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ELECTRONIC STRUCTURE OF SEMICONDUCTOR INTERFACES*

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Résumé. — Des études expérimentales récentes montrent que certains systèmes semiconducteurs, tels que $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ et des super-réseaux de couches soumises à des contraintes peuvent être fabriqués sans rugosité à l'échelle d'une couche monoatomique, et pratiquement sans imperfections. La possibilité d'obtenir des interfaces et des empilements (hétérostructure, super-réseaux) est bien sûr du plus grand intérêt sur le plan scientifique et technologique. Toutefois, la plupart des interfaces contiennent une grande variété de défauts d'origine structurale ou chimique. Actuellement, la recherche porte essentiellement sur l'identification, la modification ou la réduction de telles imperfections.

Abstract. — Although we now have a good understanding of the electronic structure of idealized semiconductor interfaces, including the nature of localized interface states, recent experimental studies suggest that the atomic structure of actual interfaces is considerably more complicated than that described by the idealized models used in current theoretical research. If we are to understand the electronic properties of interfaces more fully, it is essential that we develop more realistic structural models for interfaces. We will illustrate the strengths and weaknesses of present-day theories by discussing the electronic structure of Ge/GaAs , Si/SiO_2 , and $\text{Pd}_2\text{Si}/\text{Si}(111)$ interfaces. We will also discuss the development of improved atomic-scale models for interfaces between crystalline and amorphous semiconductors.

I. INTRODUCTION

One of the most exciting and rapidly expanding subjects in solid state physics is the study of semiconductor heterostructures and superlattices.¹⁻⁴ Improved crystal growth techniques such as molecular beam epitaxy,⁵ and the development of refined surface-sensitive spectroscopies, have stimulated wide-ranging scientific¹⁻³ and technological⁴ research efforts on such systems as Ge/GaAs , $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$, and InAs/GaSb . Recent improvements in sample preparation and measurement techniques have also inspired fundamental studies of technologically important interfaces such as oxide-passivated silicon surfaces⁶⁻⁸ and rectifying metal-semiconductor contacts.^{9,10}

In this paper we will sketch the present state of our understanding of the electronic structure of some important types of semiconductor interfaces. Most of our current ideas are based on simple, highly idealized atomic interface models. For purposes of discussion, we will define the ideal semiconductor interface as the atomically abrupt boundary between two lattice-matched, crystallographically compatible constituents. It is assumed that each of the constituents has its bulk crystal structure right up to the interface, that there is exact lattice registry at the interface, and that there are no dangling bonds at or near the interface. If the two constituents are not exactly lattice-matched, it is assumed that the residual strain is relieved by well-separated misfit dislocations. By using crystals or alloys having different chemical compositions, crystal structures, and doping profiles, it is possible to synthesize heterostructures having a wide range of physical characteristics.

Recent experimental studies indicate that some semiconductor systems, such as $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ ¹ and strained-layer superlattices,¹¹ can be made smooth on the scale of a single atomic layer, and can be grown almost free of imperfections. The availability of nearly ideal interfaces and interfacial arrays (heterostructures and superlattices) is of course of the greatest scientific and technological importance. Most interfaces, however, contain a wide variety of structural and chemical imperfections; much current research is concerned with the identification, modification, or reduction of these imperfections.

II. SEMICONDUCTOR HETEROJUNCTIONS: Ge/GaAs INTERFACES

Because of its apparent simplicity, the Ge/GaAs system has been widely studied. Ge and GaAs have compatible crystal structures and nearly identical lattice constants (Ge: 5.65735 Å; GaAs: 5.6537 Å). Since the band gaps of GaAs and Ge differ by 0.9 eV, and the conduction band edges occur at different positions in the reduced zone, there must be a band structure discontinuity at the interface which can be represented by valence and conduction band offsets. In principle, these offsets can be different for interfaces having different crystallographic orientations.

It is important to know the band offsets because they determine the depth of quantum wells in heterostructures such as GaAs/Ge/GaAs and in superlattices. Theoretical estimates^{12,13} of band offsets and experimental measurements¹⁴ are only in rough agreement with one another. This is hardly surprising: some of the estimates are based on oversimplified models,¹² while the more detailed estimates¹³ are usually based on idealized interface models which may differ in some important respects from real interfaces.

The discontinuity in crystal potential associated with the changes in crystal structure and chemical composition across the interface may give rise to localized electronic states. When the energies of such states lie within the thermal gap, they can serve as trapping and recombination centers, and hence are of considerable importance. (By thermal gap we mean the energy range between the highest occupied valence band level and the lowest unoccupied conduction band level.) Since the Ge/GaAs interface discontinuity is substantially weaker than the discontinuity at a free Ge or GaAs surface, interface states are pushed out of the valence and conduction bands to a much lesser extent than intrinsic surface states are.

Theoretical studies of ideal non-polar (110) Ge/GaAs interfaces¹⁵⁻¹⁷ demonstrate that localized interface states do not extend into the thermal gap. But localized states associated with the Ge-Ga and Ge-As bonds at the interface do occur within the "stomachs" of the projected valence and conduction bands and in the forbidden band just outside thermal gap. Localized interface states associated with Ge overlayers on GaAs have been detected by photoemission.¹⁸

In the case of ideal polar (100) Ge/GaAs interfaces, theoretical studies^{19,20} indicate that localized interface states form a band that extends into the thermal gap. Since the Fermi level passes through this interface band, this ideal interface would exhibit metallic behavior, contrary to experimental results. It must be concluded, therefore, that ideal (100) interfaces are not actually formed. It is possible that the metallic interface band is eliminated by interfacial relaxation or reconstruction, or by local interdiffusion and reordering.²¹ It is conceivable that some macroscopic polar interfaces are composed primarily of non-polar terraces and steps on an atomic scale.

Recent experimental studies^{22,23} suggest that Ge/GaAs interfaces are considerably more complicated chemically and structurally than was originally believed. Because of the similarity in atomic size of Ge, Ga, and As, it is difficult to prevent interdiffusion, so that interfaces tend to be diffuse rather than atomically abrupt. Moreover, it is found that interfacial chemical reactions take place, and that the interface is rough on an atomic scale. When GaAs is grown on Ge, antiphase boundaries can be formed in the growing GaAs, further complicating the interfacial structure. Some attempts have already been made to incorporate various types of defects into interface calculations.¹³ However, much remains to be done before we have an adequate understanding of the effects of chemical impurities, vacancies, interstitials, antisite defects, and stoichiometric mixing on

interfacial electronic structure and properties. The same applies for misfit dislocations, stacking disorder, relaxation, and reconstruction.

III. PASSIVATING OXIDE LAYERS: Si/SiO₂ INTERFACES

It is well known that suitably oxidized silicon substrates are protected from environmental contaminants and have rather low densities of localized interface states in the thermal gap. Because of the important role that surface passivation plays in MOS technology,²⁴ there is strong motivation for understanding the physics and chemistry of the Si/SiO₂ interface.⁶⁻⁸ In this section we will be concerned with the atomic-scale structure of the Si/SiO₂ interface, including the residual defects that occur near well-prepared Si/SiO₂ interfaces and give rise to residual trapping sites and fixed charge.

In contrast to the Ge/GaAs interfaces that we have been dealing with so far, the Si/SiO₂ interface connects a crystalline substrate (Si) to a non-crystalline overlayer (vitreous SiO₂, abbreviated v-SiO₂). Whatever the nature of this interface actually is on an atomic level, the observed low density of interface states is compelling evidence for the fact that nearly all of the silicon atoms on the substrate surface have their bonds saturated one way or another. How does this come about?

Before discussing the Si/SiO₂ interface itself, it is desirable to say a few words about bulk v-SiO₂. It is generally believed²⁵ that a non-crystalline material such as v-SiO₂ can be represented by a continuous random network (CRN) of SiO₄ tetrahedra joined to one another at their common oxygen positions, so that all Si and O bonds are saturated. Computer simulation studies^{25,26} indicate that the distributions of Si-O bond lengths and O-Si-O angles are relatively narrow, so that the SiO₄ tetrahedra maintain their structural integrity even when embedded in v-SiO₂. In contrast, the distribution of Si-O-Si bond angles involving adjacent tetrahedra is relatively broad. Undoubtedly, the random structure of the SiO₄ tetrahedra in v-SiO₂ is made possible by the softness of the Si-O-Si bond angle. The fact that the SiO₄ tetrahedra can accommodate themselves to different SiO₂ crystal structures must also reflect this bond angle softness. In the present context, this softness would be expected to play an important role in accommodating v-SiO₂ to a crystalline Si substrate.

What is the exact nature of this contact? Is the silicon substrate atomically smooth or rough? Does it have steps and terraces? Are the outermost silicon layers strained to accommodate the SiO₂ overlayer? Is there a transition region between the Si substrate and the "bulk" v-SiO₂ which extends over several atomic layers, or is the transition atomically abrupt? If there is a gradual change in average composition, described by the stoichiometric formula SiO_x, where x ranges from 0 (at Si) to 2 (at v-SiO₂), what are the bonding arrangements that contribute to this average composition? We do not have the space to summarize recent experimental evidence bearing on these questions,²⁴ so we will limit ourselves to discussing some of these issues in terms of two recently developed theoretical models which are highly idealized but nevertheless instructive.

The first of these is a ball-and-stick model developed by Pantelides and Long²⁷ to demonstrate that an atomically abrupt Si/SiO₂ interfaces can be formed between a CRN model of v-SiO₂ and the (100) face of Si. Using the same Si-O bond length everywhere, they were able to connect v-SiO₂ to Si on the scale of one atomic layer, but they had to distort many of the O-Si-O and Si-O-Si bond angles near the interface considerably to avoid introducing dangling bonds. The successful construction of this ball-and-stick model dramatically demonstrates the adaptability of v-SiO₂ to a silicon substrate, but does not prove that such an atomically abrupt Si/SiO₂ interface would actually form under experimental conditions.

Since the more distorted bond angles are energetically unfavorable, and hence unlikely to be realized in nature, it appears necessary to incorporate two additional ingredients into the Pantelides-Long model in order to make it more realistic. In constructing a more realistic version of this model, one can avoid excessively distorted bond angles by allowing dangling bonds to appear,

and one can saturate these dangling bonds by O and H atoms and OH groups, as undoubtedly happens during actual growth conditions.^{28,29} The extra energy needed to support dangling bonds would be largely offset by the saturation of these bonds by the entities just mentioned. (The construction of a model embodying these features is currently being investigated at our laboratory by P. Lambin and the author.)

The net effect would be an incomplete connection between a discontinuous random network of $v\text{-SiO}_2$ and the silicon substrate. There would be many voids of varying sizes present at or near the interface, but most of the dangling bonds defining these voids would be saturated by O and H atoms and OH groups. Thus, strain-relieving voids and (O,H,OH)-saturated dangling bonds are the two extra ingredients that should be added to the Pantelides-Long model to make it more realistic. The local stoichiometry described by the expression SiO_x would of course be determined in large measure by the O atoms and OH groups which saturate Si bonds and represent deviations from a continuous random network of $v\text{-SiO}_2$.

An analogous picture emerges from a totally different type of idealized Si/SiO₂ interface model that we developed recently.³⁰ In this other model, the non-crystalline SiO₂ overlayer is replaced by an idealized crystalline SiO₂ overlayer which can be brought into exact registry with the Si substrate. If one begins with a silicon crystal, expands the lattice by a factor of $\sqrt{2}$, and places an oxygen atom at the midpoint of each dilated Si-Si bond, one obtains an idealized version of the cristobalite SiO₂ structure having very nearly the same Si-O bond length as the actual structure, but straight rather than crooked Si-O-Si bond angles. This is a reasonable approximation in view of the softness of the Si-O-Si bond angle. One can now obtain exact registry between the (100) face of Si and the (100) face of idealized cristobalite SiO₂ by rotating one of these 45 degrees with respect to the other and bringing them together.

The Si atoms on the (100) substrate form a square array which can be regarded as a checkerboard with half the Si atoms occupying "red" squares and the remaining half "black" squares. At the idealized Si/SiO₂ interface, the Si atoms occupying the "red" squares are shared by the Si substrate and the SiO₂ overlayer, while the Si atoms on the "black" squares are connected only to the Si substrate, having two dangling bonds each. One can improve the realism of this model slightly by retaining the lattice topology and allowing the atomic positions to relax, but this does not change the essential features of the model.

This construction leads to a concrete, easily visualized interface model which emphasizes that the connection between the Si substrate and the (idealized) SiO₂ overlayer involves only half the Si substrate atoms directly. The remaining half of the Si substrate atoms are not attached to the SiO₂ overlayer at all. For this model to describe an actual interface, it is again essential that virtually all the Si substrate dangling bonds are saturated by H or O atoms or OH groups introduced during interface formation. Since SiO₂ has a very open structure, it is reasonable to expect such entities if present to migrate to the growing interface and saturate the dangling bonds.

Since very few experiments provide direct and unambiguous information concerning the exact nature of the atomic structure of an Si/SiO₂ interface, it is essential for theoreticians to develop atomic-scale models that can be used as a guide to interpreting experimental measurements. The two models already discussed are clearly idealizations, but they are instructive. In order to make further progress, one should consider the atomic processes by which the interface actually forms, rather than straightforward attachments between crystalline SiO₂³⁰ or amorphous SiO₂^{27,31} to a Si substrate.

There is a vast literature on defects in SiO₂⁶⁻⁸ covering interface electronics and also radiation-damaged glass. It is encouraging that increasingly refined theoretical models have begun to appear in recent years,³² as well as experimental studies based on surface-sensitive spectroscopies.^{6-8,24} Nevertheless, the identification of the defects primarily responsible for trapping and recombination at Si/SiO₂ interfaces is still largely an open question. Since the thermal (Si) gap is only 1.1 eV and the top of this gap lies about 3.1 eV below the top of the 10 eV forbidden band of SiO₂, most of the defects in the SiO₂ structure would be expected to give rise to levels that lie outside the

thermal gap. It is far more likely that defects such as dangling Si substrate bonds which are closely coupled to the Si band structure give rise to levels in the thermal gap. Support for this view comes from the fact that the deliberate introduction of hydrogen or deuterium during processing removes these defect levels, presumably by saturating these particular dangling bonds.^{28,29}

Finally, we note that there is considerable tailing of the valence and conduction bands into the thermal gap. This tailing is supposedly associated with the disordered atomic structure at the Si/SiO₂ interface, but the details are still not understood. Clearly, a great deal of additional experimental and theoretical work will have to be done before we have a more comprehensive picture of this interface.

IV. METAL-SEMICONDUCTOR CONTACTS: Pd₂Si/Si(111) INTERFACES

The formation of ohmic or non-ohmic metal-semiconductor contacts is of immense technological importance. During the past few years, many attempts have been made to understand the physical, chemical, metallurgical, and structural factors determining Schottky barrier heights in rectifying contacts.^{9,10} Although informative chemical trends have been established by correlating barrier heights with electrochemical data for many systems, the relationship between barrier height and local atomic structure at the interface remains elusive. Unfortunately, the atomic arrangements at most interfaces are too poorly characterized to provide a basis for serious theoretical analysis.

For most metal-semiconductor interfaces, lattice-matched constituents and atomically abrupt interfaces are the exception rather than the rule. The metal and semiconductor regions are usually separated by a disordered transition region which accommodates the discontinuity in lattice constant as well as the transition from metallic and covalent binding. Most of these interfaces are spatially diffuse because of interdiffusion. For some systems, chemical reactions may take place between the metal and semiconductor, leading to a transition region composed of ordered or disordered compounds. Such non-ideal systems are exceedingly difficult to treat theoretically, though some progress can be made by considering idealized lattice-matched metal-semiconductor interfaces.³³

Most elementary models of ideal rectifying contacts are based on early ideas by Schottky and Bardeen, according to which chemical equilibrium is established by the flow of electrons between the metal and the semiconductor, leading to bending of the semiconductor bands and the creation of a rectifying potential barrier at the interface. The absence or presence of localized interface states plays a crucial role in these models: In the Schottky limit (negligible interface states), the barrier height is given by the difference between the metal work function and the semiconductor electron affinity. In the Bardeen limit, there are sufficiently many interface states present to pin the Fermi level, so that the barrier height is determined by the highest occupied interface state, and is largely independent of the metal work function.

If the Fermi level is indeed pinned by localized interface states whose energy levels lie in the forbidden band of the semiconductor, how do these interface states arise? The first possibility is that they are similar to intrinsic surface states on the semiconductor, as originally envisioned by Bardeen. However, in many semiconductors, relaxation and reconstruction at free surfaces push surface states out of the forbidden band;^{13,34} the same could happen at metal-semiconductor interfaces.³⁵ Moreover, intrinsic semiconductor interface states can only partially resemble intrinsic surface states because of screening by the adjacent metallic region.

A second possibility is that electrons can be localized just inside the semiconductor by occupying the tails of the wave functions which spill over into the semiconductor from the metal. These are known as metal-induced gap states,³⁶ or MIGS. Such localized states are expected to occur when the metal is at least several atomic layers thick, but they may not occur when the metal is only one atomic layer thick. Since the Schottky barrier height may already have its limiting ("bulk") value when the metal coverage is monoatomic or sub-monoatomic for some systems, there may be no direct connection between MIGS and Schottky barrier heights for such systems.³⁵

A third possibility, particularly appropriate for "strong" (reactive) contacts, is that the frontier

metal and semiconductor atoms form chemical bonds,³⁷ and that the energy levels associated with these chemical bonds or hybridized metal-semiconductor states extend into the forbidden band. A fourth possibility is that the localized interface states arise from structural or chemical imperfections in the semiconductor.³⁸ Such imperfections include vacancies, self-interstitials, substitutional and interstitial metal impurities, metallic clusters, antisite defects, and dislocations. In the case of contacts between metals and hydrogenated amorphous silicon,³⁹ states in the gap already present because of structural disorder in the silicon are expected to play a key role in pinning the Fermi level.

Many investigators are currently making a concerted effort to interpret a rapidly increasing body of detailed experimental information in terms of different defect models.^{9,10,35,38} In view of the fact that most experimental probes do not have the spatial resolution necessary to identify structural imperfections unambiguously on an atomic scale, a general consensus has not yet been reached regarding the mechanisms responsible for Schottky barrier formation. There may well be many different mechanisms at play in different systems, or even in the same system, so sorting out the key mechanisms is an exceedingly difficult problem.

The demands of sub-micron electronics are focusing attention on rectifying contacts formed by reacting transition metals with silicon. There is considerable interest in such interfaces because the silicides form close-packed metallic structures which are impervious to bonding metals such as Al. Thus, diffuse Al-Si contacts can be replaced by relatively abrupt Al-silicide-Si contacts. Moreover, some of the silicides form epitaxial layers on Si, so there is a greater opportunity to synthesize interfaces which are more nearly ideal and hence easier to investigate experimentally and theoretically.^{9,10,40}

There have already been a number of experimental and theoretical studies of the electronic structure of bulk silicides.⁴⁰ Some attempts are currently being made to study the electronic structure of silicide-silicon interfaces theoretically, taking advantage of their epitaxial character.^{41,42} In the following, we will discuss the essential features of a model we have recently developed for understanding Schottky barriers at Pd₂Si/Si(111) interfaces.⁴² This model is of general interest because it goes beyond the idea of localized interface states being solely responsible for Schottky barrier heights.

According to our model, Pd impurities diffuse into the Si substrate in advance of the growing interface, forming triangular clusters between pairs of Si vacancies.⁴³ Since these clusters are more easily accommodated in hexagonal (2H) Si than in cubic (3C) Si, the presence of these clusters induces a hexagonal Si transition region between the cubic Si substrate and the Pd₂Si overlayer. The measured Schottky barrier height (0.71 to 0.73 eV) is readily accounted for by noting first that the forbidden band width of the hexagonal Si transition region is about 0.85 eV, and second that the Fermi level is pinned slightly above the Si valence band edge by hybridized Pd-Si states at the interface.^{41,42} The same overall effect could be achieved by having stacking disorder in the Si near the interface, rather than a coherent hexagonal crystal structure. We would again argue that the stacking disorder is induced by the presence of the triangular Pd impurities.

In short, our Pd₂Si/Si(111) model suggests that Schottky barrier heights can be determined not only by interface states which pin the Fermi level, but also by the presence of a different crystal structure or stacking disorder near the interface. Such structural features -- coherent or random -- can affect the host band structure, modifying the effective semiconductor band gap at the interface, and hence the Schottky barrier height as well. Incidentally, stacking faults have also been invoked recently to account for certain reconstructions of free silicon surfaces.⁴⁴

V. CONSTRUCTION OF ATOMIC-SCALE INTERFACE MODELS

One popular theoretical approach for determining the atomic structure of interfaces (and surfaces) involves calculating the electronic structure for a number of plausible models, and then determining which set of results agrees most closely with experiment.^{13,34} Even assuming that the experimental

data are reproducible and correctly interpreted, this approach may overlook physically significant atomic arrangements altogether, and in the end not provide insight as to why one particular model gives a better account of experiment than another.

Another popular theoretical approach involves calculating the total energy of the system, and then determining the equilibrium geometry by minimizing the total energy as a function of atomic positions. This is a very powerful approach, and has been applied with great success recently to a number of relatively simple systems.^{15,34} Because of the extensive computational effort involved, it is unlikely that this approach will soon encompass the more complicated systems that are of primary experimental interest.

So it is essential to look for still other approaches, bearing in mind that further progress in determining the electronic structure of interfaces is severely limited by our ability to construct realistic atomic models of interfaces. Instead of assuming plausible atomic positions at the outset and then relaxing these positions so as to minimize the total energy, keeping the topology or connectivity the same, we believe theoreticians should focus directly on the atomic processes by which interfaces are formed by the progressive accumulation of atoms and molecules. We should attempt to simulate the growth of covalently bonded crystals at the atomic level using computers, perhaps interactively. The challenge is to establish algorithms that will guide this growth along physically and chemically reasonable paths, possibly taking advantage of concepts arising in the field of artificial intelligence.

Computer simulation studies⁴⁵ have already provided us with considerable insight into the nature of crystal growth, but such studies have been confined almost exclusively to systems such as metals and simple liquids which can be described by hard sphere interactions.⁴⁶ Current attempts at modeling covalently bonded systems are still rather primitive,^{47,48} but this avenue of theoretical research is of the greatest importance, and deserves considerably more attention than it has received so far.

VI. FORMATION OF NOVEL INTERFACES AND SUPERLATTICES

During the next few years we anticipate increasing experimental, theoretical, and computational efforts directed at understanding the growth and stabilization of novel interfaces and superlattices, with particular emphasis on the underlying atomic processes:

- **Amorphous overlayers on crystalline substrates.** — We have already discussed the Si/SiO₂ interface as an important example of a crystalline-amorphous interface. A somewhat simpler example is the interface between crystalline Si and amorphous Si. Recent activity in laser processing and laser annealing⁴⁹ has focused attention on the fundamental processes associated with localized melting and subsequent solidification of Si into the amorphous phase, as well as with recrystallization of amorphous Si. Some attempts have already been made to model crystalline-amorphous Si transformations as well as the growth of SiO₂ on Si on an atomic scale,⁵⁰ but progress thus far has been minimal. We don't really know very much about the dynamical processes responsible for the interconversion between crystalline and amorphous phases of covalently bonded solids. If we could understand the atomic dynamics by which crystals transform into amorphous structures and vice versa, we would be able to determine the atomic arrangements at crystalline-amorphous interfaces. This is clearly a challenge for the future.

- **Metastable overlayers on solid substrates.**⁵¹ — Perhaps the best-known examples are strained-layer interfaces and superlattices.¹¹ These metastable structures have many attractive physical properties, so they are being intensively studied. An important challenge is to find ways of stabilizing such structures so that they can perform electronic functions under widely varying conditions. Other examples are low-temperature phase α tin ("grey tin") and α -Sn:Ge alloys grown on InSb and CdTe substrates.⁵² Still other examples are single-crystal (GaAs)_{1-x}Ge_{2x} alloys, whose band gaps vary non-monotonically with composition in a most remarkable manner.⁵³ This behavior has been interpreted as evidence for an order-disorder transition.⁵⁴

• Polytypism,⁵⁵ stacking disorder,⁵⁶ and random superstructures.⁵⁷ — The boundary between cubic ZnS (sphalerite) and hexagonal ZnS (wurtzite) is a classic example of a polymorphic interface.^{58,59} Long-period polytypes of SiC and ZnS can be rightfully regarded as structurally modulated superlattices. The mechanisms leading to the growth of such superlattices are still not understood, in spite of decades of study. Admixed random and non-random stacking sequences of ZnS can be formed by evaporating thin films of ZnS on suitable substrates. These films are composed of random striations of cubic and hexagonal ZnS.^{58,60} Such films are of interest because they can be used to generate photovoltages considerably larger than the band gap of ZnS. Another challenge for the future is learning to synthesize structurally modulated heterostructures as well as we have already learned to synthesize compositionally modulated heterostructures^{1,2,5,11} and modulation doped heterostructures.³ Hopefully, an improved theoretical understanding of interface formation will accelerate progress.

VII. CONCLUDING REMARKS

Recent experimental studies have provided a great deal of important information concerning the nature of semiconductor interfaces. Many experimental results can be readily interpreted in terms of electronic structure pictures based on idealized interface geometries. However, it has proved difficult to elucidate the atomic arrangements at interfaces unambiguously because even the most refined surface-sensitive spectroscopies lack the necessary resolution. Further theoretical progress on electronic structure and more incisive interpretation of experimental measurements both await a better understanding of the atomic structure of real interfaces. The development of realistic atomic structure models is a challenging theoretical problem which is ideally suited for imaginative computational analysis.

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