Contacts for Compound Semiconductors: Schottky Barrier Type ☆

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When a metal and a semiconductor come into contact, charge flows across their interface to balance electrostatic potentials. This charge exchange leads to dipole formation and bending of the semiconductor energy bands near the junction. The resultant barrier to further charge flow is of high technological value for the performance of all semiconductor devices, for example, for applications in microelectronics, optoelectronics, and energy conversion. Optimal Schottky barriers are the most demanding requirement of desirable metal–semiconductor interface properties. High-power applications require low or 'ohmic' barriers with low specific contact and parasitic resistances. High or 'rectifying' barriers are needed for high-impedance applications such as detectors, solar cells, and field-effect transistors. Additional interface electronic requirements may include high mobility (e.g., for heterojunction bipolar transistors and modulated doping structures), low recombination velocity, high reliability under environmental and bias stress, and reproducibility. Furthermore, the junction must possess certain chemical and structural properties. Chemical requirements include: shallow diffusion vertically and laterally to minimize device area and volume, low chemical degradation (i.e., against etching, oxidation, and other contamination during process fabrication), and low thermal degradation against ambient corrosion during operation. Finally, interface requirements may include structural features such as: high strength and/or flexible adhesion, extended dimensionality, minimal stress (e.g., through minimal film thickness), and possibly even resistance to radiation damage. This combination of electronic, chemical, and structural requirements places considerable demands on the choice of metal and semiconductor materials and their processing, which are further magnified as devices shrink from well below micrometer range into the nanometer regime. Therefore, the understanding and control of Schottky barrier formation can be of substantial value in designing semiconductor contact structures.

There has been considerable research into Schottky barriers over several decades, exploring microscopic charge-exchange mechanisms, as well as in preparing macroscopic contact metallizations. A number of references provide extensive overviews of this work (Brillson, 1982, 1992, 2010) Surfaces and Interfaces of Electronic Materials, Wiley-VCH, Weinheim (Palmstrøm and Morgan, 1985; Rhoderick and Williams, 1988; Shen *et al.*, 1992). A wide variety of macroscopic metallization and process techniques are now available. However, the trend toward greater miniaturization and structural complexity requires more refined control of electronic and chemical properties. With the advent of ultrahigh vacuum growth and characterization techniques, researchers are now able to alter electronic, chemical, and structural properties on an atomic scale to improve contact performance, reliability, and uniformity.

Schottky Barrier Formation

In the classical picture of interface charge transfer, the Schottky barrier formation depends strictly on the potential difference between the Fermi level (E_F) in the metal and the majority carrier band edge of the semiconductor. **Figure 1** illustrates the band bending scheme for a metal at the surface of an *n*-type semiconductor. A variety of electronic and chemical mechanisms can give rise to trapped charge and new dielectric properties which dominate the barrier formation. For a high work function metal (**Figure 1(a)**), electrons flow from the semiconductor to the metal after contact, depleting a characteristic region of majority charge. With both metal (E_{FM}) and semiconductor (E_{FSC}) Fermi levels aligned, a double layer forms with a voltage drop (qV_B) equal to the contact potential difference between the metal and the interior of the semiconductor. This double layer consists of a surface space charge region, typically $10^{-4} - 10^{-6}$ cm thick, and an induced charge at the outer edge of the metal. The depletion region is a layer of high resistance, and voltage applied to this junction will fall mostly across the surface space charge region. The barrier height (Φ_B) in this simple picture is given by

$$\Phi_B^n = \Phi_M - X_{SC}$$

where Φ_M and X_{SC} are the metal work function and semiconductor electron affinity, respectively, relative to the vacuum level E_{VAC}. The potential Φ within the semiconductor satisfies Poisson's equation

$$\nabla^2 \Phi(x) = -4\pi\rho(x)/\varepsilon_s$$

where ρ is the charge density in the surface space charge region of width d, x is a coordinate normal to the interface, and ε_s is the static dielectric constant of the semiconductor. The depletion layer width is

$$d = [q\varepsilon_s(\Phi - \Phi_0)/2\pi N]^{1/2}$$

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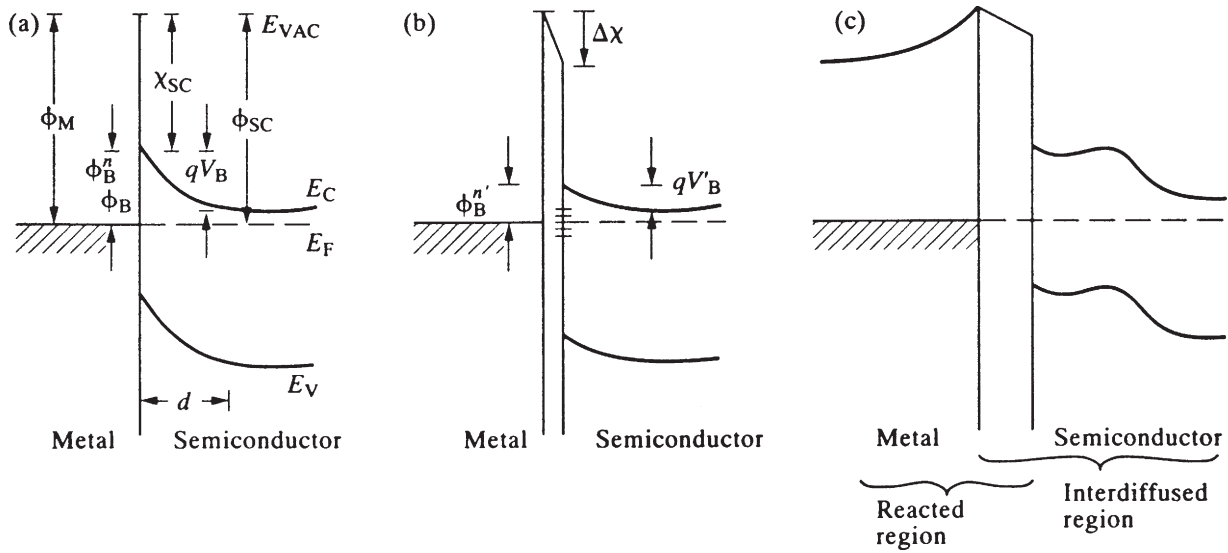
Figure 1   A schematic diagram of energy band bending after metal–semiconductor contact: (a) classical Schottky barrier, without trapped charge states or chemical interactions; (b) with screened depletion region and trapped charge states at the intimate junction but without chemical interactions; and (c) with chemical reaction and/or diffusion resulting in an extended junction.

where $N = \rho/q$ and Φ_0 is the semiconductor potential for $x > d$. A metal possessing a very low work function can produce band bending with the opposite sign, with majority carrier concentrations higher at the surface (accumulation region) than in the bulk, resulting in little or no barrier to majority carrier transport. Metals on p-type semiconductors produce analogous band bending behavior, but opposite in sign.

In practice, semiconductor barrier heights are relatively insensitive to metals with different work functions or electronegativities. For example, common metals on compound semiconductors produce a variation of only a few tenths of an electron volt in band bending, despite a difference of over a volt in metal work function. Instead of a slope S of unity for $\delta(\Phi_M - \Phi_{sc})/\delta(qV_B)$, the 'index of interface behavior,' S, can be less than 0.1. This insensitivity can be accounted for by the presence of interface dipoles due to additional, localized charge. **Figure 1(b)** illustrates schematically the effect of this additional, local dipole ΔX on the extended band bending $qV_{B'}$ and Schottky barrier Φ_{SB}^n. The presence of such dipoles reduces the movement of E_F within the semiconductor space charge region, and E_F is said to be 'pinned' (as opposed to merely stabilized) at a given energy. Such states can be due to a number of physical mechanisms which are described later.

The sensitivity of barrier height to different metals varies with semiconductor. **Figure 2** shows that the more covalently bonded compound semiconductors, that is, those with low electronegativity difference between cation and anion, vary little with metal, whereas more ionic semiconductors possess a much wider range of barriers (Kurtin et al., 1970). Significantly, the same correlation exists with respect to chemical heat of formation, that is, chemical stability. This chemical basis is underscored by a number of chemical correlations between barriers for different metals on a given semiconductor and interface heats of reaction or metallurgical phases (Brillson, 1982). **Figure 1(c)** illustrates how such chemical effects can influence the effective Schottky barrier height in terms of reacted interface regions with new dielectric properties and field gradients outside the semiconductor as well as altered, nonparabolic band bending due to defect or impurity states within the semiconductor.

Several classes of techniques are available to measure Schottky barrier heights. Conventional, macroscopic measurements of junction barriers are current–voltage (J–V), capacitance–voltage (C–V), internal photoemission, and contact resistance (Sze, 1981). The J–V measurements involve current flow mechanisms of three types, depending on the relative strength of tunneling: thermionic (tunneling negligible), thermionic-field, and field emission (tunneling dominant). Charge tunneling through the barrier rather than over it increases with increasing doping and decreasing depletion width. For low barriers, specific contact resistance is widely used as a figure of merit. The slope of the J–V characteristic also gives an 'ideality factor' of the contact. The C–V technique involves measurement of the space charge capacitance as the depletion layer width is modulated with an external voltage. Both J–V and C–V methods are subject to errors introduced by deviations from the simple Schottky picture illustrated in **Figure 1(a)** as well as charge trapping (Wieder, 1979). The internal photoemission technique involves photoexcitation of charge over the barrier and is perhaps the most direct and reliable of the macroscopic techniques for barrier determination. All three methods are affected by image-force lowering of the barrier and all are difficult to interpret if the barrier is more complex than a region of parabolic band bending; see, for example, **Figure 1(c)** (Brillson, 1982).

Inhomogeneous barriers across the metal–semi-conductor interface present another complication for macroscopic, large-area contact measurements. Two or more metallurgical or crystallographic phases with distinct, different barriers may coexist across the lateral interface plane. Depending on the substrate doping and the size of the different domains relative to the screening length,
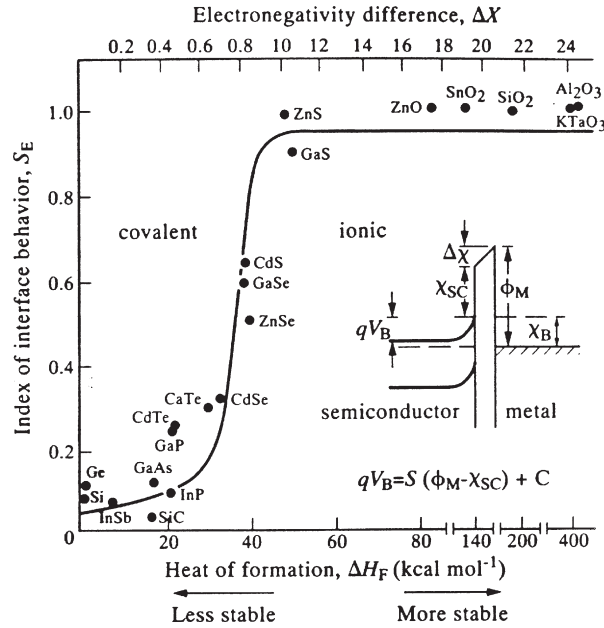
Figure 2 Transition in index of interface behavior S between covalent and ionic semiconductors vs. ionicity (top scale) and chemical heat of formation, ΔH_f (Brillson, 1978), illustrating the barrier dependence on chemical bonding and semiconductor stability (1 eV$=1.602 \times 10^{-19}$ J) (after Kurtin et al., 1970).

the higher barrier regions may 'pinch off' in varying degree the lower barriers in neighboring regions. Analytic solutions (Tung, 1991) of such effects show that the barrier height and ideality factor of the effective contact exhibit a different temperature dependence from those of the individual barrier regions.

Surface-sensitive, ultrahigh vacuum techniques provide probes of semiconductor surface electronic properties during the initial stages of Schottky barrier formation. Electron spectroscopies such as ultraviolet or x-ray photoemission rely on the short, energy-dependent escape depth of electrons from a solid to probe electronic and chemical properties from the top few monolayers. Electrostatic techniques such as surface photovoltage spectroscopy are based on the high sensitivity of band bending to relatively low charge densities (e.g., ~ 1eV (1.602×10^{-19} J) for 10^{12} with $N=10^{17}$ cm^{-3} and $\varepsilon=5$ in Poisson's equation). Tunneling spectroscopies such as scanning tunneling (STM) and atomic force (AFM) microscopy provide an atomic-scale lateral surface probe which is dependent on both atomic morphology and bond charge wave function extending into vacuum.

Buried interface techniques such as ballistic electron energy microscopy (BEEM), cathodoluminescence spectroscopy (CLS), photoluminescence spectroscopy (PL), and Raman scattering offer methods for extracting barrier heights from thin but metallic layers on semiconductors. The BEEM technique makes use of an STM tip to probe electron transmission over potential barriers on a nanometer scale laterally. CLS and even PL provide direct evidence for discrete deep-level gap states near the junction. Light scattering can provide an indirect measure of band bending in the surface space charge region, based on the electric-field induced change in semiconductor crystal symmetry.

Each class of barrier measurement techniques offers advantages and disadvantages. Conventional techniques provide convenient and macroscopic junction characteristics suitable for device evaluation, but not the microscopic features either normal to or laterally across the junction. Surface-sensitive techniques offer electronic and related chemical structure but little about the fully formed junction. Buried interface techniques provide electronic information on a nanometer scale which incorporates both near-surface sensitivity and mesoscopic junction features.

Researchers have proposed a wide diversity of physical mechanisms to account for the relative insensitivity of many semiconductor barrier heights to different metals. This 'Fermi level pinning' is due to the presence of trapped charge, as pictured in **Figure 1(b)**. Such trapped charge can be either intrinsic to the bulk semiconductor and/or metal or due to an extrinsic mechanism. Intrinsic surface or interface states may arise at the semiconductor surface where the lattice potential experiences an abrupt change and where atomic bond strength and geometry may vary. Studies of clean semiconductor surfaces in the 1970s showed that, with only a few possible exceptions, such states do not exist in the semiconductor bandgap, where they are required in order to stabilize the Fermi level. Intrinsic interface states involve charge localization near the boundary of a metal with a semiconductor without a change in the chemical or electronic properties of either medium. Significantly, wave function tunneling from the metal into the semiconductor can account for E_F pinning trends for several covalent semiconductors. However, such tunneling modes are ill-suited to account for large barrier (Φ_B) variations observed with changes in local bonding geometry and chemical composition. Extrinsic interface states can be either conventional, that is, caused by surface chemical contamination, surface structural imperfections, bulk impurities, or bulk structural imperfections, or

interface-specific, that is, due to chemically induced bonding states, localized defect states, or new phase formation. The observation of discrete deep-level states near metal–semiconductor interfaces, their dependence on interface chemical features, and the correlation of their energies with those of the stabilized Fermi level together suggest the importance of such extrinsic states in barrier formation. Nevertheless, it is a challenge to distinguish between interface state mechanisms, even under near ideal conditions and with a powerful array of techniques, based solely on a narrow range of Fermi level movements.

Macroscopic Compound Semiconductor Metallization

Technologists have developed a number of effective methods for producing low or high barriers to semiconductors which otherwise yield only a narrow range of band bending. **Figure 3** illustrates the leading metallurgical approaches to Schottky barrier control for GaAs, a representative III–V compound semiconductor. Metal contacts to this semiconductor commonly produce a barrier of 0.8 eV (1.28×10^{-19} J), shown as the thermionic emission barrier in **Figure 3(a)**. The field emission barrier illustrates that a decrease in width of the surface space charge region reduces the effective barrier height through an increase in tunneling (**Figure 3(b)**).
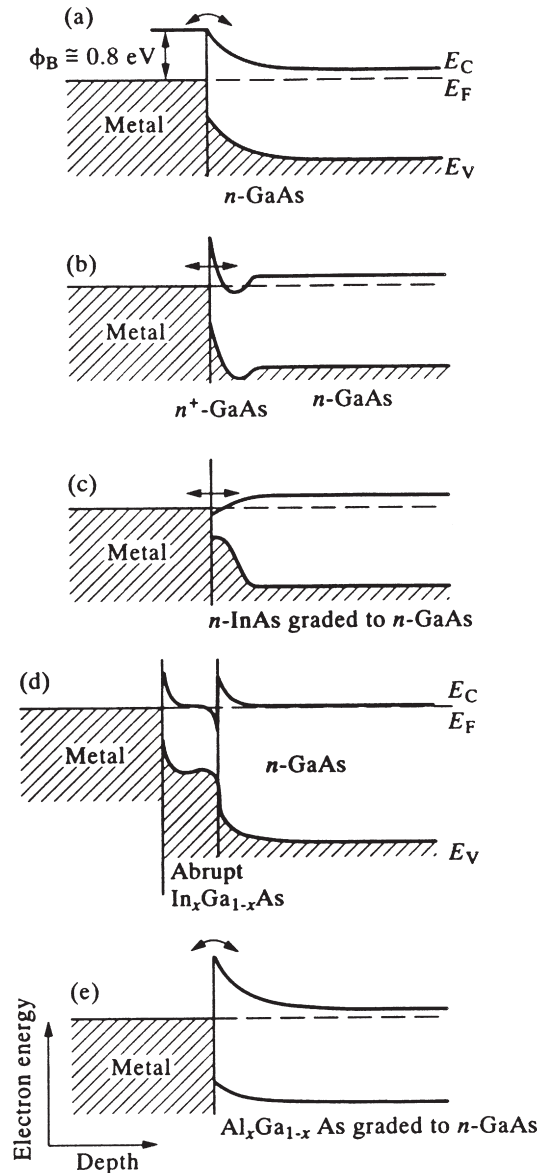
Figure 3 Metallurgical approaches to the control of Schottky barrier height: (a) thermionic emission barrier; (b) field emission (tunneling) barrier; (c) graded composition low-resistance barrier; (d) heterojunction contact reduced barrier; and (e) graded composition enhanced barrier (after Murakami, 1990; Sands *et al.*, 1990) (1 eV=1.6×10^{-19} J).

To accomplish this, a number of processes have been developed to increase the doping density near the semiconductor surface. The graded composition illustration (**Figure 3(c)**) shows another way of lowering the barrier and contact resistance. Here the narrower bandgap InAs has no *n*-type barrier and there is no band discontinuity across the graded region (Woodall *et al.*, 1981). Alternatively, reduced barriers may be obtained simply by a discrete, single-composition layer (here In$_x$Ga$_{1-x}$As) which forms two lower barriers in series, as shown in the heterojunction contact illustration (**Figure 3(d)**). Finally, graded compositions toward higher bandgap (here AlAs) or even insulating layers can enhance the barrier height (**Figure 3(e)**).

Macroscopic metallization may involve single layers, multilayers, and energy processing. For simple, single metal layer contacts, it is quite a challenge to optimize both electronic and chemical properties. Elevated temperatures are required in order to activate diffused or implanted semiconductor dopants, to grow epitaxial overlayers, or to stabilize the contact against degradation at high device operating temperatures. However, metal indiffusion, semiconductor decomposition and outdiffusion, intermetallic or new dielectric formation, and even precipitate formation may occur at above-room temperatures. This interface chemistry proceeds on a scale of micrometers and is dependent on the thermodynamics and kinetics associated with the junction's elemental constituents. In turn, such chemical changes can produce electrical changes such as those shown in **Figure 1** as well as device artifacts such as leakage traceable to compound formation or fabrication-induced lattice damage. The use of refractory metals as diffusion barriers serves to limit or eliminate such chemical effects. Metals such as molybdenum, tungsten, chromium, and tantalum have been used widely (Palmstrøm and Morgan, 1985), as well as gold–tungsten and platinum–tungsten combinations. However, such contacts still contain chemically altered regions of finite extent which are unsuitable for submicrometer-scale devices.

Multilayer contacts offer more flexibility in optimizing junction properties. Such contacts have been employed effectively in obtaining shallow, thermally stable ohmic contacts. Nonalloyed contacts produced by solid-state epitaxy (Marshall *et al.*, 1989) are planar and structurally abrupt on a scale of nanometers. They exhibit very-low-resistance, ohmic behavior ($<10^{-6}\ \Omega\ \text{cm}^2$, $<0.1\ \Omega$ mm on $N_d \sim 10^{18}\ \text{cm}^{-3}$). An example is germanium on palladium on gallium arsenide. Here, the three materials react in stages to produce a highly doped layer of solid-phase regrown GaAs(Ge) only, ~ 2.5 nm thick and a reacted intermetallic layer only slightly larger. Germanium-and indium-based contacts such as NiInW on GaAs provide comparable, low-resistance ohmic contacts with only modest alloying. Here, the addition of refractory metals prevents the formation of any low-melting-point phases, leading to self-limiting reactions and shallow junctions (~ 100 nm) even at elevated temperatures (Murakami, 1990). Epitaxial metal alloy contacts offer the means to fabricate buried semiconductor–metal–semiconductor structures such as permeable base transistors (Sands *et al.*, 1990). Chief material requirements are: crystal structure compatibility, close lattice match, high thermal stability, and morphological stability (i.e., high metal melting point to prevent agglomeration). For III–V compound semiconductors, the transition metal–group III and rare-earth metal–group V alloys satisfy these criteria. The composition-dependent lattice constant of such metal alloys permits strain to be separated from interface chemistry, geometric structure, and bonding influences on barrier height. Thus, a wide range (~ 0.5 eV (0.80×10^{-19} J)), of barriers result, depending strongly on lattice orientation and heat treatment, but only weakly on lattice mismatch (Palmstrøm *et al.*, 1992).

Besides elemental composition, energy processing is a key macroscopic tool for achieving desirable interface properties. Such processes include furnace annealing, rapid thermal annealing with flash lamps, pulsed lasers, or electron beams, and ion beam mixing and annealing. Some or all of these processes can be used to provide thermally stable reacted layers, reacted or alloyed diffusion barriers, dopant indiffusion, dopant activation, epitaxial regrowth, thermionic field emission spikes, or controlled outdiffusion. Ambient gas control during thermal processing is required to avoid unwanted side-reactions.

A wide variety of macroscopic metallization – energy-processing recipes have been developed to date for ohmic contacts to most III–V semiconductors (Palmstrøm and Morgan, 1985; Shen *et al.*, 1992; Brillson, 2010) and to some II–VI compound semiconductors (Sze, 1981; Brillson, 2010; Brillson and Lu, 2011), but further reductions in contact resistance are still desired, especially for wide-bandgap semiconductors. Techniques for the control of high barrier heights have not yet reached a comparable level of development.

Microscopic Compound Semiconductor Metallization

There has been considerable progress in understanding metal–semiconductor electronic and chemical structure on a microscopic scale. With the aid of surface science techniques researchers have shown that metal–semiconductor interfaces exhibit systematic chemical behavior on a scale not only of micrometers but even of atomic layers. Even near room temperature, there exists evidence for reaction, diffusion, segregation, and the formation of solid solutions. Compound semiconductor interface chemistry is complicated by the increased number of substrate components, their combinations with the overlayer(s), and their preferential outdiffusion. Semiconductor outdiffusion also depends on interface reactivity since reaction products can form diffusion barriers. An interface heat of reaction, ΔH_R, where

$$\Delta H_R = (1/x)[H_F(CA) - H_F(M_xA)]$$

is given for the reaction

$$M + (1+x)CA - 1(1/x)[M_xA + C]$$
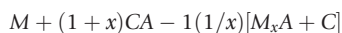
Surface science measurements confirm the existence of a critical ΔH_R dividing reactive and unreactive regimes for metals on III–V, II–VI, III–VI, II–V, and IV–VI compound semiconductors (Brillson, 1982). Ternary semiconductors exhibit pronounced chemically reacted. The heat of reaction expression above can be generalized to include metal–cation alloying.

Such measures of ΔH_R are significant in that they correlate not only with interface chemistry but also in many cases with electronic properties as well. Metal–semiconductor interfaces interdiffuse on a scale of tens of nanometers even at room temperatures. Such outdiffusion decreases with compound heat of formation, indicating that semiconductor stability is a rate limiting factor in the overall process. Furthermore, the stoichiometry of anion-to-cation outdiffusion is altered by reactive interlayer, that is, 'chemical trapping,' demonstrating the sensitivity of interface diffusion to local chemical bonding. Secondary phases may be present at the microscopic interface that are difficult to detect by micrometer-scale techniques but which are observable via transmission electron microscopy and surface science techniques. The interface phase or phases present are dependent on the combination of thermodynamics and temperature, interpretable using the appropriate isothermal section of the equilibrium phase diagram for the constituents (Sands et al., 1990). Local changes in the stoichiometry of outdiffused species affect macroscopic electronic structure: a variety of chemical interlayers –metals, gases, anions, and even other semiconductors – produce substantial barrier height changes (Brillson, 1992), implying that the strength of interfacial bonding determines the type of electrically active sites altering the band bending. Depending on the stoichiometry, high vs. low barriers can be obtained (Brillson, 1982). In general, systematic chemical interactions exist on an atomic scale, even near room temperature, that produce new microscopic chemical structure, which affects macroscopic electronic structure.

## Macroscopic Modification of Schottky Barriers

Macroscopic design principles for modifying compound semiconductor device contacts are of three types: (i) the introduction of dopants and recombination centers; (ii) the formation of interfacial chemical phases with altered, essentially bulk, properties; and (iii) altered densities and types of bulk imperfections. Besides solid-state and alloy regrowth, dopants activated to decrease or increase barrier height may be introduced via ion implantation as well as indiffusion from a contacting solid or gas source. Introduction of recombination centers can provide an effective reduction of the Schottky barrier height via localized state conduction through rather than over the bank bending region – charge 'hopping' vs. tunneling. Besides the graded or constant composition reaction layers described in **Figure 3**, ion bombardment, dry and even wet chemical techniques can provide more homogeneous reaction regions, suppressing the influence of contaminants and any lateral non-uniformities such as 'spiking.' Different crystal growth methods are known to produce substantial differences in the types and densities of deep-level defect densities. Extensive studies of GaAs show these defects to be distributed across the bandgap in energy and to vary by orders of magnitude in density, depending on whether they were grown from the melt, or by vapor-phase, molecular beam, or liquid-phase epitaxy. Furthermore, some of these defects are related to bulk dislocation densities, and both can be controlled by the stoichiometry of growth and the bulk Fermi level position. Hence, considerable flexibility exists in modifying Schottky barriers with micrometer-scale or bulk techniques.

Microscopic and Atomic Modification of Schottky Barriers

The systematics of atomic-scale chemistry have led to new methods of altering Schottky barrier heights. These involve interfacial layers, wet chemical–gas ambient processing, thermal processing, novel micro-electronic structures, or selected crystal growth and processing. Interfacial layers include reactive metals, inert gases, and semiconductors. Reactive metal interlayers alter the stoichiometry of outdiffusion and produce high or low barrier heights over ranges of 0.2–0.5 eV (0.32–0.96×10^{-19} J), which depend on the stoichiometry of semiconductor anion vs. cation outdiffusion. **Figure 4(a)** illustrates the altered doping density resulting from the thin, reactive diffusion barrier (DB). Inert gas interlayers such as xenon prevent reaction and/or defect formation by separating the semiconductor from the deposited metal, leading to more ideal interfaces (**Figure 4(b)**) and new band bending values. Semiconductor interlayers can alter band bending by yet another physical mechanism. Here the conduction band maximum of the bulk semiconductor (SC2) moves with respect to the Fermi level as the doping within the semiconductor interlayer (SC1) is changed. This can be viewed either in terms of a constant band edge discontinuity between the two semiconductors (Peng et al., 1988, **Figure 4(c)**) or a work function effect of the interlayer on the bulk semiconductor. Semiconducting interlayers may also result from interface reactions which coordinate otherwise dangling bonds (i.e., bonds of surface atoms not fully coordinated) to remove local charge sites, for example, the formation of Ga_2Se_3 at the GaAs–ZnSe hetero-interface.

Wet chemical treatments and/or gas ambient exposure have provided several examples of interface state reduction. The use of photochemical washing with bandgap light and water leads to reduced surface recombination velocity and band bending, as evidenced via luminescence and surface conductance, respectively (Offsey et al., 1986). The time-dependent nature of such features with air exposure suggests that surface oxides, water-soluble arsenic oxide in particular, lead to localized charge states and Fermi
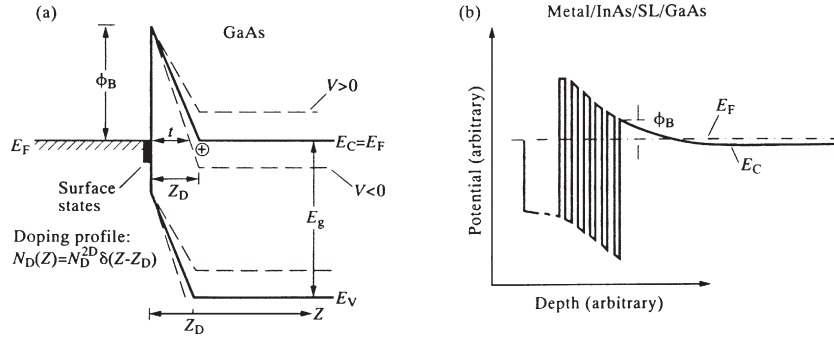
Figure 4 Schematic energy diagrams of the Fermi level and conduction band edge for (a) delta doping, GaAs (after Schubert *et al.*, 1986), and (b) strained layer superlattice (SL), metal–InAs–SL–GaAs junctions (after Peng *et al.*, 1988).

level pinning. A class of inorganic sulfides (Li_2S, $(NH4)_2S$, $Na_2S \cdot 9H_2O$) reduce the surface recombination velocity in GaAs to $10\ cm\ s^{-1}$, approaching that of the ideal AlGaAs–GaAs interface. As with the semiconductor interlayers, such reduction in interface state densities can be interpreted in terms of saturated dangling bonds or the formation of new insulating compounds. Finally, controlled exposure of III–V compound surfaces to oxygen demonstrates changes in Fermi level pinning position with metallization by as much as several tenths of an electron volt, accompanied by changes in atomic interface composition.

Thermal processing of bare semiconductor surfaces can also give rise to changes in Schottky barrier formation. Depending on the temperature, duration, and rate of anneal of GaAs(100) surfaces, subsequent Al–GaAs(100) barrier heights can range from <0.6 to >1.0 eV ($<0.96 \times 10^{-19}$ J to $>1.602 \times 10^{-19}$ J). The apparent changes in interface states can be interpreted in terms of depletion or accumulation of subsurface arsenic, alteration of interface lattice defects, or variations in morphology such as steps or dislocations.

Semiconductor crystal quality is a key factor in determining the densities of bulk native defects. Different techniques of crystal growth can produce significant variations in stoichiometry, point-defect density, dislocation density, and even elemental precipitate density. Such differences are readily apparent in deep luminescence spectra of crystals with different growth histories. Thermal processing and metallization appear to magnify the effect of these bulk deep-level differences near the metal–semiconductor interface. Indeed, GaAs crystals grown by molecular beam epitaxy have much lower midgap deep-level densities and wider ranges of band bending than crystals grown from the melt. II–VI compounds such as CdTe exhibit analogous differences in deep-level densities and band bending values. Lattice misorientation can introduce steps and expose chemically active atomic sites. Furthermore, Fermi level pinning increases with the increasing atomic site density, inclusive of misorientation axis (step direction) and angle (i.e., step density). The variation of dislocation densities across pseudomorphically grown semiconductor film surfaces also leads to changes in band bending. Here the thickness of pseudomorphic growth controls the dislocation density, the higher barrier height whose depletion region 'pinches off' the lower barrier height within the range of the screening distance. The effective barrier height thus depends on both the dislocation and doping densities. Elemental precipitates located near the interface can play a similar role (Brillson, 1992).

Epitaxial metal–semiconductor interfaces provide the best-defined atomic systems for barrier modification. Such interfaces are free of extended chemical reaction, diffusional mixing, and lattice disorder. Nevertheless, different bonding arrangements at interfaces of the same metal and semiconductor are capable of yielding distinct differences in macroscopic barrier height. Most notable have been barrier differences of ~ 0.2 eV (0.32×10^{-19} J) in nickel–silicon and, more recently, lead–silicon junctions with epitaxial arrangement. Barrier variations of 0.2–0.3 eV (0.32–0.48×10^{-19} J) are reported for NiAl overlayers to GaAs(100) with varying nickel–aluminum stoichiometry, while barrier variations of over 0.4 eV changing orientation of the GaAs(100) growth surface (Palmstrøm *et al.*, 1992).

Finally, novel microelectronic structures represent perhaps the most sophisticated growth method of controlling Schottky barriers. Taking advantage of the atomic-scale control of semiconductor crystal growth now available with molecular beam or atomic-layer epitaxy, researchers have engineered new band structures using, for example, delta doping and strained layer superlattices to adjust space charge barrier widths and heights. **Figure 5** illustrates these two innovations. In delta doping, a high density of donors distributed in a two-dimensional plane are located a distance Z_D from the interface (Schubert *et al.*, 1986). The thickness of the tunneling barrier depends in part on the applied voltage. Distance Z_D is only a few angstroms, leading to an extremely thin tunneling barrier and contact resistances in the $10^{-6}\ \Omega\ cm^2$ range and ranges predicted theoretically that are orders of magnitude lower. This structure relies on a strongly pinned Fermi level deep in the bandgap as well as an atomically abrupt interface morphology. The strained layer superlattice consists of alternating large and small bandgap materials. Charge transfer from the large to the small bandgap materials (here GaAs and InAs, respectively) lowers the effective barrier height, and carrier tunneling through the depleted regions is high (Costa *et al.*, 1991). The multiple interfaces of the superlattice serve to reduce the generation or propagation of dislocations and any associated lattice defects. Contact resistances of $10^{-8}\ \Omega\ cm^2$ are reported.
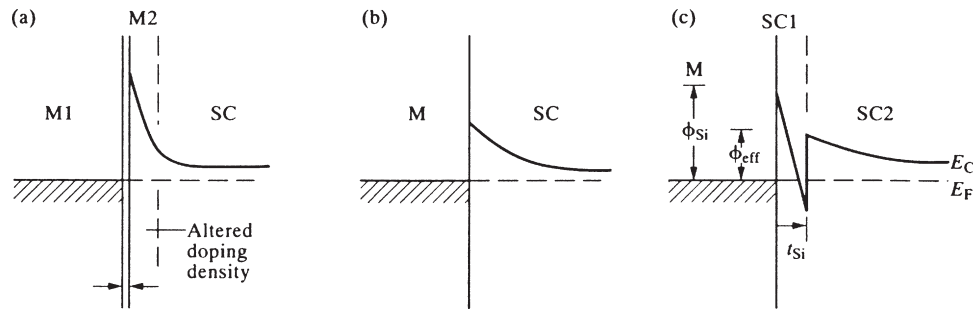
Figure 5 Schematic diagram of the Fermi level and conduction band edge for a metal–semiconductor interface with (a) reactive, (b) inert, or (c) semiconducting interlayer (after Costa *et al.*, 1991).

New Directions

The application of increasingly sophisticated growth and characterization methods will serve to increase both our understanding and control of Schottky barrier formation. Further developments on Schottky barrier engineering require metallurgical growth and processing techniques which permit specific, thermally stable spatial and bonding distributions of interface atoms. Compound alloys are needed for higher temperature diffusion barriers and enhanced reliability. Atomic-scale techniques may prove useful in processing to create extremely uniform surfaces for spatially homogeneous chemical reactions and junction electrical properties with a high degree of reproducibility. Finally, new *in situ* characterization techniques may provide new tools for device fabrication. Such tools could identify desired surface chemical or electronic features at early stages of device fabrication, thereby providing feedback mechanisms for optimization and improved yield.

Acknowledgment

References

Brillson, L.J., 1978. Transition in Schottky barrier formation with chemical reactivity. Phys. Rev. Lett. 40, 260–263.
Brillson, L.J., 1982. The structure and properties of metal–semiconductor interfaces. Surf. Sci. Rep. 2, 123–326.
Brillson, L.J., 1992. Surfaces and interfaces: atomic-scale structure, band bending and band offsets. In: Landsberg, P.T. (Ed.), Handbooks on Semiconductors, vol. 1. Amsterdam: Elsevier.
Brillson, L.J., 2010. Surfaces and Interfaces of Electronic Materials. Weinheim: Wiley-VCH.
Brillson, L.J., Lu, Y., 2011. ZnO Schottky barriers and ohmic contacts. J. Appl. Phys. 109, 121301.
Costa, J.C., Miller, T.J., Williamson, F., Nathan, M.I., 1991. Unpinned GaAs Schottky barriers with an epitaxial silicon layer. J. Appl. Phys. 70, 2173–2184.
Kurtin, S., McGill, T.C., Mead, C.A., 1970. Fundamental transition in the electronic nature of solids. Phys. Rev. Lett. 22, 1433–1436.
Marshall, E.D., Lau, S.S., Palmstrøm, C.J., *et al.*, 1989. Ohmic contact formation mechanism in the Ge/Pd/*n*-GaAs system. Mater. Res. Soc. Symp. Proc. 148, 163–168.
Murakami, M., 1990. Development of ohmic contact materials for GaAs integrated circuits. Mater. Sci. Rep. 5, 273–317.
Offsey, S.D., Woodall, J.M., Warren, A.C., *et al.*, 1986. Unpinned (100) GaAs surfaces in air using photochemistry. Appl. Phys. Lett. 48, 475–477.
Palmstrøm, C.J., Cheeks, T.L., Gilchrist, H.L., *et al.*, 1992. Effect of orientation on the Schottky barrier of thermodynamically stable epitaxial metal/GaAs structures. J. Vac. Sci. Technol. A 10, 1946–1953.
Palmstrøm, C.J., Morgan, D.V., 1985. Metallization for GaAs devices and circuits. In: Howes, M.G., Morgan, D.V. (Eds.), Gallium Arsenide: Materials, Devices and Circuits. New York: Wiley, pp. 195–261.
Peng, C.K., Ji, G., Kumar, N.S., Morkoc, H., 1988. Extremely low resistance nonalloyed ohmic contacts on GaAs using InAs/ InGaAs and InAs/GaAs strained-layer superlattices. Appl. Phys. Lett. 53, 900–901.
Rhoderick, E.H., Williams, R.H., 1988. Metal–semiconductor contacts. In: Hammond, P., Grimsdale, R.L. (Eds.), Monographs in Electrical and Electronic Engineering, 2nd ed. Oxford: Clarendon Press.
Sands, T., Palmstrøm, C.J., Harbison, J.P., *et al.*, 1990. Stable and epitaxial metal/III–V semiconductor heterostructures. Mater. Sci. Rep. 5, 99–170.
Schubert, E.F., Cunningham, J.E., Tsang, W.T., Chiu, T.H., 1986. Delta-doped ohmic contacts to *n*-GaAs. Appl. Phys. Lett. 49, 292–294.
Shen, T.C., Gao, G.B., Morkoc, H., 1992. Recent developments in ohmic contacts for III–V compound semiconductors. J. Vac. Sci. Technol. B 10, 2113–2132.
Sze, S.M., 1981. Physics of Semiconductor Devices. New York: Wiley. Chapter 5.
Tung, R.T., 1991. Electron transport of inhomogenous Schottky barriers. Appl. Phys. Lett. 58, 2821–2823.
Wieder, H.H., 1979. Laboratory Notes on Electrical and Galvanometric Measurements. Amsterdam: Elsevier.
Woodall, J.M., Freeouf, J.L., Pettit, G.D., Jackson, T., Kirchner, P., 1981. Ohmic contacts to *n*-GaAs using graded bandgap layers of Ga$_{1-x}$In$_x$As grown by molecular beam epitaxy. J. Vac. Sci. Technol. 19, 626–627.