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SECTION I
METAL-SEMICONDUCTOR INTERFACES

THEORETICAL MODELS OF SCHOTTKY BARRIERS

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A review is presented in which existing theories of the formation of Schottky barriers are analyzed. The list includes macroscopic dielectric approaches and various microscopic quantum mechanical treatments. The central role of interface states and their different physical origins are assessed. Simple concepts, able to predict general trends in barrier heights, are examined along with detailed microscopic theories applied to individual contacts.

1. INTRODUCTION

The interface between a semiconductor and a metal is of great technological interest because of its rectifying properties. Early related experimental work dates back over 100 years to the studies by Braun¹ on contacts between metal wires and crystals. Intensive research in the field started in the 1930s and 1940s and is now a large branch of semiconductor and device research. It was also in the 1930s that the first microscopic quantum mechanical pictures emerged. The pioneering work by Tamm² and Shockley³ predicted that surfaces (clean and idealized) can bind new states, so-called surface states. These states are localized at the surface and decay, both into the bulk of the crystal and into the vacuum outside the crystal. This concept of surface states has strongly influenced and guided modern surface science. Surface states were observed spectroscopically in the early 1970s on clean semiconductor surfaces in ultrahigh vacuum using photoelectron emission techniques⁴. The observations stimulated a wealth of both experimental studies and realistic theoretical calculations with the goal of understanding the electronic structure of clean surfaces (see for example ref. 5). In particular it was realized that the chemical composition and the detailed structural arrangement of the atoms at the surface produced characteristic spectroscopic "fingerprints" due to the specific distribution of surface states, which can be interpreted theoretically to obtain information about the atomic arrangements.

The focus on surface- or interface-induced electronic states also strongly

influenced theoretical efforts to understand Schottky barriers. A variety of model ideas, as will be described in the next section, were proposed mainly to explain the one key question: what determines the rectifying barrier height if a metal is brought into contact with a semiconductor? The belief in the existence of simple unified descriptions, however, was fast shattered by new elaborate experimental findings and today researchers are mostly concerned with the detailed understanding of some small classes of Schottky contacts or even individual systems. Studies of the details in chemical bonding across the metal–semiconductor interface (this includes some selvage regions on either side) reveal many new situations, such as atomic interdiffusion, formation of metastable compound phases, creation of defects etc. These detailed studies, however, have to date not produced any generally accepted microscopic picture for Schottky barrier formation. The theoretical development is thus marked today by the search for new concepts which ultimately will allow a more unified description.

In Section 2 an overview of past and present theoretical concepts for microscopic descriptions of Schottky barriers will be presented. The selection is incomplete, yet the main ideas will be described. In Section 3 we shall discuss some simple trend studies, their successes and their failures. In Section 4 a particular interface system, GaAs/Al, will be investigated in detail. This includes a description of the various experimental and theoretical approaches as they are specifically applied to the determination of the *structure* of the interface. Finally, Section 5 concludes this article.

2. GENERAL MODELS FOR THE RECTIFYING MECHANISM OF SCHOTTKY DIODES

If a metal and a semiconductor are brought into contact, their individual Fermi levels will adjust to be identical on either side of the interface. The adjustment occurs on a local microscopic scale (1–10 Å range) near the interface where electronic charge can flow from the metal to the semiconductor or vice versa and build up a small interfacial dipole Δ . This local charge rearrangement can, for example, be the consequence of tunneling of metal electrons into the semiconductor or of the formation of new chemical bonds or of the charging of newly created defects or so on. Whatever the mechanism for this local Fermi level adjustment, the bulk semiconductor, which is doped either n or p type and thus has a well-defined Fermi level inside the bulk, adjusts in turn by long range (1000–10 000 Å) band bending. The situation is depicted in Fig. 1 for an n-type semiconductor. The rectifying barrier height Φ_B is the energy necessary to transport a metal electron into the semiconductor conduction band as indicated in Fig. 1.

In the simplest model, due to Schottky⁶, the metal and semiconductor are assumed to be in equilibrium but no direct interaction or charge flow at the contact and therefore no interface dipole ($\Delta = 0$) is considered. As shown in Fig. 1 the barrier height Φ_B is then just the difference between the metal work function Φ_M and the semiconductor electron affinity χ_S , i.e. $\Phi_B = \Phi_M - \chi_S$. In this picture, the barrier and therefore also the degree of rectification vary linearly with the work function of the metal. If the work function of the metal is less than the electron affinity of an n-type semiconductor no rectification should occur. For a p-type semiconductor the reverse is true, i.e. a low metal work function gives high rectification. It was soon

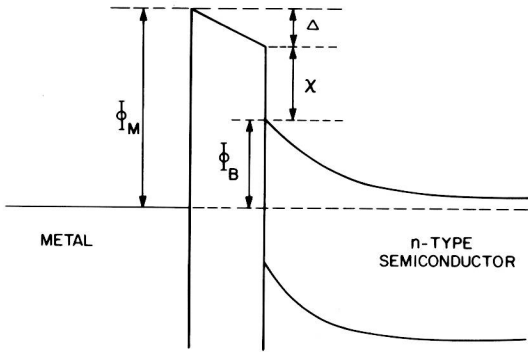


Fig. 1. Energy band diagram of a metal in contact with an n-type semiconductor. The interfacial dipole layer extends over atomic distances (less than 10 Å) while the long-range band bending extends over dielectric distances (about 1000 Å).

recognized that this model was too simple to describe a number of experimental findings. In particular, it was found that the barrier heights for many metals in contact with silicon were practically independent of the metal work function. This led Bardeen⁷ to propose a model in 1947 in which surface states, located energetically in the semiconductor gap, played the central role. Bardeen recognized that a relatively low density of surface states (about one per 1000 surface atoms) on the *free* surface would be sufficient to “pin” energetically the Fermi level at the surface and thus to make the work function independent of the doping in the interior as had been observed for silicon. Therefore, if the semiconductor is brought into contact with a metal, charge can flow from the metal into these surface states and set up a microscopic interface dipole potential (Δ in Fig. 1) such as to compensate the difference between the metal and semiconductor work functions. Bardeen pointed out that there are two limiting cases: (a) the case of a low (or vanishing) density of surface states (in this case the microscopic dipole $\Delta \approx 0$ and the original Schottky picture applies, *i.e.* $\Phi_B = \Phi_M - \chi_s$) and (b) the case of a high density of surface states (*i.e.* more than one state per 100 surface atoms). In case (b) charge flows easily across the interface and the interface dipole Δ can form freely to compensate the difference between the metal and the semiconductor work functions. The rectification properties are then mainly independent of the work function of the metal.

The main feature of the Bardeen model, *i.e.* variable Fermi level pinning by some kind of interface states, has remained the key ingredient for most interface theories until today.

In 1965 Heine⁸ commented on the nature of these interface states. Bardeen had introduced them in the spirit of surface states on free semiconductor surfaces and was not specific as to what changes would occur in the case of an intimate metal–semiconductor contact. Heine pointed out that, strictly speaking, localized states cannot exist at such a junction because of the coupling to a continuum of free-electron-like states on the metal side. He argued, however, that these metal wavefunctions will decay into the semiconductor and their tails will play the role of Bardeen’s surface states. He estimated typical decay lengths of 3–10 Å for free-electron-like metals in contact with silicon.

In the early and mid-1970s a large amount of theoretical work⁹⁻¹¹ appeared in which Bardeen's and Heine's ideas were further investigated and refined. Most of the work focused on the nature of one-electron metal-induced interface states in contrast with intrinsic surface states. One common feature of the various different theoretical approaches was the description of the metal by a featureless "jellium" of continuum states. This model neglects any structural effects and de-emphasizes the role of strong local chemical bonds between the semiconductor and the metal. The models are thus weak-interaction models and correspond to a linearization of the complex problem: $\Phi_B = F(\text{metal, semiconductor})$. This linearization facilitates study of the trends in Schottky barrier behavior which we shall discuss in more detail in the next section. Figures 2 and 3 illustrate some typical results of the Bardeen-Heine-type model calculations. The results are based on self-consistent pseudopotential calculations by Louie and coworkers¹⁰. The system is a silicon-jellium interface, modeling Si-Al. The total electronic valence charge distribution is shown as a profile in Fig. 2(a). The distribution changes abruptly from the strongly modulated behavior on the semiconductor side, which is due to the strong covalent bonds in silicon, to the featureless behavior on the metal side. This rather abrupt change-over is also visible in the valence band spectrum. Figure 3 shows the space-resolved density of states for each of the six regions indicated in Fig. 2. On the metal side (region I) the density of states shows free-electron character (*i.e.* varies as $E^{1/2}$), while on the semiconductor side (region VI) it exhibits the characteristic three-peak structure of silicon. The change-over takes place on a scale of approximately 5 Å between regions III and IV. The feature of interest here is the filling of the semiconductor gap (around E_F) with a smooth and featureless density of gap states. This is in contrast with the free Si(111) surface where peaked structures appear due to dangling bond surface states. The states in the gap can thus be thought of as strongly resonance-broadened surface states, coupled to the metal continuum. The charge profile for these states, located energetically in the semiconductor gap, is shown in Fig. 2(b) and supports this interpretation. The exponential decay length of this charge is about 3 Å which is somewhat smaller than, but not too different from, Heine's original estimates. The charge spill-over of the metal-induced interface

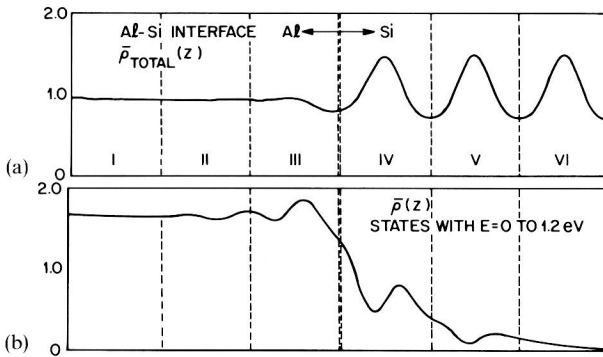


Fig. 2. (a) Calculated total valence charge density profile averaged parallel to the interface and plotted along the direction perpendicular to the interface. The metal is simulated by a jellium and the semiconductor is silicon. (b) The charge profile only for states found energetically in the semiconductor gap. (After Louie and coworkers¹⁰.)

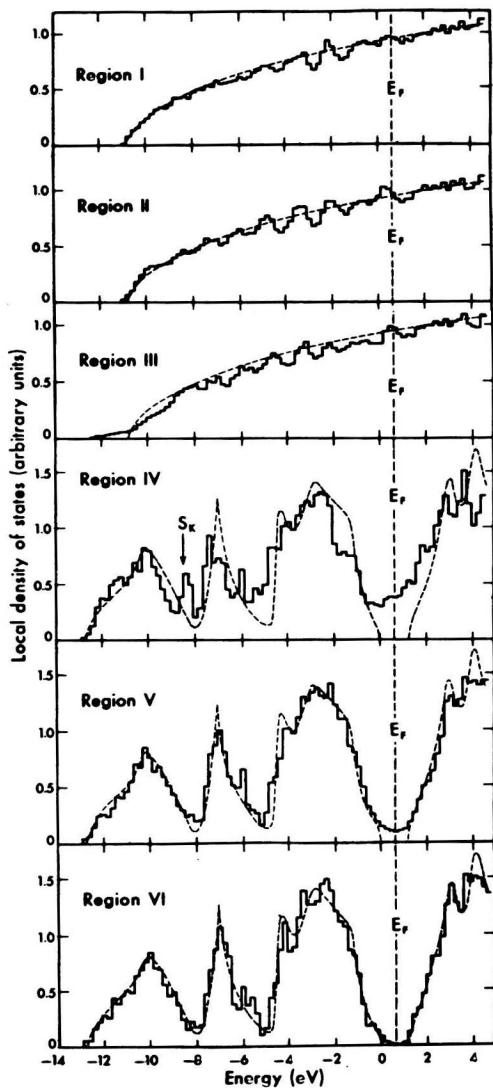


Fig. 3. Calculated local density of states diagrams for a silicon-jellium (Al-Si) interface. The spatial regions I-VI are those indicated in Fig. 2. (After Louie and coworkers¹⁰.)

states produces a dipole potential (Δ in Fig. 1) to align the Fermi levels in the metal and the semiconductor. For high densities of such states large dipoles can be formed without much local Fermi level motion. In this case the rectifying barrier height will be mainly independent of the metal work function. Quantitative trend studies involving different semiconductors and different metals (*e.g.* jellium with different electron densities) have been carried out by Louie and coworkers¹⁰ and will be discussed in the next section. These calculations make the Bardeen-Heine model quantitative and predictive within its limits, which are set by the underlying model assumptions.

The key assumption of weak interaction, *i.e.* the neglect of strong chemical bonding across the interface, has been challenged for its general validity. Alternative models stressing the importance of strong chemical bonds have first been put forward by Phillips and coworkers^{12, 13}. Phillips' arguments are based on a series of observations which show a strong variation in silicon Schottky barrier heights ($\Delta\Phi_B \approx 0.4$ eV) when brought into contact with different transition metals. He proposed a simple but general model in which one or more bulk-like compounds are formed between the semiconductor and the metal which in turn influence the value of the barrier height. Plotting the heat of formation ΔH_f of transition metal silicides against the measured barrier height Φ_B shows excellent correlation (Fig. 4) which stresses the importance of the concept of chemical bonding. Phillips pointed out, however, that according to Pauling's picture strong chemical bonding should produce a correlation of the form $\Phi_B \sim (-\Delta H_f)^{1/2}$ and not the observed linear behavior. He thus proposed a model of weak or moderately strong chemical bonding for which the degree of hybridized bonding and thus charge transfer (or dipole potential Δ) between transition metal and silicon atoms would be linear in ΔH_f .

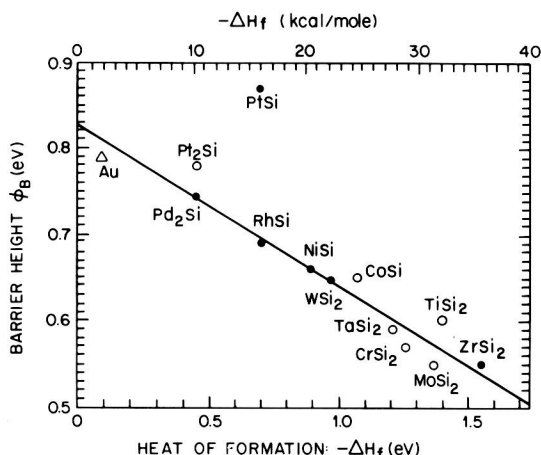


Fig. 4. Schottky barrier heights of transition metal silicide-silicon interfaces plotted against the heat of formation ΔH_f of the silicide compounds: ●, identified silicide; ○, assumed silicide. (After Andrews and Phillips¹³.)

A similar thermochemical analysis of Schottky barrier behavior has been done by Brillson¹⁴ for a variety of systems involving compound semiconductors. Brillson too noted that the barrier heights exhibit a systematic dependence on chemical reactivity. Figure 5 illustrates this relationship between the barrier heights and heats of formation of the most stable known metal-anion bulk compounds. The curves show a strong transition between reactive ($\Delta H_f < 0$) and non-reactive ($\Delta H_f > 0$) junctions. They also exhibit deviations from the linear behavior which Phillips discussed for the weakly reactive transition metal silicides to a non-linear regime for higher reactivities. While the various analyses of Schottky barrier data shown here do not produce any explicit microscopic pictures for Fermi level pinning and barrier formation yet, they clearly indicate the need for a theory able to distinguish between