeed, such structures were first grown by workers at AT&T Bell Laboratories and Tokyo Institute of Technology in 1980.

More recently, the Bell Labs group grew NiSi₂ layers less than 50 Å thick on Si(111) and showed that these very thin layers can be continuous and uniform and can have a high degree of perfection. They showed¹¹ that one can modify the growth hierarchy Ni₂Si → NiSi → NiSi₂ by forming sufficiently thin layers of nickel. In this case, the Bell Labs researchers converted the disordered, room-temperature, nickel-rich silicide directly to epitaxial NiSi₂ by low-temperature annealing. Furthermore, they showed that NiSi₂ forms on silicon through two distinct growth patterns. In the type-B structure the silicide is crystallographically rotated 180° about the normal to the silicon surface, whereas in type A there is no rotation. Again, controlling the formation procedures makes it possible

to grow templates with either structure. Subsequent deposition of nickel at elevated temperature produces thick, uniform layers of single-crystal type-A or type-B silicides.

High-resolution transmission electron microscopy has made it possible to image¹¹ the morphology of these silicide-silicon interfaces. Figure 6 shows electron micrographs of NiSi₂/Si samples that were cross-sectioned, ion-milled to make them transparent to the electron beam and imaged by directing the beam parallel to the crystallographic [110] direction. As one can see, the interface is flat and localized to a single interplanar spacing, and the A and B structures are easily identified. From such micrographs, one can determine the structure of the interface. A group in Amsterdam at the Foundation for Fundamental Research on Matter has also identified¹² the interface structure using medium-energy ion scattering. They have evidence that for the A orientation of NiSi₂ on silicon, there is a reduction, relative to the bulk, in the spacing between the layers composing the boundary.

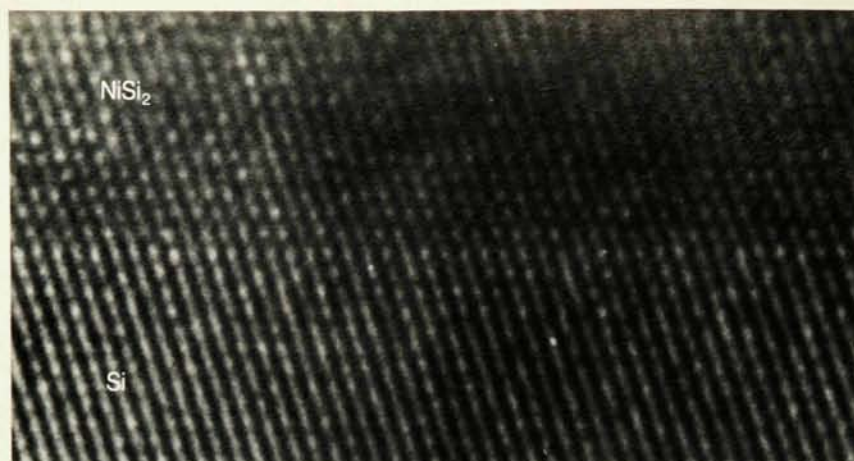
That one can prepare two inequivalent silicide-silicon boundary regions makes it possible to examine the role of structure in the formation of Schottky barriers. Although investigators have long recognized that the Schottky-barrier voltage cannot be determined from the metal work function or semiconductor affinity, there is no consensus regarding the microscopic origin of the Schottky barrier.¹³ Hence there was considerable interest when recent stud-

ies of the NiSi₂/Si interface showed¹⁴ that one could obtain different barrier heights by choosing A-type or B-type silicide growth on the silicon (111) surface. Although this continues to be a controversial issue,¹⁵ it is clear that our understanding of the formation of Schottky barriers will increase through such detailed studies of the nickel-silicon interface.

These basic studies of metal-semiconductor interfaces have led to the discovery of new materials and structures. For example, CoSi₂ has the same structure as NiSi₂ but much better electrical conductivity. Single-crystal films as thin as 100 Å of CoSi₂ on silicon were found¹⁶ to have electron-scattering lengths of 1000 Å at liquid-helium temperatures. This is very surprising and implies that electrons are scattering specularly at the surface and interface, as if these boundaries were highly reflecting mirrors. Some recently constructed heterostructures of Si/CoSi₂/Si have remarkably thin layers of CoSi₂. In these heterostructures transistor action with the silicide acting as the base has been seen¹⁶ for the first time.

Modifying reactivities and barriers

Our characterization of interface morphology would be incomplete if we failed to note that one can control reactivities in predictable and favorable ways by depositing ultrathin surface layers of adatoms. This control has two extremes: enhanced reactivity, where formation of a desired product is accelerated, and suppressed reactivity,



a



b

where extended intermixing is minimized.

For an example of enhanced reactivity, consider the oxidation of silicon. It is well known that silicon reacts with oxygen slowly at room temperature but that when the atomic order of the surface atoms is disrupted by deposition of any of a number of metals onto the silicon, the intermixed surface is significantly more reactive with oxygen than was the clean silicon surface. We can understand this microscopically by noting that the silicon sp^3 bond is more stable with respect to oxidation than the silicon-metal hybrid bond. Based on the modeling results discussed above, we can then predict that the reactivity of the interface will depend critically on the detailed complex morphology of the interface. Indeed, the rate of oxidation of germanium is increased by addition of a vanadium overlayer.

Diffusion barriers also give us a means of microscopic control of interface reactivity, but their role is to prevent atomic intermixing. As discussed above, the thickness of an interface is controlled by the detailed chemistry and morphology of the system. Materials that very readily diffuse away from their optimal positions

would be poor choices for devices that must be fabricated at elevated temperatures. Therefore one commonly introduces a metal interlayer during processing to form a barrier against intermixing. Any microelectronic device contains examples of diffusion barriers. In the MODFET of figure 1, for example, a tungsten layer isolates the gold connection from the gold-germanium mixture that reacts to form the ohmic contact on AlGaAs.

I have focused in this article on interfaces prepared under ideal conditions: carefully characterized, atomically clean surfaces with overlayers deposited—and analyzed—in ultrahigh vacuum. Actual device processing involves somewhat less perfect conditions, namely the sputter deposition of overlayers in modest vacuum onto surfaces with native oxides, carbon impurities, defects and structural imperfections. Understanding and controlling these "real life" multicomponent systems clearly represents a major challenge for interface research.

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Interfaces between $NiSi_2$ and $Si(111)$. These ultrahigh-resolution transmission electron micrographs show the abruptness of the interface and the two types of highly perfect $NiSi_2$ overlayers. **a:** Type-A overlayer. **b:** Type-B overlayer. (Micrographs courtesy of John Poate.) Figure 6

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