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A photoemission study of samarium on silicon

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Iowa State University

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A photoemission study of samarium on silicon

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An-Ban Yang

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I. INTRODUCTION

In recent years the study of rare earth/semiconductor interfaces has become a topic of great interest because of the stability of the strongly chemically-reacted compounds (silicides) forming at the surface and the resulting low Schottky barrier height (of the order of 0.4 eV on n-type silicon\(^1\)), which make the applications of rare-earth semiconductor interfaces possible in very-large-scale-integration (VLSI) technology. Moreover, it is of both practical significance and theoretical interest to understand what interactions are involved at the metal-semiconductor interface due to the essential role it plays in microelectronic device performance, especially in VLSI applications. Understanding the growth behavior of rare earth/semiconductor systems is valuable for understanding the behavior of others, such as noble-metal semiconductor interfaces. For most integrated-circuit devices, the electronic characteristics and stability of entire circuits is greatly determined by the microscopic properties of metal-semiconductor interfaces. As microelectronics manufacturers achieve large and large-scale circuit integration, the role of interfaces become even more critical. Boundary regions will become a greater and greater fraction of the volume of smaller and smaller devices. Nevertheless, little is known of the electronic structure of the rare earth silicides or of the interfaces themselves.
Therefore, it is worthwhile to investigate the growth behavior and the electronic properties at the rare earth/semiconductor interface.

Samarium/silicon interface properties will be studied in this thesis. In order to obtain a complete growth study of Sm/Si, three different kinds of silicon substrates are used: crystal Si(111), amorphous Si (a-Si), and hydrogenated amorphous Si (a-Si:H). From the comparison between the two different kinds of amorphous Si substrates we can learn what influences hydrogen has on the chemical reaction between Sm adatoms and Si substrates. Also, from comparison between the single crystal Si substrate and the two different amorphous ones, we can examine the potential complexity arising from roughness of the substrate surfaces. Although crystalline semiconductors have received the most attention in the past, scientists are now expanding efforts toward understanding the amorphous ones. One reason for this increase in interest lies in their applications in solar-cell technology. Besides, amorphous elements are usually cheaper to manufacture than crystalline ones, so the widespread use of amorphous elements in electronics could lead to a significant reduction in cost.

The amorphous elements usually contain many voids which can absorb gases such as hydrogen, fluorine, oxygen, etc. Due to the high reactivity of the dangling bonds present, these molecules are broken down to their atomic constituents, thereby passivating the dangling bonds. Empirically it has
been found that the passivation of dangling bonds by introducing some additional passivating agents (usually hydrogen) into amorphous elements (such as amorphous Si) results in better device characteristics.\textsuperscript{3,4}

The adatom-substrate interaction is generally rather complicated and, at the same time, is of crucial importance in determining metal-semiconductor-interface properties. However, samarium is an excellent test system for study of the interaction between chemisorbed metallic overlayers and the Si substrates not only because Sm doesn't diffuse through Si but also because Sm exhibits strong chemisorption on Si following a multi-stage process.\textsuperscript{5,6} Therefore, more information can be extracted than from some weakly-reacted or one-step-process systems. Moreover, the special characteristics of Sm 4f electrons can make the interfacial study non-ambiguous and clear. We will see this in the following.

\textbf{A. The Characteristics of Samarium}

The onset of a chemical reaction at an interface is usually difficult to observe in most cases because the changes of the chemical state of the interface components are small. However, rare-earth atoms, in general, and Sm atoms, in particular, exhibit 4f spectral "fingerprints" sensitive to the atomic valence configuration. These features are well known and for Sm have been used to identify the valence state
in bulk compounds,\textsuperscript{7} surfaces,\textsuperscript{8} and clusters.\textsuperscript{9}

The Sm 4f levels, like all the rare-earth 4f levels, energetically lie in the midst of valence band. But they act as core levels in the sense that, spatially, they lie deep within the atom and exhibit shifts (in configuration center) rather similar to the core levels that have a much larger binding energy. This is to be expected considering the relative orbital dimensions. For Sm, the average radius\textsuperscript{10} is 0.1 Å for 3d and 0.5 Å for 4f, while for valence shell, it is 1.4 Å for 5d and 2.58 Å for 6s. It is only the large kinetic energy of the 4f shell (introduced by angular nodes) that causes it to fall, energetically, in the valence band. Since the 4f orbits are spatially too localized to overlap well with orbitals on adjacent atoms, they do not exhibit band-type dispersion but final-state multiplets in the photoemission spectrum. The 4f electrons participate in chemical binding only indirectly by acting as a reservoir of electrons that can donate an electron to, or accept an electron from, the 5d6s valence band when it is energetically favorable to do so. For example, the free Sm atom is divalent 4f\textsuperscript{6}6s\textsuperscript{2}, whereas in the bulk metal it is trivalent 4f\textsuperscript{5}6s\textsuperscript{2}5d\textsuperscript{1}. The valence of Sm atoms in situations between these two ultimate configurations (i.e., free atom and pure bulk metal) is greatly dependent on particle size,\textsuperscript{9} where mixed-valence behavior is exhibited; samarium is primarily divalent at small particle size, while the trivalent state becomes progressively more abundant with
increasing size, becoming the dominant state for the bulk metal.

In the Sm 4f photoemission spectrum of pure metal, as shown in Fig. 1, the divalent (6H, 6F, and 6P) and trivalent (5I, 5F, 5G, and 5D) 4f configurations show a large core-level binding-energy separation of about 5 eV due to surface core-level shifts, and the final-state multiplets of the divalent component overlap with the 5d valence band region near the Fermi level; this gives us a clear distinction between the two possible valence-state configurations and a high level of surface sensitivity at photon energies near the 4d absorption threshold, ranging between 133 and 155 eV (the Sm 4d photoabsorption spectrum is also shown in Fig. 1). Therefore, use of the final-state 4f multiplet structures, 4f^5 and 4f^4, to identify the 4f (and thus the 5d6s valence electrons) initial-state occupancies is sometimes superior to the use of deeper core levels. Additionally, the divalent and trivalent states of Sm show different resonant behavior; the resonant enhancement of the divalent state occurs at a photon energy of 135 eV, but the resonance of the trivalent state is at 140 eV, as shown in Fig. 2. Consequently, this special resonant behavior of Sm enable us to investigate the valency of Sm adatoms at the interfaces unambiguously.

A general tendency for the surface valence of rare earths to be lower than in the bulk was first suggested by Wertheim and Crecelius, and is readily understandable in terms of
Figure 1. EDC of Sm metal at 135 eV (upper) and the partial yield spectrum (lower) in which the energy range spans the 4d core energy of Sm.
Figure 2. Comparison of CIS spectra of the Sm$^{+3}$ to Sm$^{+2}$ 4f levels. Notice the different resonant photon energies for the trivalent and divalent states.
valence-band narrowing due to reduced surface coordinations and also understandable from a thermodynamic aspect proposed by Johansson. In Johansson's model, a trivalent atom forms stronger bonds than a divalent one, and so loss of bonding in forming a surface is always more costly in energy terms in the divalent case. According to Johansson's calculation, in Fig. 3 we show that forming a Sm trivalent surface requires energies of about 21 kcal/mol, whereas forming a divalent surface costs only about 9 kcal/mol. The relative stability of the divalent surface relative to the trivalent surface is therefore 12 kcal/mol more favorable than their relative bulk stabilities. Moreover, the trivalent Sm metal is stable by about 6 kcal/mol (0.26 eV/atom) relative to the divalent metal. Therefore, the divalent surface is about 6 kcal/mol more stable than the trivalent surface. This story takes no account of the fact that the divalent surface atoms will be in contact with trivalent atoms in the second layer, and corrections for this would reduce the divalent advantage somewhat, but overall the calculation suggests that Sm surfaces ought to be looked at very carefully! However, there are at least two possibilities even if divalency proves favorable. Either a divalent layer forms, or dynamical valence fluctuations may occur at the surface. What actually happens was originally controversial, but it now seems agreed that Sm is in the trivalent state in the bulk and in the divalent state at the surface, by careful interpretation of
Figure 3. Energy diagram for Sm atom, metal and surface, where $E_{coh}$ represents the cohesive energy required to remove an atom and to put it into a state that often has a different valence from that in the metal. An energy $0.2 E_{coh}$ is needed to form a mole of surface in liquid metals (see Ref. 15)
some surface sensitive experiments. XPS (X-ray Photoemission Spectroscopy) measurements of Sm metal, in which the take-off angle of the photoelectrons was varied from near normal to grazing exit, indicated that the Sm surface layer has a prominent divalent component.\textsuperscript{8,16,17} This was suggested by the appearance of multiplet structures due to $4f^5$ (trivalent) and $4f^6$ (divalent) initial states in both core level and valence band spectra under conditions of enhanced surface sensitivity. Afterwards, more resonant photoemission experiments by Gerken et al.\textsuperscript{18-20} established complete divalency for the Sm metal surface, as opposed to mixed valent character.\textsuperscript{21} This is in agreement with the theoretical predictions of Rosengren and Johansson.\textsuperscript{22} Gerken et al. based their conclusions regarding the completely divalent character of the Sm surface layer on the absence of surface core level shifts of the trivalent Sm multiplet structures. Because the completely divalent Sm atoms exist only at the surface, using this special characteristic of Sm in the coverage-dependent interface study of the nucleation and growth processes occurring in thin film formation at the interface surface has its own great advantage. It provides a clear indication of the growth behavior at the interface, whether the island, layer plus island, or layer growth mode is involved.

Based on the above knowledge of samarium's unique characteristics makes it an extraordinarily suitable system for the study of interface properties between chemisorbed
metallic overlayers and different kinds of substrates.

B. Overlayer-growth Morphology (Growth Modes)

It is generally accepted that there are three possible modes of crystal growth on surfaces. In the island or Volmer-Weber mode, small impurity-atom clusters nucleate directly on the substrate surface and then grow into islands of the condensed phase. This happens when the atoms (or molecules) of the deposit are more strongly bound to each other than the substrate. The layer-by-layer, or Frank-van der Merwe mode, displays the opposite characteristics. Because the atoms are more strongly bound to the substrate than to each other, the first atoms to condense form a complete monolayer on the surface, which becomes covered with a somewhat less tightly-bound second layer. Providing the decrease in binding is monotonic, towards the value for a bulk crystal of the deposit, the layer-by-layer growth mode is obtained. The layer-plus-island, or Stranski-Krastanov, growth mode is an interesting, intermediate case. After forming the first monolayer or a few monolayer, subsequent layer growth is unfavorable and islands are formed on top of this "intermediate" layer. There are many possible reasons for this to occur, and almost any factor which disturbs the monotonic decrease in binding energy may be the cause.

Other phenomena play significant roles in growth-mode
behavior. Real surfaces have defects, steps, and terraces. These features may affect the quality and detailed processes of the overlayer. Surfaces with complex corrugations, such as the Si(111) reconstructed surface, have many possible "special sites" for overlayer atom adsorption. The overlayer may chemically react with the substrate. Interdiffusion, intermixing, and surface segregation sometimes occur in thin films.

C. The Purpose of This Study

Sm/Si(111) system has been previously studied by Franciosi and Weaver et al., in which the Sm-Si(111) interface has shown a complex morphology involving sequential formation stages with different Sm valence states and exhibited a critical coverage corresponding to the onset of a strong chemical reaction and a large resulting chemical shifts indicative of substantial charge transfer in the reacted phase. However, unlike other rare-earth/Si interfaces, such as Ce/Si, no such lowering of the Schottky barrier has been observed, as expected as the basis of recent results for technological samples. Many questions besides this still remain about the structural and electronic properties and the growth behavior at the interface surface.

The purpose of this work is to use ultraviolet photoemission spectroscopy to study the chemical and physical
phenomena underlying the formation of samarium on silicon.
The following questions that need to be addressed in resolving
the problem of the Sm/Si interface are: 1) What are kinds of
adatom-substrate chemical reactions are involved at the
interface? 2) Where dose the energy come from to break the
Si-Si bonds and trigger the strong chemical reactions between
Sm and Si? 3) What growth processes occur in the thin film
formation of Sm on Si? Do they depend on the surface
conditions such as surface roughness? and finally 4) Does
hydrogen play any role in the formation of Sm on hydrogenated
amorphous Si? The questions leads to the photon energy
dependent study of the energy distribution curves which
includes the valence-band and core-level information of the
system. From this information we can infer a model to explain
what happens in the interfacial formation of Sm on Si and
answer all the questions above.
II. THE PHYSICS OF PHOTOEMISSION

A. The Three-step Model

Although the photoelectric effect was first observed by Hertz in 1887, this effect was not understood until Einstein proposed the quantization of light in 1905. The basis of photoemission is the relation

$$E_{\text{max}} = h\nu - \varphi$$

(1)

The maximum kinetic energy of a photoemitted electron $E_{\text{max}}$ equals the energy $h\nu$ of a quantized packet of light, where $\nu$ is the classical electromagnetic frequency, minus the work function $\varphi$ required to remove the electron from the emitted solid. The relation assumes that the total energy of the incident photon is absorbed by single electron in the excitation process (the independent-or one electron-approximation).

The experimental photoemission spectra can be qualitatively interpreted in terms of the "three-step" model of Berglund and Spicer and others. Within this model, photoemission is treated as a sequence of 1) optical excitation of an electron from an occupied initial state to an unoccupied final state, 2) transport of the excited electron through the solid, which includes the possibility for inelastic scattering by the other electrons in the solid, and
finally 3) the escape of the electron through the sample surface into the vacuum. This is shown schematically in Fig. 4. On the left in the figure, a hypothetical \( P(E, h\nu) \) has been sketched, illustrating the initial optically excited distribution. Changes in the distribution as electrons approach the surface and after the escape into vacuum are indicated. Customarily, the photoemission intensity is separated into two contributions which are a primary distribution of electrons \( I_p(E, h\nu) \) and a secondary distribution \( I_s(E, h\nu) \) for those electrons that have suffered an energy loss due to inelastic scattering. Furthermore, the primary distribution can be factorized according to the "three-step" model into a distribution of photoexcited electrons \( P(E, h\nu) \), a transport function \( L(E, h\nu) \), and an escape function \( K(E) \). The photoemission intensity can be, therefore, written as

\[
I(E, h\nu) = I_p(E, h\nu) + I_s(E, h\nu)
\]

\[
= AP(E, h\nu)L(E, h\nu)K(E) + I_s(E, h\nu),
\]

where \( A \) is a constant.

1. **Optical excitation**

An incident photon of sufficient energy absorbed by a material may cause the optical excitation of an electron from a filled initial state to an empty final state. The Hamiltonian \( H \) of an electron (charge \(-e\)) in the presence of an
Figure 4. Schematic of the three-step model for the photoemission process (from Ref. 33)
electromagnetic field characterized by vector potential $\mathbf{A}$ and scalar potential $\phi$ is

$$H = \left( \mathbf{p} + \frac{e\mathbf{A}}{c} \right)^2/2m + V(\mathbf{r}) - e\phi. \quad (3)$$

By choosing the gauge such that the scalar potential is zero and ignoring terms of order $A^2$. Eq. (3) becomes

$$H = \frac{p^2}{2m} + V(\mathbf{r}) + \frac{e(\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A})}{2mc}$$

$$= \frac{p^2}{2m} + V(\mathbf{r}) + \frac{e\mathbf{A} \cdot \mathbf{p}}{mc} + \frac{e[p, A]}{2mc}$$

$$= \frac{p^2}{2m} + V(\mathbf{r}) + \frac{e\mathbf{A} \cdot \mathbf{p}}{mc} - \frac{i e h V \cdot \mathbf{A}}{4\pi mc} \quad (4)$$

The term $\nabla \cdot \mathbf{A}$ is usually assumed to be small or zero in the bulk. Therefore, Eq. (4) can be simplified to

$$H = \frac{p^2}{2m} + V(\mathbf{r}) + \frac{e\mathbf{A} \cdot \mathbf{p}}{mc}. \quad (5)$$

The last term in Eq. (5) is the perturbation term in the Hamiltonian mixing the initial and final states.

The Fermi Golden Rule of time-dependent perturbation theory now gives the distribution of optical transitions from an initial state $|i\rangle$ with initial energy $E_i$ to a final state $|f\rangle$ with final energy $E_f$ as

$$P(E, h\nu) = (2\pi/h) \sum_{i,f} \langle f | (e\mathbf{A} \cdot \mathbf{p}) | i \rangle^2 \delta(E_f - E_i - h\nu) \delta(E_f - E). \quad (6)$$

The first delta function ensures conservation of energy and the second selects from all possible transitions the emitted electrons with the final energy $E_f$ equal to the energy set by the electron analyzer. In addition to energy conservation,
momentum conservation is also required in the physical sense. This leads to the fact that a free electron can not absorb a photon since energy and momentum can not be conserved simultaneously in such an absorption process. The extra source of momentum in photoabsorption is provided by the solid. For a single crystal, if no phonon participates in the radiative transition, the wavevector of an electron persists during the photoexcitation process, because the exciting photon carries a momentum negligible with respect to the crystal momentum. This transition is the so-called direct optical transition, which appears vertical in a reduced Brillouin zone. The use of optical transitions that conserve \( k \) in the photoexcitation process is a direct consequence of the assumed translational symmetry inside the bulk of the crystal. It would make no sense for an amorphous material.

2. **Transport**

The distribution in energy of photoemitted electrons is similar to the distribution in energy of electrons in the solid after optical excitation. However, the distribution is modified by inelastic scattering involving other electrons or phonons since the electrons must move through the solid to the photoemitting surface before escaping into vacuum. Under the assumption that 1) the distribution in the direction of the excited electrons is isotropic, 2) only inelastic scattering events need be considered, and 3) the probability of inelastic
scattering can be described in terms of a mean free path \( \lambda(E) \) (also called the escape depth), dependent only upon the electron energy, a first approximation of the transport function was given by Berglund and Spicer\(^{29} \) as

\[
L(E,\hbar \nu) = \frac{\lambda(E) \alpha(\hbar \nu)}{1 + \lambda(E) \alpha(\hbar \nu)}, \tag{7}
\]

where \( \alpha(\hbar \nu) \) is the photoabsorption coefficient of a solid at frequency \( \nu \). Typically, over the energy scale of a photoemission spectrum, \( L(E,\hbar \nu) \) is a slowly varying function of the electron energy, so it does not give rise to any structure in the distribution. However, its dependence on the electron energy plays a very important role in the use of photoemission spectroscopy as a probe of surfaces because it translates into a variation in the effective sampling depth of the technique. The energy dependence of the escape depth permits an experimenter to estimate the electron energy at which the minimum in the escape depth occurs and to select photon energies to obtain optimal surface sensitivity. This leads to comparable sensitivity for bulk states and localized electronic surface states and make photoemission a fine tool to study surface chemical processes. In particular it makes it possible to monitor chemisorption and physisorption processes with sufficient sensitivity to observe changes induced by fractions of a monolayer of adatoms.
The general behavior of the escape depth $\lambda(E)$ as a function of electron energy is first a sharp decrease with increasing electron energy, then a fairly flat minimum in the range 50-500 eV with a remarkably small escape depth (~ 5 Å), and finally an increase with increasing electron energy (see Fig. 5). The finite escape depth of the photoexcited electron is a result of various scattering processes. When an electron is photoexcited within the solid, it may reach the emitted surface without being scattered or undergoing scattering. Electron-electron scattering between the excited electron and the valence electrons, and electron-phonon scattering with the crystal lattice are the two important processes that determine the scattering probability. Scattering between the electron and lattice defects (or impurities) is also possible as are plasmons or other collective excitations. Scattering by phonons may influence the direction and momentum of the outgoing electron, but the energy losses are very small compared to the energy resolution in such cases, typically a few millielectron volts (meV), and the process is quasi-elastic. Additionally, the mean free path is fairly energy-independent for electron-phonon scattering but extremely dependent on the electron energy for electron-electron scattering. In fact, the mean free path is limited over most of the energy range by electron-electron interaction except for an electron energy below twice the band gap of an
Figure 5. The general behavior of the inelastic mean free path of electrons as a function of their kinetic energy. The dots are experimentally-determined values for a variety of materials as compiled in Ref. 35. Energies are referenced to the Fermi level.
insulator or semiconductor, where electron-electron collisions are not possible and electron-phonon events, therefore, limit the escape depth. More significant electron energy losses come from electron-hole pair production or by the generation of collective electron oscillations,\(^6\) or plasmons. They are typically several electron volts. At low electron energies, electron-hole pair production is the dominant loss mechanism. Plasmon creation becomes significant at electron energies on the order of 100 ev.\(^7\)

3. **Escape from sample**

The escape of an electron from the solid surface into vacuum is possible only for an electron with a sufficient kinetic energy component normal to the photoemitting surface to overcome the potential barrier \(E_F + \bar{\phi}\), where \(\bar{\phi}\) is the work function of system, which is a measure of the strength of this potential barrier. It is customary to define it as the difference between the potential immediately outside the solid surface (but sufficiently far so that the potential has become position-independent) and the electrochemical potential or Fermi energy \(E_F\) inside the solid. The potential "immediately outside" the solid surface is sometimes called the vacuum level. The escape probability is assumed to be unity if the above condition is satisfied. Using a free-electron model for the excited photoelectron, an escape cone with an opening angle relative to the surface normal can be defined as
\cos \theta = \left[ (\varnothing + E_f)/E \right]^{1/2}. \quad (8)

For an isotropic distribution of electrons inside the solid, the escape function \( K(E) \) is then given by

\[
K(E) = \begin{cases} 
1 - \left[ (\varnothing + E_f)/E \right]^{1/2} & \text{if } E > \varnothing + E_f, \\
0 & \text{elsewhere.}
\end{cases}
\quad (9)
\]

\( K(E) \), like \( L(E, \hbar \nu) \), is a smooth function of the photoelectron energy \( E \).

4. Discussion

In the spirit of the "three-step" model, any structure in the photoemission spectra is now given through the bulk optical excitation process. The matrix element, the transport, and escape functions will only modulate the intensity of peaks. However, due to the existence of the two delta functions in Eq. (6), the initial and final densities of states are implicitly convolved in a complex way into the expression of the energy distribution. It is therefore unrealistic to expect every feature in the initial state band structure to show up in the photoemission spectra or attribute all features in the energy distribution curve (EDC) to initial density of states structure. To interpret features in the EDC then requires a study of both initial and final state structures, as can be done by changing the photon energy. As for matrix-element effects, one can learn about them much more easily using synchrotron radiation than with conventional
photon sources.

As mentioned earlier, the photoemission technique can provide extreme surface sensitivity by working around the minimum of the electron escape depth, where the probing depth is about 5 Å. Since inter-atomic distances in a solid are also typically a few Å, at these very small escape depths, photoemission only probes the outermost atomic planes of the solid and the validity of the three-step model becomes more and more questionable. The separation of the photoemission process into excitation, transport, and escape obviously loses its meaning when the escape length turns out to be of the order of the atomic dimensions, which is the case in the energy region 30-200 eV. But it is quite surprising what a great success in explaining photoemission data the three step model has had, considering its conceptual deficiencies. These deficiencies fall into two categories: 1) the almost complete neglect of all surface effects (except for the escape function); and 2) the use of one-electron eigenfunctions to determine all the possible transitions. A proper description of the photoemission process as the response of an interacting multielectron system to an electromagnetic field would contain these effects. Several more sophisticated models have emerged during the last decade, where the photoemission process is treated as a one-step quantum-mechanical event. Rather than present the more rigorous models and formulas here, it is better to take the three-step model as a first
approximation and amend it to account for these effects.

The surface effects arise from the presence of the solid-vacuum interface where an abrupt discontinuity in media occurs. Generally speaking, the surface effects can be divided into two parts according as the effects arise from either contributions peculiar to the photoexcitation process or purely intrinsic electronic properties of the surface. In other words, we can define surface optical effects as those absorption phenomena that are produced in the vicinity of the surface as different from the optical absorption in the bulk, and electronic surface effects, in contrast, as those features that are introduced by the surface as distinct from the bulk: namely, bound "intrinsic" surface states; "extrinsic" or absorbate induced states; and including unbound "resonances," degenerate with the vacuum continuum, that exist above the vacuum threshold of the emitting surface. Let us consider these effects in more detail as follows.

In the optical excitation step of the three-step model, we have assumed that the spatial variation in the vector potential \( \mathbf{A} \) is small on the scale of atomic dimensions, and ignored the \( \nabla \cdot \mathbf{A} \) term. However, the boundary conditions of Maxwell's equations at the solid-vacuum interface lead to the continuity of the component of the radiation field parallel to the surface, while the perpendicular component of the transverse field has a discontinuity at the surface whenever
the dielectric constant is not equal to 1 inside the material. Such a step function discontinuity in \( \mathbf{A} \) may make the spatial variation of \( \mathbf{p} \cdot \mathbf{A} \), not small compared to \( \mathbf{A} \cdot \mathbf{p} \). This gives in addition to the \( \mathbf{A} \cdot \mathbf{p} \) term a \( \partial A_z / \partial z \) term in the matrix element \( \left( \nabla \cdot \mathbf{A} = \partial A_z / \partial z \right) \). Furthermore, the discontinuity in the component of the field normal to the surface means that \( \nabla \cdot \mathbf{E} \neq 0 \), so there will be a charge imbalance in the surface region. This charge imbalance can set up longitudinal fields caused by the interaction of the electrons in the solid with the surface charge.\(^4^4\) Such a longitudinal field will differ significantly from the long-wavelength transverse field. The nature of the longitudinal field depends on the frequency-dependent dielectric response of the system. For a nearly free-electron metal, the electron gas is incompressible below the plasma frequency \( \omega_p = (4 \pi n_0 e^2 / m)^{1/2} \) (\( n_0 \) is the electron density), which means that the longitudinal fields may exist only in the surface region and are evanescent into the bulk. This produces Friedel oscillations,\(^4^5\) with wavelengths much shorter than the wavelength of the incident light. On the other hand, above the plasma frequency the longitudinal waves can propagate into the solid without damping (i.e., plasmons). Due to these internal induced fields and the charge imbalance in the proximity of the surface, substantial variations in the one-electron potential \( V(\mathbf{r}) \) are expected in the surface.
region. Essentially, the one-electron potential in the surface region suffers other major variations in addition to the variations resulting from the electromagnetic fields. In the bulk the ions form a regular structure, whereas at the surface there may be departures from this regularity in order to relax the surface structure and lower the total energy of system. Both the rearrangements of ions as well as the responding distribution of electrons in the surface region would make a great change in the potential from the bulk. Therefore, the solutions of the single-particle Hamiltonian in the solid are affected by the introduction of such a surface. Additionally, the wave functions in the solid have to fulfill the proper continuity requirements at the surface, which are to match continuously, with a continuous derivative, to an outside solution in the vacuum. This leads to amplitudes of the wave functions in the surface region different from the bulk. There exist additional solutions, called surface states. For states below the vacuum level the wave functions must vanish at large distances from the solid. For states above the vacuum level the wave functions must look like plane wave at large distances. A simple pictorial representation of the wave functions is shown in Fig. 6. We distinguish between the extreme case of weak and strong damping. Wave functions (c) and (f) in Fig. 6 correspond to the states which are only very weakly evanescent into the interior of the solid and are termed Bloch-like because of their strong resemblance to the
Figure 6. Schematic representation of the wave functions of initial states (a), (b) and (c), and final states (d), (e) and (f), involved in optical transitions giving rise to photoelectron emission. States (c) and (f) correspond to bulk Bloch states hardly modified by the presence of the surface. States (b) and (e) are more strongly evanescent (surface resonances). States (a) and (d) have essentially no amplitude in the interior of the solid and correspond respectively to a true bound surface state and the case of band-gap emission (from Ref. 46)
Bloch states in conventional bulk-band theory. There are also states characteristic of the surface itself. Below the vacuum level there are highly localized surface states such as (a) and these may be occupied or unoccupied. The analogous state above the vacuum level is the "band-gap" state (d). A band gap is by definition an energy range in which an infinite solid can not support electronic states. Electrons impinging externally on the solid in this energy range are therefore totally reflected. Their wave functions however have an evanescent tail extending a short distance into the solid, so that optical transitions to these states are possible. States of intermediate character are the surface resonances. These are Bloch-like evanescent states which have their largest amplitude at the surface. Of course, the categories are not distinct. There are cases of bands of states whose character varies continuously from surface state to surface resonance to Bloch-like state. In a word, the so called "classical" surface photoemission effect, relating to the influence of the shape of the surface potential barrier, and emission arising from the behavior of the vector potential field within the surface region, are the cases in point.

If the solid is crystalline, k-vector conservation arising out of the three-dimensional translational symmetry properties is also changed by the loss in translational symmetry at the solid-vacuum interface. In the original three-step model, the wavevector is conserved in the
photoabsorption process for all three dimensions. To account for the loss in the translational symmetry in the direction normal to the surface, a small imaginary part, \( \text{Im}(k_\perp) \), is introduced to the real \( k \)-vector component \( \text{Re}(k_\perp) \) that is perpendicular to the surface. This leads to a momentum broadening effect in photoemission because of the uncertainty of momentum normal to the surface caused by the decay of the final wavefunction, and a change from the delta functions \( \delta(k'_\perp - k_\perp) \) which describe the conservation of \( k \)-vector in the direction normal to the surface to a Lorentzian

\[
\delta(k'_\perp, k_\perp) \sim \frac{1}{([k'_\perp - \text{Re}(k_\perp)]^2 + \text{Im}(k_\perp)^2)^{-1}}. 
\]

Nevertheless \( k \)-conservation in the two directions parallel to the surface remains. The decay constant of the wavefunction amplitude which is given by the imaginary part of the wavevector is related quite simply to the mean free path in the direction perpendicular to the surface through the formula

\[
\lambda = 1/[2\cos \theta \times \text{Im}(k_\perp)] ,
\]

where \( \theta \) is the angle between the group velocity of the electron and the surface normal. Combining the relaxed selection rule with our knowledge of average electron mean free paths, we can proceed to the different effects of these in three regions. In the weak damping limit, the mean free path of the electron is greater than the typical dimension of the unit cell. Equation (10) then represents a sharply peaked
function around the direct transition $k' = k$. This is the region where the $k$-conserving three-step model is a good approximation. It covers the range of photon energies below 20 eV. As the mean free path approaches its minimum around 40 to 100 eV and the $k$-vector selection rule in the direction normal to the surface is to a large degree relaxed, surface effects become more prominent. Beyond electron energies of 100 eV the mean free path increases again and the uncertainty in $k_1$ decreases. In this region, the final state becomes nearly free-electron-like. This leads to a situation where the requirement of quasidirect transitions is readily fulfilled due to both a small freedom in $k$ and abundance of final states. We then observe the initial density of states in the EDC.

A single-electron theory of photoemission in the three-step model often provides not only an excellent starting point but also a quite adequate description of the energy distribution spectrum from solids. But one-electron eigenvalues of a multielectron system (e.g., of an atom or group of atoms) do not represent a real physical property of the system in its initial or ground state. In reality, individual electrons do not, in the ground state of a system, have distinct energies associated with them. The energy of the system is best thought of as shared simultaneously (as it must be for a many-body system) among all the electrons. The
physical significance of this should not be ignored. Nevertheless, one-electron eigenvalues are useful when viewed as a first-order approximation to observed electron binding energies. This is particularly true when the initial single-electron state is spatially extended, as in the case of a Bloch function, and when the bandwidth of such states is comparable with collective mode energies. However, there is a sizable class of photoemission events, usually typified by the breakdown of Koopmans' theorem, in which independent- or non-interacting electron theory provides a qualitatively inadequate description. The simplest example of these is the 2-electron or Auger process. This is normally associated with the excitation of a core electron. After excitation, the core hole is filled with an electron whose binding energy is less than that of the core level, e.g., the valence band electron, and another electron is emitted from the solid. The emitted electron leaves with an energy corresponding to the difference between the core hole state and the state from which the electron was in that filled hole. Since this process relies only on the presence of the core hole, a feature will be present in the EDC above the threshold energy corresponding to the excitation of the core level. The energy associated with this process is independent of the photon energy and will, therefore, always appear at the same kinetic energy.

The emitted electron energy can also be changed due to the response of the system to the excitation. This response
can be in the form of relaxation or screening. After excitation of the electron, the system is now in an N-1 electron state with a positive hole remaining. The effective potential seen by the remaining electrons should be different between before and after the removal of the electron, and the surrounding electrons would tend to screen this hole and readjust themselves into eigenstates of a new Hamiltonian in order to lower the energy of the system. This so-called relaxation energy, defined as the change in the total energy of the system upon allowing all the other electrons to relax, is then transferred to the emitted electron which leaves the solid with a slightly higher kinetic energy. The relaxation energy is calculated in the adiabatic limit corresponding to an excitation just above threshold. In this limit, the time scale for which the excited electron leaves the region is long and, therefore, the entire system can always remain in its ground state configuration. This configuration is determined by the instantaneous charge density. The relaxation energy depends greatly on the local extent of the initial electron state. For localized levels, the relaxation energy is greatest with the energy decreasing as the state becomes more band like.

Departure from the adiabatic limit introduces a non-vanishing probability that the target will be left in an excited state, causing the photoejected electron to be emitted with less energy than in the adiabatic limit. The emitted
electron is referred to as satellite or shake-up electron and leaves the system behind in the excited state. If the amount of energy transferred to the system from the photoexcited electron is large enough, a second electron may be excited to a high enough energy to leave the solid. The feature due to this process is called a shake-off satellite. Of course, multiple electron ejection is possible, in which case a continuous shake-off spectrum is observed since the discrete energy can be arbitrarily divided between the emitted electrons.

It is convenient to think of the photoexcitation process as switching on a time-dependent potential $V_h(r,t)$ which describes the changes in the effective potential of the system due to the creation of a positive hole, and $\lim(t\to\infty)V_h(r,t)$ represents the fully relaxed potential due to the hole, neglecting the decay process. Suppose the potential is instantly switched on at $t = 0^+$, i.e., $V_h(r,t) = V_h(r)u(t)$, where $u(t)$ is the product of a function dependent only on time, which describes the behavior of the potential after switch-on, and a step function. This potential changes discontinuously in time at $t=0^+$ and has Fourier components at all frequencies. Therefore, this suddenly-switched-on potential can transfer energy to the electron gas leading to a satellite structure. On the other hand, if the electron is excited closer to threshold, it remains in the vicinity of the
hole longer and the electron gas sees no significant change in net potential. The short-time Fourier components (the high-frequency terms) are small, resulting in low intensity shake-up satellites. With a very long switch-on time, the adiabatic limit is reached. Depending on the photoelectron kinetic energy, the switching can span the entire time domain with the satellite intensity varying accordingly.

In terms of energy eigenstates, the shake-up satellite corresponds to an excited state of the N-1 electron ion. These states could be thought of as excitations of an electron to a higher orbital by the sudden loss of a core electron and the accompanying sudden change in the potential. Although this is an incorrect physical picture of the shake-up feature, since it uses a one-electron picture, it does give some qualitative insight into the problem. In reality, the shake-up states are simply eigenstates of the N-1 electron ion. Transitions to these states are allowed in exactly the same way as to the primary hole state.

Amending the three-step model to include the many-body and surface effects gives a reasonable qualitative theory of the photoemission process. Admittedly this procedure is not rigorous and does contain some unjustified approximations, but has been shown to be quite adequate in describing the experimental features.

As mentioned earlier, in the transport step of the three-step model, when the photoexcited electron moves through
the solid, it may experience an inelastic collision. Those electrons which escape from the photoemitting surface after scattering contribute to the secondary electron distribution. Usually to an experimenter the tendency has been to concentrate exclusively on the spectral interpretation of the region which contains the so called "primaries" or "elastically" emitted electrons, while the "secondaries" or "inelastic" electrons are almost ignored in spite of the fact that they constitute the major content of the photoemitted current. We can find many examples in the literature where the discussion focuses solely on interpretation of structure in the primary spectrum, i.e., peaks or dips, and their movement with excitation energy or emission angle, disregarding the much larger "background." Valid and interesting conclusions may be derived from such an analysis. However, much valuable information is also contained in the often disregarded inelastic part of the spectrum. For instance, important information, relating to the photoabsorption coefficient of a system, can be extracted from the analysis of the inelastic electron spectra. Although the secondary electrons may not provide any information in terms of the energy distribution, they do play a role in terms of the yield spectrum. The total yield spectrum at a given photon energy is given by the total integrated intensity of the energy distribution curve. This is the sum of the primary, secondary, and Auger distributions and the major
contribution to this is the secondaries. The number of secondaries at energy $E$ is proportional to the total number of excited electrons with energies greater than $E$. This is due to the fact that any electron with energy $E'$, greater than $E$, can be inelastically scattered in some manner to give it a final energy of $E$. Therefore, the same information extracted from the total yield spectra can be gained by determining the intensity at very low kinetic energies, where the secondaries are dominant. The spectra obtained by scanning the photon energy while sampling electrons at very low kinetic energies are the so called partial yield spectra. Both this and the total yield spectra show the same features as the photoabsorption spectra. Through photoemission, we can not only observe the energy levels of the solid in direct emission, but can also get a measure of the dipole matrix elements involved in the photoemission process.

B. Photoemission Spectroscopies

Four different photoemission spectroscopies were used to study metal-semiconductor systems in this thesis. They are angle-integrated electron energy distribution curve (EDC) spectroscopy to measure the valence band DOS, constant initial-state (CIS) spectroscopy to characterize the valence band features, constant final-state (CFS) spectroscopy to investigate the photoabsorption behavior of the system, and core-
level spectroscopy to deduce the structural details of the system.

1. **Angle-integrated energy distribution curve (EDC)**

   The classical, and still by far the most common, photoemission technique is the measurement of an energy distribution curve of the photoemitted electron at a particular photon energy. In this mode, the photon energy $h\nu$ is fixed and the intensity of emission as a function of electron kinetic energy is recorded. The emitted photocurrent is collected over a wide solid angle, so as to sample over all possible emission angles of photoelectrons. Data so obtained give a distorted replica of the occupied bulk and surface density of states, distorted by the inelastic background and a convolution over the final density of accessible states. With the tunability of the synchrotron radiation over a large photon energy region, it is possible to take a series of EDCs at selected photon energies to obtain different surface sensitivity by optimizing the two most important parameters: photo-ionization cross sections (matrix element) and electron escape depths for the particular problem being studied. The tunability of synchrotron radiation has also made two other photoemission techniques possible, which are constant initial-state (CIS) spectroscopy and constant final-state (CFS) spectroscopy (also named partial yield spectroscopy).
2. **Constant initial-state spectroscopy (CIS)**

In CIS the photon energy and kinetic energy of the photoemitted electrons are scanned synchronously to keep $E_k - h\nu = \text{constant}$, where the constant is the electron binding energy of initial state, relative to the vacuum level. This can be achieved by making a synchronous scan of the optical monochromator and the electron analyzer. The initial density of states is fixed by this method and all the excitations from one given filled state to different empty states are recorded. A CIS spectrum, therefore, provides a picture of the density of unoccupied states weighted by the matrix element. If the final states do not cause any new features in this picture, quite frequently the case, such a CIS spectrum obtained under this assumption reveals the electron-configuration characteristic of the initial state through the matrix element and can be used to characterize the valence band features.

3. **Constant final-state spectroscopy (CFS)**

In CFS, the photoemitted electrons with a fixed kinetic energy are detected while the photon energy is continuously varied. When the photon energy is scanned, electrons from occupied states are excited into this fixed final state energy window. As mentioned previously, when this fixed energy window is selected in the regions where inelastic secondaries are prominent and the energy distribution of these inelastic scattering electrons is independent of photon energy, a
spectrum obtained by this method reflects the optical absorption coefficient and is proportional to the total yield spectrum. This is why CFS is also named partial yield spectroscopy. However, electrons of increasing kinetic energy being selected, the escape depth is reduced and surface state contributions to the yield are enhanced. In this thesis, the partial yield data were taken by setting the electron energy of the analyzer to 2.5 eV and scanning the monochromator through the desired photon energy range.

4. **Core-level spectroscopy**

Although core-level spectroscopy is same type of spectroscopy as EDC, it probes the tightly-bound atomic core levels instead of valence band structure. Since the exact binding energy of a core-level electron is sensitive to the details of the local environment, high-resolution core-level line shape studies can provide very valuable information about the chemical and physical properties of solids and surfaces, and become one of the most widely used diagnostic tools for routine surface analysis. These measurements are usually done in an angle-integrated configuration to obtain the maximum photocurrent signal.

There are many causes for the core-level binding-energy shifts. In order to simplify the theoretical computation in the core-level binding-energy shifts, we often break the core-level shift problem down into contributions from the
initial and final states of the system. They separately reflect the results of differences in the initial-state properties (chemical and configurational effects) and the final-state properties (screening and/or relaxational effects) between atoms in inequivalent sites.

One very important conceptual problem in defining an initial-state contribution to a core-level binding-energy shift arises from the fact that photoemission is indeed a final-state spectroscopy. The technique does not really probe initial-state properties directly. In general, the initial-state properties can only be inferred indirectly, if at all. What photoelectron spectroscopy probes is the spectrum of energy differences between the ground state of the sample and the numerous final (or ionized) states of the sample. Thus, since there is only one ground state for a particular sample, the photoelectron spectrum consists of the spectrum of final states. Figure 7 presents a schematic illustration of this point.

To see the conceptual dilemma, it is useful to define a system in which an initial-state property is the only cause for a core-level binding-energy shift. Consider a sample in which the same element is present in two different chemical environments in the same sample; call them site A and site B, as in Fig. 7. Suppose that in site A the element has a larger total electron density than the element in site B and all other things are equal. It will require less energy to create
Figure 7. Illustration of the shift in core-level binding energy for the same element in two different environments, A and B. The initial and final states in a total energy difference framework are illustrated in (a), the core-level peaks in (b) and total energies of the states in (c). Final states of the type in (c) will be referred to throughout this view with $A^*$ described as the state of lower total energy and $B^*$ described as the state of higher total energy (from Ref. 58)
a core hole in A than in B, due to a distinct difference in the electrostatic potential at the core of each element, and the photoelectron spectrum of the sample will then show that in A the element exhibits a smaller core-level binding energy. One would naturally think that an initial-state contribution was responsible for the such a core-level binding-energy shift between A and B. However, to view photoemission properly, there is only one ground state of the system and two final states (a core hole at A or B) so the shift observed in the spectrum actually represents the difference in energy between the two final states.

The crux of the dilemma is now apparent. What is observed in the spectrum is an energy difference between two distinct final states of the system. But the apparent cause of this difference in energy between two final states is a property of the initial or ground-state charge distribution; that is, although an initial-state distribution makes its contribution only by having an effect on the energy difference between the two final states, the shifts in the core-level binding energy completely correspond to the difference in the initial-state properties. Such an effect can quite properly be called an initial-state contribution to a core-level binding-energy shift.

The above qualitative description of an initial-state contribution as being based on a difference in initial-state charge density has a rigorous basis in theory. Shifts in
the core-level eigenvalues turn out to correspond directly to what may be called the initial-state contribution. This correspondence occurs because of the way a one-electron Hamiltonian treats each electron as moving in a smeared-out, static field of all the other electrons. Changes in the initial-state charge density on an atom will directly change the potential in the core of the atom, thus shifting the core-level eigenvalues. Therefore, it is equivalent to defining the initial-state contribution as the core-level eigenvalue shift.

The phenomenon of the core-eigenvalue shift can easily be understood by noting that it is directly analogous to the classical electrostatic case of the potential inside a uniformly charged spherical surface. Viewed in this manner it is clear that excess negative charge in the valence shell of an atom will raise the electrostatic potential at the core and thereby reduce the energy required to remove a core electron. However, this simple classical picture will not hold very well for shallow core levels. For example, the 3s and 3p core orbitals of copper are similar in their radial extent to the valence 3d orbitals. Upon changes in the valence charge, the 3s and 3p orbitals will experience only part of the electrostatic effect that occurs deep in the core. Therefore, for shallow core levels, the magnitude of the initial-state contribution is reduced when compared to that of deep core levels. In this electrostatic potential model, however, it
shows that the exact binding energy of a core-level depends on the valence charge $q$. For a change $\Delta q$, the binding energy changes by

$$\Delta E = b\Delta q.$$  \hspace{1cm} (12)

In the simplest approximation for this so-called chemical shift, the $q$'s are regarded as the charges localized on the valence shell with radius $R_v$. The corresponding potential shifts all inner core levels with radii smaller than $R_v$ by equal amounts $b = 1/R_v$ per unit charge transfer $\Delta q$. However, in solids, a charge $\Delta q$ on one atom is often compensated by opposite charges on neighboring atoms: that is, the net shifts in core-level binding energy is usually less than expected.

Through the foregoing discussion, the concept of an initial-state contribution can be well understood. Anything that changes the electrostatic potential at the atom under study takes the form of an initial-state contribution. For example, the shifts in the core-level binding energy are due to a chemical-reaction difference or a configuration change. However, there are some ways, which may not be immediately obvious, in which initial-state contributions can occur. One such initial-state contribution is the Madelung contribution. In an ionic solid, this effect is particularly important since the electronic charge on the atom under study is generally opposite to that on the nearest-neighbor atoms. Thus the electrostatic potential at the core of the atom under study
must be expressed in the form of a Madelung sum. This sum generally reduces the magnitude of the core-level shift that would be predicted on the basis of the charge on one atom alone. In other words, this Madelung effect reduces the proportionality constant \( b \) in Eq. (12) to \( b' = \frac{1}{R_v} - \frac{\alpha_m}{a} \), where \( \alpha_m \) is the Madelung constant and \( a \) the lattice constant. 

In Si, the proportionality constant \( b' \) has been estimated from studies on oxygen-induced shifts by Grunthaner et al.,\(^{61}\) where \( b'(Si) \approx -2.2 \text{ eV/electron} \). Other examples of initial-state contributions are band bending at semiconductor surfaces and interfaces, and adsorption of an atom in a surface electrostatic dipole layer.

One particular initial-state contribution which has not been mentioned above and has received much attention lately is the so-called surface core-level shifts of pure metals. This can be understood from the application of the electrostatic approach. This application is based on the assumption that narrowing of the valence band at the surface of a metal is primarily responsible for the initial-state contribution to the bulk-to-surface core-level shift, commonly known as the surface core-level shifts. The basic idea\(^{62-64}\) is illustrated in Fig. 8 for the case of a less-than-half-filled band. The band width at the surface is presumed to be more narrow for the surface layer of metal atoms due to the reduced number of
neighboring atoms. However, merely narrowing the valence band about its centroid pushes occupied states above the Fermi level. Therefore, the highest occupied states of this valence band must be depopulated to avoid having electrons rise above the Fermi level. This depopulation could occur either by donating a fraction of an electron into the bulk or by dropping one whole electron into an unfilled core shell. In the former case, a net positive charge relative to bulk atoms has been built onto the surface layer of atoms. The effect of this net positive charge is to shift both the surface valence-band centroid and the surface core-level eigenvalues downwards due to the electrostatic attraction. This simple form predicts a monotonic relationship: the more the surface valence band is narrowed, the more it and the core-level eigenvalues are shifted. In the latter case, however, the surface core-level shift becomes a more complicated problem due to its extra dependence on which unfilled core level we deal with. As mentioned earlier in Chapter I, the surface core-level shifts of Sm is such a classic example as this. However, caution should be taken in using the band narrowing argument on the core-level shifts.

The band narrowing argument is a convenient way of thinking about the core-level shift problem but in reality it is only the excess charge at the surface or in the bulk that constitutes a real property of the ground state of the system. The band width is not a true ground-state property, but is a
Figure 8. Illustration of how the narrowing of the d-band of a rare earth metal at the surface leads, by charge transfer and simple electrostatics, to a core-level shift.
first-order approximation to the spectrum of hole states. Thus the charge density, not band narrowing, is the true physical basis for this initial-state contribution.

Departing from the initial-state contribution, the final-state contribution also plays an important role on the core-level binding-energy shifts. The main contribution from the final states is the relaxational or screening effect. The fundamental concept of this effect has already been discussed in the previous section. To put it briefly, for the fully screened core hole, the screening always reduces the core-level binding energy in contrast to the initial-state contribution, where the initial-state contribution can go either way depending, roughly, on whether the atom under study donates electron density to or accepts electron density from the surroundings.

For solid-state systems, it is convenient to break the screening effect down into two parts: intra-atomic screening and extra-atomic screening. This breakdown is especially useful for the more elementary treatments of the problem since one then assumes the intra-atomic part to be independent of chemical environment. This approach is probably a fairly good assumption, as long as the ground-state valence configuration of the atom is independent of the chemical environment. The simpler problem can then be addressed of how the extra-atomic part varies with chemical environment. It is fortunate that the intra-atomic part varies little with
chemical environment since the energy associated with intra-atomic screening is usually much larger than the observed core-level shifts. However, when the valence configuration differs, serious errors may be expected.

So far we have been discussing only the core-level binding-energy shifts arising from either the initial- or final-state contributions. But the line shape of a core level is also changed due to incomplete relaxation around the core hole, and the lifetime of the core hole due to the different decay mechanisms opened to it. In the absence of lifetime effects, and for perfect energy resolution in the analyzer, the line shape of a core electron would appear as a infinitely sharp peak in the spectrum. The lifetime of the core hole left behind results in broadening because of the uncertainty principle, and the infinitely sharp peak changes to a Lorentzian function

\[ \mathcal{L} = \frac{\Gamma}{2\pi[(E - E_C)^2 + (\Gamma/2)^2]}, \]  

(13)

where \( (\Gamma/2)^{-1} \) is the hole lifetime. Thus this function is more appropriate to describe a core-level line shape corresponding to leaving the system in something close to the electronic ground state in the presence of the core hole. However, the larger binding energy side of this function can be also modified by incomplete screening. In photoemission spectra of metals, the core-level line often exhibits an asymmetry, skewed to larger binding energy, due to the
creation of low-energy electron-hole pairs concurrently with core ionization. Such a skewing of the core-level line is generally known as the Doniach-Sunjic lineshape, the expression for which is

\[ I = \frac{\gamma(1-\mu)\cos\left[\frac{1}{2}\mu \arctan\left(\frac{E}{\beta}\right)\right]}{(E^2 + \beta^2)^{(1-\mu)/2}}, \]  

where \( \gamma \) is the gamma function, \( \mu \) the asymmetry factor, \( 2\beta = \Gamma \) the full width at half maximum of the Lorentzian lifetime broadening, and \( E \) the energy.

In semiconductors and insulators the Doniach-Sunjic asymmetry in core-level peaks is generally not observed because the band gap eliminates the possibility of exciting low-energy electron-hole pairs.

Core level spectra can be also used to identify the composition of specimens within the sampling depth of photoemission. From the three-step model, the intensity of a core level \( j \) from an element \( Z \), \( I(j,Z) \), is related to the concentration \( C(Z) \) of this element according to

\[ I(j,Z) = A\eta(j,Z,\hbar\nu)C(Z)L(E)K(E)T(E), \]  

where \( \eta(j,Z,\hbar\nu) \) is the photoelectron cross section of the core level and \( L(E) \) and \( K(E) \) are the transmission and escape functions, respectively. \( T(E) \) is the energy dependent transmission function of the analyzer and \( A \) is an energy-independent scale factor that takes photon intensity and
Performing core-level spectroscopy with synchrotron radiation allows experimental control over the sensitivity of the measurement. This provides a means to isolate spectral features specific to the surface by comparing relatively bulk-sensitive to surface-sensitive spectra.

Figure 9 provides a practical illustration of this point. It shows Si-2p core-level spectra for the clean Si (111) surface taken at incident photon energies of 110 and 130 eV. The intrinsic line shape is a spin-orbit-split doublet, with 2p₁/₂ and 2p₃/₂ components. Each spin-orbit component is represented by a Voigt line shape (a convolution of a Gaussian and a Lorentzian) to account for core-level lifetime broadening and instrumental resolution effects. The line shapes of Fig. 9 are not simple doublets; rather, it is experimentally observed that they consist of three spin-orbit-split components.⁷³⁻⁷⁷

The data clearly suggest that two features, a small bump on the low-binding-energy side, and the filling-in of the valley between the two spin-orbit-split peaks, are surface-derived. The relative intensity of these are larger in the 130-eV spectrum, where the mean free path is 5.3 Å,⁷⁴,⁷⁶ than in the 110-eV spectrum, where it is 10 ~ 12 Å. Therefore, surface sensitivity and relative intensity are therefore directly correlated.
Figure 9. Si-2p core-level spectra for clean Si(111) taken at the indicated incident photon energies. The lower spectrum includes mainly emission from the bulk; the upper emphasizes surface features. The dashed curves represent the three spectral components; B is bulk in origin and S1 and S2 are surface-derived. The binding-energy scale is referred to 99.14 eV below the Fermi level.
III. EXPERIMENTAL

A. Apparatus

The discussion of the experimental apparatus is divided into four sections. The first section briefly describes the light source for experiments, - the Aladdin electron storage ring at the University of Wisconsin Synchrotron Radiation Center, Stoughton, Wisconsin, and the AMES/MSU Erg-Seya combined monochromator used to obtain and focus the incident photons on the sample. Section two and three describe the experimental hardware: the stainless-steel ultra-high vacuum (UHV) chamber where the data were taken and the electron-energy analyzer used to collect them. The last section provides a general description of photoelectron spectrometer operation.

Much of the experimental apparatus mentioned in the last three sections was developed by C. G. Olson and D. M. Wieliczka and the Erg-Seya combined monochromator was designed by C. G. Olson.78

1. Light source and baseline

It is well known that accelerated charges emit electromagnetic radiation.79 For non-relativistic motion the radiation shows the characteristic \( \sin^2 \theta \) Larmor radiation pattern. At ultra-relativistic velocities, the radiation is
beamed into a highly collimated, narrow cone in the direction of the velocity vector. This synchrotron radiation, as it is called, has a broad frequency distribution covering the visible, ultraviolet, and X-ray regions. It is strongly polarized in the plane of particle motion.

The source of synchrotron radiation for these experiments was the Aladdin electron storage ring at the University of Wisconsin Synchrotron Radiation Center (SRC), Stoughton, WI. In storage rings such as these, electrons radiate as they are accelerated by bending magnets. Radio-frequency energy in the proper phase with the electrons' motion compensates for radiation loss and maintains the charged particles' orbit. Details concerning Aladdin have been given in the literature. Briefly, it operates at an energy of 800 MeV. Synchrotron radiation beamline ports were provided and connected to monochromators provided by the facility and individual user.

Incident photon energies of 10 to 1000 eV (or wavelengths ranging between 12.4 and 1240 Å) were used to probe valence-band and core-level states in these experiments. Monochromatized radiation of the required energy was provided by the AMES/MSU Erg-Seya combined beamline. Figure 10 shows its optical layout. Briefly speaking, its two monochromators share a common refocusing mirror and only the movement of a single plane mirror is required to change the monochromator illuminating the sample. The operating principles of these two monochromators have been described in the literature.
Extended Range Grasshopper - Seya Namioka Monochromators

Figure 10. Optical layout of the Ames/MSU EGR-Seya combined beam line located at Sychrotron Radiation Center, Stoughton, Wisconsin
Essentially, each of the monochromators consists of an entrance slit, a dispersive element, usually a diffraction grating, and an exit slit. However, differences in design details between the Seya and Erg results in distinctly different performance characteristics. The resolution varies from 0.04 to 0.5 eV, depending on photon energy, the entrance and exit slit widths, the ruling density of grating, and the radius of the grating. Finally, wavelength tuning was accomplished by changing the relative geometry of the grating and the exit slit via computer- or manually-controlled stepping-motor adjustments.

2. Photoemission chamber

In order to avoid surface contamination, the maintenance of ultra-high vacuum (UHV) conditions is critical. Thus all photoemission experiments were carried out using a stainless-steel UHV chamber. Metal seals and UHV-compatible material were used throughout. The chamber was pumped by a Thermionics Laboratory Inc. Model IP 200 differential-ion pump (pumping speed = 200 liters/sec) and a Balzers TPU110 turbomolecular pump (pumping speed = 110 liters/sec). After closing the chamber, the chamber was initially pumped down by the turbomolecular pump, then baked for a period of about 10 hours to reach minimum pressures. After the pressure equilibrium was reached, the pumping was switched to the ion pump by closing the gate valve between the chamber and the turbo and leaving
the chamber still under bake. A new lower pressure equili-
brum would be obtained after about another 10-hour bake, then
the heaters were turned off, and the chamber gradually cooled.
During the cool-down period, some degassing procedures of the
filaments were carried out. When the chamber was completely
cool, the base pressure was typically about \(6 \times 10^{-11}\) Torr or
less. The internal chamber pressure was monitored by a nude
ion gauge protruding from the chamber and located as far from
the pumping port and the probing area as possible. The
chamber was mounted on a frame with an air-floated-pad stand
and a kinetic mounting system, so it could be positioned such
that the foci of the electron-energy analyzer and the light
source were coincident at the sample position.

The sample was mounted at one end of a commercial
precision manipulator which provided the movements of the
sample to the different positions for the individual purposes:
changing, sputtering, or probing sample.

The chamber also had facilities for sample characteriza-
tion and preparation. A 0-to-10-kV electron gun and a CMA
(cylindrical mirror analyzer) electron-energy analyzer
comprised an AES (Auger Electron Spectroscopy) system to
monitor surface chemical composition, or an EEL (Electron
Energy Loss) system to monitor surface chemical properties. A
sputter-ion gun and an argon gas supply allowed for the
cleaning of samples inside the chamber. An evaporation system
with two evaporators allowed for the deposition of a thin-film
overlayer onto substrates. A removable sample-storing rack in the chamber allowed for the changing of samples without breaking vacuum. Many windows in the chamber allowed good sample visibility during most processes.

The electron-energy analyzer (described below) was located on the top of the chamber. The sputter-ion gun and the evaporators were located at a lower level; this protects the analyzer from unwanted material deposition during evaporations. The samples were oriented at an angle of about 45° with respect to the axis of the analyzer in order to sample over all possible emitted angle of the photoelectrons and obtain a truly angle-integrated spectrum. We will see why this orientation angle was chosen shortly.

3. **Electron-energy analyzer**

A commercial double-pass cylindrical mirror analyzer (PHI Model 15-255G) was used to determine the emitted electron energies. The analyzer consists of two hemispherical pre-retarding grids and two cylindrical mirror velocity analyzers in series in a single instrument. The two cylinders of radii \( r_1 \) (inner) and \( r_2 \) (outer) are positioned accurately coaxially and regarded as a dispersing element. As electrons traverse the region between these cylinders, they follow trajectories dependent upon their kinetic energies, the specific analyzer geometry, and the potential between the cylinders. Only electrons within a certain kinetic-energy range will be
directed through apertures and enter the detector. The pass energy is the kinetic energy an electron must have in order to pass through the dispersing element and apertures. The pass energy of a commercial CMA is usually 1.7 times the potential difference between the cylinders, and the entrance angle $\beta$ of the sampling cone is chosen to be $42'18''$, since at that angle the CMA becomes a second-order focusing device. A typical angular aperture $\Delta \theta$ would be $6'$. From these characteristics of geometry, it now becomes obvious why the particular sample-orientation has been chosen.

The energy resolution of a CMA is determined by the aperture size and the pass energy. The commercial CMA often has two aperture sizes; the smaller one (intended for Auger spectroscopy) provides a resolution of 0.6% of the pass energy, while the larger one (which was used for all of the spectra in this thesis) give a resolution of 1.6% of the pass energy. These values are given by the manufacturer. For the double-pass CMA, the effective energy resolution is set by the first stage and the sensitivity by the second stage, although the two functions are clearly not independent (or uncoupled).

Due to the dependence of resolution on pass energy, the band pass of the analyzer would increase as the electron energy increases. To overcome this, the analyzer can be run using the two spherical pre-retarding grids centered on the source position of the samples. These grids are used to
change the kinetic energy of the emitted electrons to a previously set value, the pass energy. The potential applied to the grids is equal to the difference between the fixed pass-energy and the electron energy. Therefore, we can operate a CMA analyzer in two different modes: the constant-transparency mode and the constant-resolution mode. For Auger spectroscopies, the double-pass CMA is operated in its "normal" (constant transparency) mode. In this mode, the retarding grids and the inner cylinders are grounded. Simply scanning the negative potential applied to the outer cylinders of the CMA gives the energy distribution of electrons passing through it directly. Quite often, the negative potential of the outer cylinders is modulated by a small sinusoidal signal, as is normal in Auger spectroscopy, and a differential distribution of electron energy is obtained. If pre-retarding were attempted with AES, grid scattering would reduce the transmission undesirably. For photoemission spectroscopies, however, the constant-resolution mode is used. In this mode, the potential difference between the outer cylinders and the inner cylinders is kept constant. Both cylinders are floated at the scanning potential of the retarding grids. In this way, the energy of the electrons which pass through the analyzer is constant; that is, the resolution is kept constant over the range of the scan.

Operating the analyzer in the retarding mode solves the problem of varying resolution, but introduces a new problem, a
loss of count rate. There are two effects of the pre-retardation on the count rate at a given energy. The first effect is that by going from a kinetic energy of $E_0$ to a fixed analyzer band-pass energy $E_p$, the energy resolution is improved by a factor $E_p/E_0$. At the same time, the effective source volume is collapsed by a factor $(E_p/E_0)^{1/2}$. The second effect, which is opposed to the effect of the collapse of the source area on retardation and coupled with the effective source area increase due to grid scattering, is a function both of kinetic energy and pass energy, and is somewhat difficult to estimate. The combined effect for any chosen pass energy will not necessarily be zero, or even linear with kinetic energy. However, as long as features close in energy are compared, the transmission function should not be a large source of error.

When dealing with a flooded source, we can often neglect the effect of grid scattering. This can be seen by the fact that the number of electrons scattered out of the proper trajectories are compensated for by electrons scattered into those trajectories. A flooded source is one in which the radiation spot size on the sample is greater than the photoelectron sampling diameter without retardation. Again, if this criterion does not hold, it will introduce only small errors, provided that spectral features close in energy are compared.

After the electrons pass through the CMA, they enter an
electron multiplier. The electron multiplier is a channeltron mounted on the other side of the CMA exit aperture. When traversing the channeltron, a primary electron is accelerated by the electrostatic field and produces several secondary electrons when it hits the inner wall of the channeltron. The secondary electrons will produce more secondaries. At the exit end of the channeltron, an original electron can be amplified typically by a factor from $10^7$ to $10^8$. This pulse (the bunch of electrons) will be collected and sent to the pulse-counting electronics composed of either a computer in conjunction with a scaler, or a ratemeter with a built-in digital-to-analog converter. The number of pulses, therefore, can be recorded in digital form by the computer and displayed as they are recorded on an X-Y plotter.

4. **Spectrometer operation**

The spectrometer was controlled by a Kinetic System 3885 microcomputer via a CAMAC interface crate. The computer could set the monochromator output photon energy to a desired value by calculating the desired grating position and sending the appropriate number of pulses to the monochromator controller, or run the monochromator in the scanning mode. The photon flux could also be read by the computer via an analog-to-digital converter (ADC). For scanning the kinetic energy, a ramp generated by the computer [via a 16-bit digital-to-analog converter (DAC)] was sent to the input of a CMA controller.
box, and the output of the controller would set the CMA to the proper operation mode. Figure 11 schematically illustrates this spectrometer operation.

During the collection of photoemission spectral curves, a software driving subsystem generated the scanning ramp as desired in EDC or CIS, collected the electron counts with the pulse-counting electronics, monitored the actual kinetic energy the analyzer was "tuned" to by reading the voltmeter, drove the X-Y recorder's X-axis, and in the case of CFS or CIS, scanned the monochromator through the desired photon energy range in a suitable manner. The CAMAC contained a DAC, an ADC, a data scaler, and a programmable timer for ramp generation and scaler gating. The details of spectrometer-system hardware and software operation have been documented in manual form by C. G. Olson.

B. Sample Preparation and Characterization

1. Silicon substrates

There are three different kinds of silicon substrates used in this thesis: crystal Si(111), amorphous Si, and hydrogenated amorphous Si. The crystal samples were commercially polished Si(111) wafers. They were n-doped, but high purity (the impurity concentrations ranging between 1 and $2 \times 10^{14}$ atoms/cm$^3$). The amorphous and the hydrogenated amorphous samples came from the Ames laboratory, made in situ
Figure 11. Block diagram of the electronics used to control the CMA analyzer and collect data. The parts which control the analyzer operation are shown on the left; on the right is the signal electronics.
by plasma-assisted ac sputtering in either an argon or argon-hydrogen atmosphere. The Ar was 99.999% pure and H₂ 99.99% pure. The total pressure during sputtering in both cases was about 40 mTorr; for hydrogenated films the H₂ partial pressure was about 15% of the total. The targets, polished single silicon crystal, were held at about room temperature by water cooling mounted on the anode of a radio-frequency capacitive reactor; the silicon sources, also cooled by water, were mounted on the cathode supplied with the radio-frequency ac power in addition to a dc bias. The power was about 500 Watts. This operation gave a deposition rate of about 0.8 microns per minute. The thicknesses of those deposited films ranged from 1 to 3 microns. All of the individual samples consisted of about 8 x 10 mm rectangular sections cut from the crystal, amorphous, or hydrogenated amorphous silicon wafers. The thicknesses of these samples ranged between 20 and 30 mils and the resistivities between 5 to 10 ohm-cm.

All of the rectangular Si substrates were chemically etched prior to insertion into the vacuum chamber in order to remove the heavy-oxidation layers and chemically clean and smooth the substrate surface. The etching process was done in the following sequence: first using methanol then water separately to rinse those substrates, then etching with concentrated hydrofluoric acid by dropping the acid over the surfaces continuously for a few minutes, finally rinsing again
with methanol and water in order. The substrates were then
dried by blowing away the residual moisture with helium. This
etching process was unlikely to have changed the substrate
surface structures but would cut the surface-oxide layers down
to only a few Å. However, the growth rate of oxidation was
about 2 Å/hour in air after etching. Therefore, etching just
before loading the substrates into the chamber was crucial.

To obtain a clean substrate surface, sputtering and
heating was used. For the Si(111) substrates, a good quality
Si(111) surface was obtained by heating for 15 seconds
("flashing") once or twice at about 1250 C. The results were
confirmed by taking core-level and valence band spectra, which
revealed the expected Si(111) surface core levels and the
surface states, respectively, and showed no signs of
contamination. Unfortunately, a LEED (Low Energy Electron
Diffraction) system was not available in the experimental
chamber. The reconstruction of the Si(111) surface was,
therefore, not able to be identified, but it showed no
influence on the results of Sm/Si(111) interface study in this
thesis. Moreover, clean surfaces of the amorphous and the
hydrogenated amorphous silicon films were obtained by a series
of sputterings. Each sputtering was carried out in situ by
using a sputter-ion gun at 10 mA emission current and 1 kV
accelerating voltage with argon for about 30 minutes. The Ar
pressure during sputtering was 10^-5 Torr. The quality of
those thin-film substrates were monitored by valence band
spectra taken at 40 eV photon energy. Ultraviolet photoemission spectroscopy (UPS) is very sensitive to atomic contamination on the solid surface. To identify this contamination, one can simply observe the appearance of characteristic spectral features. For a few common absorbates, there are well-known signatures which can usually serve as a guide in the assessment of surface cleanliness. Oxygen, for example, typically introduces a relatively broad bump at -6 eV; at heavy coverage (where the character of the surface should not be in doubt), a double-structured oxygen 2p-derived feature appears. Hydrogen is generally observed as a relatively narrow chemisorption state at -5.0 to -5.5 eV. Carbon is more difficult to detect and may be better seen in Auger spectroscopy or in a carbon 1s core-level spectrum. However, the two carbon monoxide features are easily detected near -8 and -11 eV. All of the electron binding energies mentioned above were relative to the Fermi level of the system.

2. Samarium film evaporation

The samarium films deposited upon the Si substrates came from bulk samarium obtained from the Ames Laboratory. An analysis of residual elements is given in Table 1. The most important impurities are other rare earths, typically with a concentration of a few tenths atomic parts per million (ppm).

The samarium had been electropolished and sealed in an
Table 1. Spark source mass spectrometric analysis of samarium used (impurity levels are in atomic ppm)

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Conc.</th>
<th>Impurity</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
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<td>In</td>
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</tr>
<tr>
<td>Be</td>
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<td>Sn</td>
<td>&lt;0.06</td>
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<td>Sb</td>
<td>&lt;0.02</td>
</tr>
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<td>Te</td>
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</tr>
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</tr>
<tr>
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<td>Cs</td>
<td>&lt;0.004</td>
</tr>
<tr>
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<td>Ba</td>
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</tr>
<tr>
<td>P</td>
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<td>Hf</td>
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</tr>
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</tr>
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</tr>
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<td>Re</td>
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</tr>
<tr>
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<tr>
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<td>Ho</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Rh</td>
<td>&lt;0.05</td>
<td>Er</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Rd</td>
<td>&lt;0.1</td>
<td>Tm</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;0.02</td>
<td>Yb</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.04</td>
<td>Lu</td>
<td>&lt;0.2</td>
</tr>
</tbody>
</table>
evacuated ampoule. The seal was not broken until just before placement of the samarium in the evaporator basket and subsequent closing of the vacuum chamber. The cleanest films were obtained only after a prolonged degassing procedure of the evaporator. After mounting the basket in the chamber, the chamber was sealed and evacuated to approximately $10^{-7}$ Torr. The basket was then heated until the pressure recovered to the value prior to the heating of the basket. The system was allowed to cool and the chamber brought up to atmospheric pressure using dry nitrogen gas. The samarium was then placed in the basket and again the chamber was sealed, pumped, and baked. The degassing procedure of samarium did not begin until the pressure of the chamber was less than $10^{-9}$ Torr. Heat was applied slowly to the evaporator, keeping the pressure less than $10^{-9}$ Torr, until the samarium began to sublime. After sublimating, the pressure was kept below about $5 \times 10^{-10}$ Torr until the desired evaporation rate was reached. Following this procedure, we were able to obtain a high percentage of clean films. A tungsten basket has been used as the evaporator to deposit the samarium onto the clean silicon substrates. The thickness of evaporated samarium was monitored by a quartz crystal and the chamber pressure was less than $4 \times 10^{-10}$ Torr during evaporation. The evaporation rate was about 0.5 Å/minute for small coverages and about 1 Å/minute for large coverages.
C. Data Analysis Techniques

A digital record was taken of all photoemission spectra collected in this thesis. The section discusses two specialized data-analysis techniques used upon certain digitized spectra, which are core-level deconvolution and data smoothing.

1. Core-level deconvolution

A photoemission spectrum has an observed spectral width that includes a broadening due to instrumental factors. These factors include the resolving power of the spectrometer and the line width of the photon source used. If one knew the exact contribution due to these factors and could construct a function $B$ that described them, then it would be known that the observed spectrum was a convolution of the "true" spectrum $F$ and this instrumental function. The "true" spectrum could then be obtained by the deconvolution of the observed spectrum $F'$ that arises from the way in which the experiment is constructed. The observed spectrum is related to the desired "true" spectrum by a "convolution" equation:

$$F' = F \times B.$$  \hspace{1cm} (16)

The retrieval of $F$ from $F'$ is referred to as "deconvolution." In this thesis, the instrumental function was assumed as a Gaussian.

As discussed previously in the last chapter, high-resolution core-level spectra may contain structural inform-
ation (viz., the presence or absence of atoms at inequivalent sites). Core-level deconvolution is a useful procedure to extract this information. It can give a quantitative description of a core-level lineshape and binding energy, from which it is possible to further deduce the concentrations of atoms responsible for the observed spectrum and their chemical environments which cause the core-level shifts. The deconvolutions done in this thesis were performed on a Zenith-8086 microcomputer (IBM XT compatible), using a BASIC program written by the author. The fitting model and procedure will be outlined below.

The program was designed to fit simultaneously the background and the core peaks, using a model function of count rate vs. electron-kinetic energy, composed of a background distribution function and several spin-orbit-split doublets. The Si 2p doublet can be described well by the convolution of a Lorentzian, which takes into account the lifetime of the core hole, and a Gaussian, representing the instrumental broadening effect (the combined resolution of monochromator and electron analyzer) and the broadening effects for those due to the potential irregularities or fluctuations. This convolution is called a Voigt function. The net width of the Gaussian is then partitioned into a contribution $\sigma_{\text{exp}}$ due to the experimental resolution obtained from a spectrum of single crystal silicon measured under identical conditions and a
contribution $\sigma_{\text{else}}$ which takes the additional broadening into account such that $\sigma_{\text{exp}}^2 + \sigma_{\text{else}}^2 = \sigma_{\text{total}}^2$. Each of the two peaks comprising a doublet was assumed to be the same; a Voigt function with the same width parameters was used for each. The number of doublets used in fitting was determined by two things: the type of Si substrates and the number of newly produced doublets due to the chemical reaction between the substrates and the adatoms. For the crystal Si(111), as mentioned before, there are two more surface-related core levels in addition to the bulk pair. However, for the Si 2p core level spectrum of hydrogenated amorphous Si, the data can be fitted with a minimum of four doublets: an unshifted doublet corresponding to emission from Si atoms not bonded directly to hydrogen (Si$_0$) and three components representing Si$_{4-n}$-Si-H$_n$ configurations (referred to as Si$_n$ hereafter), where $n$ can be 1, 2, or 3.

In some fits the Gaussian width for the two surface-component doublets of crystal Si core levels was allowed to vary independently with respect to the bulk width to simulate the contribution of the momentum broadening effect or multiple, unresolved shifts.

For the hydrogenated amorphous Si, in order to accord with the additivity of chemical shifts a fixed chemical shift $\Delta E_H$ between Si$_n$ and Si$_{n+1}$ configurations was assumed. The fit also assumes that the Gaussian width decreases with increasing
n towards the experimental Gaussian width.  

In order to deal with the problem of the contribution in a core level spectrum due to inelastic electron scattering, the model function for fitting should also contain a background function properly describing the contribution of the secondaries. Two different kinds of the background functions were used in this thesis: A cubic polynomial function and a proportional-to-primary background function (see Fig. 12). For the core level spectra taken in the region where the dominant contribution to the photocurrent is the inelastic secondaries, the core level peak causes only a small perturbation to a smoothly-varying background, which is then well-described by a polynomial. In the region where the secondary electron contribution arising from the inelastic scattering of the cores is pronounced, a proportional-to-primary background function is used to take this non-linear background term into account, in which a additional quadratic polynomial is incorporated. The function representing the non-linear background term was first proposed by Shirley, who considered the background at any point due to inelastic scattering of electrons of higher kinetic energy and was thus proportional to the integrated primary photoelectrons with higher kinetic energies.

To simulate differences in the final-state effects, the doublet branching ratio was allowed to vary independently from one fitted spectrum to another. Other spectrum-specific
Figure 12. Comparison of the background functions, describing the contribution of the secondary electrons, of Si-2p core-level spectra at 110 (lower) to 130 eV (upper). The background of bulk sensitive photoemission spectrum (lower) is well-described by a cubic polynomial; in addition, a proportional-to-primary background function is incorporated in surface sensitive spectrum to take a non-linear background term into account.
attributes, such as the energy location of the bulk component, its Gaussian width, and the parameters representing the inelastic background, were also allowed to vary separately.

The fitting itself was accomplished using the Marquardt scheme of estimating non-linear parameters by the method of least squares, where the Marquardt algorithm is a combination of a gradient search and an expansion of the fitting function. The Voigt functions were evaluated with a Fast Fourier Transform algorithm developed by Cooley and Tukey. In this way, the computations are simpler and faster than using an integral method to evaluate directly the Voigt function, due to the convolution theorem and the Cooley-Tukey algorithm. The convolution theorem can be simply stated as follows: the Fourier inverse transform of a product of Fourier transforms is the convolution of the two original functions. The Fourier transform of a Gaussian function is still a Gaussian function, and the Fourier transform of a Lorentzian function is a simple exponential function. A modified version of Bevington's CURFIT routine was used for computation. The deconvolution program was written in manual form, and is easily used.

2. **Data smoothing**

It was not uncommon during these experiments for the digitized spectral data to have a rather noisy appearance, even though the photoelectron count rate was rather high
(10,000 counts/sec or greater). Many small spikes derived from statistical fluctuations would be present. They were distinguishable from true spectral features by their characteristic width, always much narrower than the typical instrumental resolution (usually between 0.1 and 0.5 eV).

This noisy appearance was due to the use of more data channels than necessary for the data collection (frequently data channel widths would be 1/5 of the instrumental resolution or less), and the lack of time constants in the data collection.

This "noise," actually an artifact of the data collection process, sometimes turned out to be a hindrance to the analysis of data. A digital filtering method was therefore devised to eliminate it. Of course, the removal of as much of this noise as possible without, at the same time, unduly degrading the underlying information is of fundamental importance.

The filtering method used in this thesis to smooth fluctuating data, and yet avoid signal degradation, was proposed by Savitzky and Golay. The method was based on the usual least squares minimization procedure, which fitted a polynomial to a set of data points minimizing, in a least squares sense, the deviation of any point from the best fit. This polynomial would then be used to evaluate a new best-fit data point as the center point to the selected cluster of points. The data set would then be moved one point (throw away the old point at one end of the group and add a new one
at the other end), and the process repeated until a whole new array of smoothed data was obtained. All of the error (noise) has been assumed to be in the ordinate and none in the abcissa in this usual least squares minimization procedure. But calculations using such a procedure can be quite time consuming. Fortunately, as pointed out by Savitzky and Golay in their now-classic paper, if the abcissa points are uniformly spaced, this procedure is analogous to convoluting the data with a moving average smoothing filter, provided that the correct weighting coefficients are used. Savitzky and Golay presented tables of these coefficients for the various filters (quadratic-cubic, quartic-quintic, derivatives, etc.). These tables have since been revised. Thus, we can construct an extremely simple and versatile algorithm by using these previously calculated convoluting coefficients that can be used to smooth digital data. A computer routine was written to implement this operation.
IV. RESULTS AND DISCUSSION

The presentation of Chapter IV is divided into five sections. The first section is devoted to Si-2p core-level studies. The second describes the resonance photoemission spectra of Sm-4f electrons as the Sm coverage increased. The third is a study of the structural and electronic properties of the Sm thin-film overlayers via the investigations of valence-band spectra. The fourth section shows the variation of work function with Sm coverages. Finally, the fifth section summarizes the results obtained in the sections above and presents a growth model for the Sm/Si system, which is capable of explaining all the phenomena observed in the photoemission spectra.

A. Core Levels

Figure 13 shows background-subtracted, high-resolution scans of the Si 2p core levels of five Sm-covered Si(111) surface at an incident photon energy of 130 eV. From bottom to top the Sm coverages are clean (no Sm), 0.14 ML, 0.34 ML, 0.68 ML, 1.03 ML, and 5.13 ML Sm, where a monolayer (ML) is defined here to be one-half of one Si(111) double layer, or \(7.83 \times 10^{14}\) atoms/cm\(^2\) which equals 2.59 Å apparent thickness. As mentioned before, the energy dependence of electron escape depth causes these spectra to emphasize surface-related
Figure 13. Si-2p core-level spectra for clean and Sm-covered surfaces at 130 eV. Binding energies are referred to bulk component of the clean-surface Si-2p$_{2/3}$
features. Additional spectra emphasizing the bulk contribution were taken with 110 eV photons; for simplicity these spectra are not shown here.

In order to gain additional insight into the evolving character of the interface, we have decomposed all the spectra in Fig. 13 into components indicated by the dashed curves by using the core-level deconvolution routines. Each component in a spectrum consists of a Si-2p core doublet which is described by two Voigt functions with Lorentzian and Gaussian widths, and separated by a spin-orbit splitting. The intensity ratio (branching ratio), the spin-orbit splitting, and the Lorentzian width of an individual doublet have been assumed the same in all the spectra, which have been obtained from the best least-squares fit for the clean spectrum. They are 0.592 eV for the spin-orbit splitting, 0.162 eV for the Lorentzian full width at half maximum (FWHM), and 0.533 for the branching ratio; however, due to the final state effect, the branching ratio, obtained and used in this thesis for the bulk-sensitive spectra taken at 110 eV, is 0.492 instead. The peak position, the intensity, and the Gaussian standard deviation sigma (2.355σ is the Gaussian FWHM) of a doublet have been treated as adjustable parameters, and the non-linear backgrounds (already discussed in Chapter III) have been assumed for a surface-sensitive core-level spectrum. The tolerance of fitting for all of the parameters being fitted
has been set to 0.5% accuracy. The solid lines, in Fig. 13, representing the composite line shape, are in reasonable correspondence with the experimental data (dots) for all the spectra.

In the clean spectrum of Fig. 13, there are two features in addition to a bulk component (labelled by B): the small shoulder (S2) on the low-binding-energy side of the bulk doublet and the filling-in of the valley (S1) between the two spin-orbit-split peaks. These features have already been observed and analyzed in the literature. They correspond to two surface components shifted relative to the bulk component due to surface reconstruction. From the intensity ratio of surface to bulk emission, the number of surface atoms with shifted core-level binding energies can be determined by using a discrete layer model:

\[ \frac{R_s}{R_B} = \frac{N_s}{[1 - \exp(-d/\lambda)]^{-1} - N_s}, \]

where \( R_s/R_B \) is the intensity ratio, \( d \) is the spacing between double layers [3.14 Å for Si(111)], \( \lambda \) is the escape depth, and \( N_s \) is the surface-atom concentration in Si(111) ML. From the fit for the 130 eV spectrum, using \( \lambda = 5.3 \) Å from Ref. 72 and solving for \( N_s \), Eq. (17) gives \( N_s = 1.17 \) ML, in agreement with the results in the literature. At a coverage of 0.14 ML, the spectrum simply shows a rapid attenuation of the bulk component and slight shifts of the two surface components.
whose relative binding energies are a little closer to that of the bulk, as compared with the clean spectrum; otherwise, the two spectra appear quite similar. The attenuation of the bulk component can be understood by the presence of Sm adatoms at the interface, providing an additional chance for inelastic scattering of the electrons escaping from the bulk and Sm surface atoms. Although the electrons emitted from the surface components also can be scattered by the Sm adatoms, the probability is greatly reduced. Moreover, at this point, the presence of the two surface components with binding energies slightly shifted from the bulk suggests that the interface interaction between Sm adatoms and Si surface atoms is very weak and the magnitude of surface charge transfer between them is insignificant; that is, the Sm atoms are weakly adsorbed on the surface at a coverage of 0.14 ML and probably locate at their special sites as theoretically predicted by Xide and Kaiming,\textsuperscript{92} where the threefold site chemisorption is preferable. However, which of two surface components corresponds to the weakly-chemisorbed state can be determined by the spectrum of the 0.34ML-Sm-covered Si(111) surface. At a coverage of 0.34 ML, comparison with the two previous spectra reveals some obvious changes, such as the absence of the high-binding-energy surface component and the appearance of an additional component shifted (indicated by a tic mark) farther to low binding energy relative to the residual surface component. This suggested that the weakly-
adsorbed surface component is the one left and it is located at lower binding energy. Furthermore, emergence of the additional shifted component indicates that a new interface has begun to form at a coverage between 0.14 and 0.34 ML, in which a chemical shift in core-level binding energy occurs. From the evolutinal study of this first shifted component with coverage, one finds that the coverage which corresponds to the onset of the chemical reaction is about 0.2 ML (0.52 Å). Beyond this point, the component, which grows as the coverage increases and whose relative binding energy relative to the bulk component is 0.83 eV lower, can be characterized by a line shape which is slightly broader than that of the non-reacted crystal substrate and a binding energy whose centroid is a constant. The magnitude of the shift also indicates the chemical reaction is rather strong, which corresponds to a charge transfer between the reacted Sm and Si atoms of about 0.38 electrons, using the calibration factor of 2.2 eV/electron mentioned earlier in Chapter III. Moreover, this ionic compound is best assumed to be the disilicide, by comparison of the chemical shift with the theoretical calculation. The spectrum of the 0.34 ML-Sm-covered Si(111) surface also shows that there is a rigid shift of about 210 meV to higher binding energy due to band bending, as confirmed by bulk-sensitive spectra at a photon energy of 110 eV, in contrast with the earlier reports in Refs. 5 and 24, where no such lowering of the Schottky barrier was found. For
coverages above 0.68 ML, a second shifted component is observed at about 1.2 eV lower binding energy than the bulk. This component also shows a slight shift to low binding energy at higher coverage and is characterized by a line sharpening with coverage. It is significantly sharper than the bulk component, suggesting a more atomic Si bonding configuration. The presence of the weakly-reacted surface component at a coverage more than 1 ML indicates the Sm overlayer grows, forming clusters at high coverage. However, the rapid decay of all components at high coverage reveals no evidence of surface segregation. A heterogeneous interface is also indicated by the coexistence of two reacted species, and the formation of the second reacted component occurs above the first-reacted surface component because it is the only species observable for high coverages.

The analysis of Si-2p core levels for the H:a-Si and a-Si substrates has revealed the same interface formation as on the single crystal substrate. However, the growth rates of the two reacted components depend on the substrate, probably as a result of the number of available Si atoms to participate in the chemical reaction. For the hydrogenated substrate there is the least nearly-free Si available to participate in the chemical reactions due to the large fraction of Si atoms already involved in forming the strong H-Si bonds, so the growth rates are slowest. For the undoped amorphous Si, plenty of nearly unbound Si atoms are available for the
chemical reaction, so the growth rates are faster, even a little faster than for the Si(111). Figure 14 provides evidence of this point.

Finally, the absolute hydrogen concentration of a hydrogenated sample can be also determined by its core-level spectrum, because the distribution of the H atoms among the different configurations is simply related to the areas $I(Si-H_n)$ under the component lines.

$$N(H_n) = n I(Si-H_n) \quad \text{and}$$

$$N(Si) = \sum_{n=0} I(Si-H_n)$$

are the number of H atoms in the configuration Si-H$_n$ and the number of Si atoms within the photoelectron sampling depth, respectively. The hydrogen concentration $C(H)$ is, therefore, given in terms of $N(H_n)$ and $N(Si)$ by

$$C(H) = \frac{\sum_{n=1} N(H_n)}{[\sum_{n=1} N(H_n) + N(Si)]}. \quad (20)$$

The H concentration of the H:a-Si sample used in this thesis is about 15 at. % by using this model, in agreement with photoconductivity measurements.

### B. Resonances

The resonant photoemission technique provides an excellent tool for distinguishing the particular resonant features from others because of its special emphasis on the resonant features. Figure 15 presents a practical illus-
Figure 14. Si-2p core-level spectra of Sm on Si(111) (left), H-a:Si (middle) and a-Si (right) at 110 eV with three different coverages, i.e., zero (clean), 1.77 and 4.43 Å.
Figure 15. EDCs of Sm/a-Si:H at 132 (solid), 135 (dashed) and 140 eV (dot-dashed) for 0.18, 0.89 and 2.66 Å Sm-covered surfaces (from bottom to top). Notice the enhancement of the Sm$^{+2}$ and Sm$^{+3}$ related features.
As mentioned before, the 4f states of divalent Sm exhibit a resonant behavior at a photon energy of 135 eV, whereas the states of trivalent Sm are enhanced at 140 eV. Both states are off-resonance at 132 eV. In Fig. 15, the lowest spectrum clearly shows only divalent states existing when the Sm coverage is 0.18 Å. At a coverage of 0.89 Å, the trivalent states of Sm appear. At the higher coverage of 2.66 Å, trivalent species become dominant, giving rise to a characteristic Sm$^{+3}$ multiplet between 4.5 and 12 eV below the Fermi level.

In Fig. 16 we show a series of the resonance photoemission spectra, taken at a photon energy of 140 eV, for Sm-covered a-Si:H surfaces. The spectra are normalized to the incident-photon flux monitored by a nickel mesh and are given in arbitrary units. The lowest spectrum is for an 0.18 Å Sm-covered surface, representative of the weakly-reacted stage, in which Sm adatoms are purely divalent. The spectrum at a coverage of 0.53 Å shows a little strength from trivalent species (as confirmed by the CIS and CFS spectra) and a great loss of the divalent features, suggesting that the Sm clusters are formed by collecting the scattered divalent adatoms so that the resulting larger particle size induces a valence change$^9$ and the mixed valency of clusters occurs. A coverage of about 0.53 Å, therefore, corresponds to the onset of the strong chemical reaction. The same onset coverage has been obtained by the resonant photoemission studies of Sm/Si(111)
Figure 16. Resonant photoemission spectra at 140 eV for a-Si:H surfaces with increasing Sm coverages. The binding energy scale is referred to the Fermi level.
and Sm/a-Si, in agreement with the results from the core-level studies in last section. At coverages between 0.53 and 0.89 Å, representative of the chemically-reacted stage, the trivalent 4f species grow with increasing coverage, as does the first shifted Si-2p component, in agreement with intensity studies. This suggests that the reacted phase in this coverage range arises from the formation of trivalent-Sm silicides, what is consistent with a semi-theoretical prediction from a thermodynamic point of view by Fujimori et al. Furthermore, the intensity studies of the Si-2p core levels and Sm divalent features for Sm/Si(111) system in this regime confirm that the divalent Sm is associated with the weakly-chemisorbed core-level component assigned in the last section. In this regime the core-level binding energy of the trivalent Sm 4f state is independent of coverage, but there is a slight change in the divalent 4f region. Comparison of the binding energy of divalent Sm 4f core between the 0.53 and 0.18 Å also reveals a binding-energy shift of the divalent Sm 4f features. The variation in divalent Sm 4f is probably due to the coexistence of its two different forms, the weakly reacted Sm and the non-reacted divalent Sm in the reacted clusters. Therefore, mixed valent character is expected in the reacted clusters, where trivalent Sm is the reacted species. At a coverage of more than 1.77 Å, corresponding to the final reacted stage, the trivalent species gradually shifts to lower binding energy with a sharper line shape as
the Sm coverage increased and finally reaches the saturation line which is the same as that of pure Sm metal. In addition, the spectrum at a coverage of 8.85 Å shows an enormous gain in the strength of divalent features, suggesting that the coalescence of clusters occurs at about this point.

The shift in core-level binding energy and the sharpening of the line shape can be understood in terms of cluster growth. In very small clusters the final-state core hole is screened by the polarization of the neighboring atoms. Therefore, the binding energy depends only weakly on cluster size and the core-level line width is essentially broad. On the other hand, in larger, metallic clusters the hole is screened by conduction electrons, with the missing charge appearing at the surface of the cluster. This leads to a core-level binding-energy shift with coverage by the Coulomb energy of the charged final-state cluster and a sharper line width due to a more atomic bonding configuration than in a smaller cluster. Finally, when the clusters begin to coalesce and form a contiguous metallic layer, the binding energy rapidly approaches that of the bulk metal, as does the line width. However, the divalent Sm 4f features show no obvious evidence of the core-level binding-energy shifts for coverages above 1.77 Å. This indicates the Sm divalent atoms stay on the top surface of the metallic clusters as expected in the pure Sm metal.
The valence band spectrum is usually used in the study of the structural and electronic properties of the system. However, choosing a proper photon energy is of importance because of the great energy dependence of the photoionization cross section of valence states. In order to observe the true valence-band features instead of the Sm 4f's, a low energy photon is needed because the photoionization cross section of Sm 4f is nearly zero at low photon energies.

In Fig. 17 we display a series of normalized EDC spectra for the valence band emission at a photon energy of 25 eV from several Sm-covered a-Si:H surfaces. At 25 eV the Sm 4f features are greatly suppressed due to their extremely low photoabsorption cross section, and they are barely seen in the spectra until very high coverages. The lowest EDC is for clean a-Si:H, while the spectra at coverages of 0.18, 0.53, and 1.77 Å are representative of three different interface morphologies, respectively. Below a coverage of 0.53 Å, the spectrum shows the valence band emission simply attenuated by the presence of Sm atoms on top of the Si surface, confirming that the Sm adatoms are weakly reacted with the Si substrate in this stage, consistent with the prediction of the Si-2p core level study. However, in the coverage range between 0.53 and 0.89 Å, the valence-band features show some changes, gaining strength and narrowing as compared to the previous
Figure 17. Valence-band spectra at 25 eV for clean a-Si:H and for surfaces with increasing Sm coverages. The binding energy scale is referred to the Fermi level.
formation stage, suggesting that a reactive interdiffusion stage occurs and the silicide compounds are formed. The same conclusions were obtained in the last section. Beyond a coverage of 1.77 Å, the valence-band spectra show a gain of strength of the Sm 5d conduction electrons near the Fermi level as the coverage increases, indicative of the existence of metallic solid-solution formation in this regime and the start of the configurational transition from the atomic to the metallic Sm on top of the reacted cluster. This, and the Si-2p core-level studies in this coverage range, suggest that the second shifted Si component, growing with the strength at Fermi level and characterized by a line shape which sharpens with coverage and a binding energy which shifts to reach a saturation line, is contributed by reacted Si atoms completely coordinated by Sm metal atoms, and the additional shift is due to the extra-atomic screening from the surrounding metallic Sm atoms. The sharpening of Si-2p core-level line shape and the gradual shift in its binding energy are therefore expected as discussed in previous section.

D. Work Functions

Changes in surface potential are usually revealed by measuring work function changes. Deposition of Sm, in general, causes a decrease in work function, which is ascribed to positive outward dipoles created when the Sm atoms are
located outside the surface, because the Sm atom normally forms a cation during chemical reactions due to its low Pauling electronegativity. A decrease in work function is equivalent to the establishment of a positive surface potential due to chemisorbed Sm on the surface.

The measurement of the work function was carried out by negatively biasing the measured specimen with respect to the spectrometer in order to obtain the low-energy cutoff which represents electrons at the specimen vacuum level, or what can be defined as the true zero of kinetic energy. Following Fadley's definitions, the low-energy cutoff thus establishes the zero of kinetic energy, and a distance $h\nu$ above this on the measured spectral scale corresponds to the point at which excitation from states at the specimen vacuum level, $E_v$, would occur. On the same scale, the high-kinetic-energy cutoff observable for metal specimens is caused by excitation from occupied states at the Fermi level $E_f$. The difference between these two positions is the specimen work function $\varnothing$. That is, if the measured difference in kinetic energy between the two cutoff levels is $\Delta E$, then

$$\varnothing = h\nu - \Delta E \quad (21)$$

However, for semiconductor specimens, the high-kinetic-energy cutoff, which corresponds to the Fermi level of the specimen, is unobservable but can be indirectly obtained by measuring the Fermi level of any metal specimen in the same experimental
conditions, such as the same bias and the same photon energy. Assuming that electronic equilibrium is fully established between the measured specimen and spectrometer and a tiny voltage drop across them (typically a few millielectron volts or less), caused by internal resistivity of the specimen and the photoemitted current, is negligible, the Fermi level remains constant and independent of the specimen measured. That is, the spectra yield the same high-energy cutoff. Therefore, the work function of a semiconductor specimen can be evaluated.

Figure 18 shows the changes of work function of Sm on a-Si:H with coverage. Sm deposition at the lowest coverage used [0.35 Å (0.14 ML)] was sufficient to cause an enormous decrease in work function by about 1.05 eV. At 0.7 Å (0.28 ML) coverage the work function slightly increases by 100 meV as compared to the previous coverage and essentially remains constant with coverage up to 2.1 Å. It is followed by a gradually decreasing work function as coverage increases. Eventually the work function reaches its saturated value of 2.8 eV after a coverage larger than about 8.85 Å. This is a little (100 meV) larger than the work function of pure Sm metal.97

Combining with what we have learned in the last three sections, the changes of work function can be easily understood in terms of the surface dipole potential. At coverages less than 0.53 Å (about 0.2 ML), only a weakly
Figure 18. Changes of work function of Sm on a-Si:H with coverage. Sm deposition at the lowest coverage used (0.35 Å) is sufficient to cause an enormous decrease in work function by about 1.05 eV. The work function of the clean a-Si:H (~15 % H₂) is about 4.6 eV (not shown).
interacted phase exists at the Sm/Si interface surface and the Sm atoms are simply located outside the Si substrate surface. The relatively low electronegativity of Sm (1.05 for Sm; 1.75 for Si\textsuperscript{98}) causes the valence electrons of Sm to move slightly toward the Si substrate, and thus well-oriented positive outward dipoles are built at the interface surface. This leads to a great decrease in work function. At coverages from 0.53 to 2.1 Å, some of the well-oriented dipoles begin to loosen due to the collection of Sm adatoms. Although ionic compounds (silicides) are formed in this regime, the constant work function suggests that the net electric dipole moment of each ionic compound is either nearly zero or oriented at random; that is, no macroscopic dipole is further established. This leads to a little restoration of the work function, as shown in Fig. 18. After 2.1 Å coverage, the Sm-metal-solution formation starts building on top of the reacted cluster. Therefore, the work function exhibits a tendency of decrease, approaching that of Sm metal. Finally, at about 8.85 Å, the saturated work function is reached, suggesting that the clusters coalesce and a complete Sm metallic layer is formed upon the surface.

As seen above, the work-function change with coverage provides further information in the interfacial study, which is complementary and consistent with results obtained by other techniques, such as core-level, resonance, and valence-band photoemission.
E. The Growth Model of Sm/Si

An interface with behavior demonstrated by Figs. 13-18 is complex, but the results presented above allow us to formulate a model for Sm/Si which describes its heterogeneous growth. The simplest model, shown pictorially in Fig. 19, for the growth behavior of Sm on Si is as follows. At very low coverage, less than about 0.53 Å (0.2 ML), the Sm adatoms interact weakly with the Si substrate and they are scattered and located outside the substrate surfaces. The photoemission spectra of both Si-2p core levels and valence bands are similar on both the clean and Sm-covered surfaces. The binding energy of the bulk component relative to the Fermi level is essentially unchanged, but the work function is greatly reduced due to the redistribution of electron density at the interface surfaces by the presence of the weakly adsorbed Sm atoms. For the single crystal Si substrate, the surface charge redistribution, however, causes core-level shifts of two surface components to new energy positions close to that of the bulk component. At about 0.53 Å (0.2 ML), coalescence of the scattered Sm adatoms into Sm clusters occurs in terms of conversion from the layer growth to the reactive intermixing cluster and the liberated energy is used to break Si-Si bonds and promote a Sm 4f electron to a 5d conduction electron. Therefore, a strong chemical reaction is
Figure 19. A model pictorially describes the heterogeneous growth behavior of samarium on silicon.
triggered. However, the energy probably is not enough to break the Si-H bond due to the stronger bonding for H-Si than for Si-Si (the bond energy is 2.35 eV for Si-Si, 3.4 eV for H-Si). Therefore, fewer Si atoms in a-Si:H can be involved in the reaction. This leads to the different growth rates of the reacted species on the three kinds of substrates [Si(111), a-Si, and a-Si:H]. After the critical coverage corresponding to the onset of strong chemical reaction, the reacted Si species is in an amorphous configuration, resulting in a negligible change of the work function and in an increase of the line width. The lowering of the Schottky barrier is observed for the Si(111) substrate but not for H:a-Si or a-Si. After the coverage at which the metallic Sm solution is formed, the second shifted species is observed and the work function starts to decrease, gradually approaching that of Sm metal. Finally, at the coverage corresponding to the coalescence of clusters, the work function reaches its saturated value, the components underlying the solid solution are almost unobservable, and the final component is rapidly attenuated. Therefore, no surface-segregated behavior is indicated.
V. SUMMARY AND CONCLUSIONS

From the spectroscopic information and the modeling of morphological development of the Sm/Si interface, several conclusions can be drawn.

1) The existence of three different interface-formation regimes which correspond to the weakly-adsorbed, chemically- and metallic-reacted stages, respectively, has clearly been indicated by the core-level data.

2) The nucleation and growth processes occurring in Sm thin film formation have also been indicated to be sublayer plus island (or Stranski-Krastanov) growth mode, where a critical coverage for the chemical reaction and cluster formation has been exhibited.

3) At a critical coverage corresponding to the onset of strong chemical reaction, cluster formation is the origin of triggering the chemical reaction and the liberated energy promotes the breaking of Si-Si bonds and changing the Sm valency from a divalent to trivalent atom.

4) During interface formation, two chemically reacted species have been observed and identified as silicide phase and solid solution, respectively.

5) The first reacted component, whose Si-2p core width is slightly broader than that of the non-reacted crystal substrate but whose energy centroid is a constant, has exhibited a chemical shift which is consistent with the
formation of a compound having about 50 at. % Si.

6) The second component, which is characterized by a line shape which sharpens with coverage and a binding energy which shifts to reach saturation, has been described as a solid solution, in agreement with intensity studies.

7) The chemical shifts for these two components have shown analogous behavior on three different substrates, suggesting that morphological and surface structure differences in the reacted films play a secondary role in determining the chemical shift.

8) On the contrary, the growth rates of these two components have exhibited a dependence of the substrate on the degree of available Si atoms to participate in the chemical reaction, so the hydrogen in the hydrogenated substrate simply plays the role of slowing down the reaction rate in the interface formation.

9) The Si atoms have shown no sign of surface-segregation behavior as Ce on Si(111), but the same Schottky-barrier-lowering phenomenon has been observed, in contrast with the previous studies of Sm/Si(111) in Refs. 23 and 24.

These conclusions have provided a more detailed understanding of the nucleation mechanisms, overlayer morphologies, and electronic properties of the fundamentally interesting and technologically important rare-earth/group-IV semiconductor interfaces. A significant point has been established, which is that high-resolution photoemission studies of reactive
interfaces make it possible to distinguish the chemical environments of the constituents, i.e., that specific bonding configurations form which can be identified even for intermixed interfaces where long-range order is absent and the scale of the interface is limited to a few monolayers. Hence, we can conclude that strong local bonding determines the character of the evolving interface species. Comparison to bulk compounds will show how the interface phase fits into the hierarchy of the bulk phase diagram. For Sm/Si, we find no evidence that more than a single silicide phase exists, and whatever stoichiometry gradients might exist between the reacted patches and the unreacted Si are too small for identification. By studying the variation of each component with nominal metal overlayer coverage, even complex interfaces can be modeled. The implications of these conclusions are major because they indicate the limitations of modeling of interface properties based on homogeneous overlayers and they show the importance of microscopic fingerprinting of interface phases.
VI. BIBLIOGRAPHY


14. An analogous results was obtained by Herbst and coworkers in Refs. 12 and 13, where they showed that in bulk metallic Sm, the energy required to promote a 5d conduction electron from the Fermi energy into an empty 4f state is only 0.2 eV.


53. See, for example, papers in Proc. Symp., Electronic Density of States, edited by L. H. Bennett, National Bureau of Standards Special Publication, No. 323.


77. The curve-fitting procedure used to obtain these results will be discussed in more detail in Chap. III.


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