Silicide–silicon Schottky barriers

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In honor of Emanuel Mooser's 60th birthday

Abstract. The properties of a large number of silicide–silicon Schottky barriers are analyzed. An almost linear relation is found between the barrier height and Miedema's electrochemical potential for the metal atom. Although this type of correlation is usually connected to the Schottky model and its extensions, the results point out that silicon Schottky barriers obey a model that emphasizes the role of the interfacial electronic structure. Defects are significant, but not dominant in defining the barrier height.

1. Introduction

Understanding the parameters that determine the height of Schottky barriers is technologically important. It is also a fundamental challenge and the subject of an intense activity. Silicon Schottky barriers should be an obvious proving ground for theoretical models. As an elemental semiconductor, silicon is devoid of many of the interfacial complexities of compound semiconductors. Its surface can be cleaned thoroughly in ultra-high vacuum and a high degree of structural perfection of the substrate surface can be obtained. Silicon also forms silicides with all transition metals with essentially the same type of p–d bonding [1]. Provided that sharp interfaces are formed, the interfacial reaction between the metal and the substrate moves the interface below the semiconductor surface, away from initial contaminants and structural defects. Such intrinsic interfaces should exhibit much more reproducible properties than interfaces containing extrinsic defects. The bulk metal parameters such as electrochemical potential and stoichiometry can be varied over a wide range. Some silicon-silicide junctions offer the opportunity to study epitaxial interfaces which should presumably display the most simple interfacial geometry.

Extensive reviews of the present status of Schottky barrier models have been published recently [2, 3]. In the first section of this paper, models will be discussed only to the extent required to test their relevance for silicon Schottky barriers. In the second section, an analysis of the properties of a large number of silicide-silicon Schottky barriers will be presented and confronted to the models.

2. Models

The models developed for Schottky barriers can be categorized into two broad groups. In the first group one would find the linear theories, i.e. the

Schottky model and its extensions. They predict that the barrier height depends essentially on bulk parameters of the metal and the semiconductor, and that the barrier changes linearly for small variations of these parameters. The second class regroups the non-linear models. In these, the interfacial electronic structure plays a dominant role, and if furthermore the interface is disordered, they must deal with the influence of electrically active defects. The chemical nature and the position of the nuclei near the interface must be known accurately in order to develop a barrier model and then to check for its validity.

2.1. Linear models

Schottky's early model [4] proposed that the barrier height is defined by one bulk property of the metal-semiconductor couple, namely the difference in electrochemical potentials. This model requires that there be no interaction between the metal and the semiconductor.

The electrochemical potential is difficult to measure directly, so traditionally this quantity has been substituted with the work function. The work function, however, contains a surface contribution, so later one has used Pauling's electronegativity [5] as a measure of the electrochemical potential in an attempt to minimize the spurious contribution due to the surface term. Pauling's electronegativity scale was deduced from the properties of molecules. A scale more appropriate for bulk metals should be Miedema's electronegativity scale [6] which has been deduced from data on solid alloys.

In any case, whatever the details of the charge redistribution between the bulk of the metal and the bulk of the semiconductor and the complexities of the interfacial electronic structure, it remains true that the electrochemical potential difference gives rise to an electrical dipole which appears entirely across the depletion layer in the Schottky model, and splits into a depletion and an interfacial contribution in the general, non-linear case.

Heine [7] has pointed out that the metal states do not terminate abruptly at the stuctural interface: they decay over a finite distance into the gap of the semiconductor. Such metal-induced gap states (MIGS) can establish the position of the Fermi level with respect to the semiconductor bands, and they may exchange charge with the metal as required by the electrochemical potential difference. MIGS is somewhat a misnomer, since the original model envisions metal-induced gap state *tails*. This distinction has implications, for instance on lifetimes while probing the MIGS with perturbations that attempt to change their occupancy. The MIGS model has been further developed by Louie et al [8, 9, 10] and Tersoff [11]. In their calculations, these authors represented the metal by a featureless jellium, neglecting possible effects of the strong chemical reactions that often occur at the interface. This approach represents the most advanced weak interaction models for sharp metal-semiconductor interfaces. They may even be valid for interfaces where strong chemical reactions are known to occur, provided that MIGS are dense enough and penetrate deep enough into the semiconductor to mask the details of the local interface properties. Indeed, in such a situation, the MIGS properties are essentially defined by the semiconductor, and the Fermi level position in the atomic layers scanned by the MIGS is determined by the condition that the charge distribution be nearly neutral. A subsequent change in

the electrochemical potential will then result in a small charge transfer between the MIGS and then metal bulk [11].

Within this framework, one can understand the analysis presented by Kurtin et al. [12] and later reviewed by Schlüter [13]. From their compilation of experimental data on a large number of metal-semiconductor interfaces, these authors extract for each semiconductor a parameter S by fitting the experimental data to the linear law

$$d\Phi = S \cdot d\mu, \tag{1}$$

where Φ is the barrier height and μ the chemical potential difference. If only because of the uncertainty in establishing the electrochemical potential scale, the fits display a large amount of scatter, but the overall results exhibit trends which are in agreement with the MIGS model: The S parameter represents essentially the reciprocal of the density of MIGS. The density of gap states increases if the gap decreases, and indeed one observes small values of S for small gap semiconductors such as Ge or Si, and large values of S for large gap semiconductors and insulators such as ZnS or SiO_2. One also observes, as expected, that the uncertainty on the value of S, and on the validity of the linear model, is large for large gap semiconductors: In such cases the density of MIGS is small and interfacial effects become more important.

2.2. Non-linear models

After the discovery of surface states, Bardeen [14] proposed that the charge transfer required by the electrochemical potential difference could take place between the metal and interface states. This was in effect the first non-linear model. If the interface state density is large enough at the Fermi level, charge transfer can be accomplished at the expense of a small change in the interface Fermi energy, and the barrier height is essentially defined by the position of the Fermi level in the interface states with respect to the band edges. If furthermore the interface state distribution does not change when the semiconductor is interfaced with another metal, one reaches the Bardeen limit in which the Fermi level is pinned at the interface and the barrier height is metal independent.

Detecting the presence of an interface state distribution represents a delicate experimental task: During its formation, the interface may be exposed to various contaminants. Strong chemical reactions may be taking place. Finally, when the interface is completed, it is a buried structure: The measurement technique must be able to separate the substrate and bulk metal contribution and isolate the interfacial component. At this point, even in the most well defined interfaces it remains difficult to separate bulk, interfacial, or defect contributions to the barrier height.

There is experimental evidence that occupied interface states have been observed by electron spectroscopy techniques at the interface between Pd_2Si and Si (111) [15, 16, 17, 18]. An enhancement of the electron density was detected at the Fermi level in the interfacial region. However, the mere existence of interface states does not prove that they play a significant role in defining the barrier height. Unfortunately, the amount of charge exchanged between the metal and the interface could not be established on the basis of these measurements.

Real interfaces may often be more intricate in their atomic and electronic structure than the abrupt interface required by simple models: Consider, for instance, Schottky barriers on III–V semiconductors: The highly non-linear behavior of barrier height versus metal parameters has led several authors [19, 20] to propose models in which interface defects are responsible for the Fermi level pinning. However, a global understanding of Schottky barriers on III–V compounds cannot be derived from such models alone.

First of all, the correlation between information derived from ultra-high vacuum studies at sub-monolayer metal coverage and the interface states at junctions with massive metallization must be analyzed carefully. In particular, the interplay between the MIGS and the defect states must be evaluated. Furthermore, the relative chemical instability of compound semiconductors may lead to many interfacial reactions [21], some of which catalyzed by surface contaminants [22], with the result that the chemical composition and structure of the interface may differ markedly from that of a simple, ordered, sharp, interface. In view of such complexities, it is remarkable that Freeouf and Woodall [22, 23] are able to explain a large number of III–V barriers displaying an excess of type V atoms at the interface by a simple, effective work function, Schottky model.

Secondly, when MIGS, interface states and/or defect-related states are significant in establishing the barrier height, a fraction of the interfacial electrical dipole is supported by an interfacial layer of atomic dimension, in the immediate vicinity of a metallic region. Consequently, the charge transfer required to build the interfacial dipole is much larger than the charge transferred from the depletion region. For Si, the charge transfer would amount to about 0.03 electron per interface atom. This means that in the presence of MIGS or interface states, a rather large concentration of defect-related states is required to modify the barrier height, or, in other terms, that the barrier is relatively stable against interfacial defects [24]. On the contrary, when dealing with adatoms at a vacuum-semiconductor interface, the density of defects required to pin the Fermi level is much smaller. Its amounts to the depletion layer charge: about 10^{-4} electron per surface atom for moderately doped silicon.

Several authors have stressed the importance of strong interfacial interactions by proposing correlations between the barrier height and chemical parameters of the system. In 1975, Andrews and Phillips [25] found a striking correlation between barrier height and heat of formation of silicides at junctions between silicon and transition metal silicides. Since then the spectrum of silicide–silicon systems studied has broadened and the values of the heat of formation of noble and near noble metal silicides have been revised [26], so that the correlation is less convincing. More recently, Ottaviani et al. [27] have found a correlation between a eutectic temperature of the silicon-transition metal couple and the Schottky barrier height. Explaining this correlation in terms of microscopic properties of the interface remains an open problem.

2.3. Disordered interfaces

Substantial chemical and structural disorder may occur at the interface, especially when a compound is formed or when the semiconductor itself is a compound [28]. This may lead to serious difficulties both in characterizing the interface and in predicting its properties. Another limitation to the applicability of

simple interface models is that real interfaces may not display a sharp stoichiometric and structural transition. As a result of atomic interdiffusion, the chemical composition might change quasi-continuously over many layers. It is very doubtful that a sharp interface model can be applied to such a situation [29, 30]. It can be argued, however, that if the composition transition occurs in such a gradual fashion, interdiffusion should also give rise to a large number of gap states inside the depletion region. The electrical properties of such junctions would therefore be more ohmic than Schottky-like. The gap states would also quench the photocurrent in junction photoresponse measurements. It is thus easy to recognize that one is dealing with a complex interface for which simple models are not adequate.

3. Silicon–silicide interfaces

3.1. Experimental results

Silicon (111) and (100) interfaces with silicides of Zr, Nb, Mo, Ni, Ru, Rh, Pd and Pt have been prepared. The 10 ohmcm wafers were cleaned by standard chemical procedures and about 30 nm of metal were deposited with an electron gun evaporator. Subsequently, heat treatment were performed in a Helium furnace. The barrier heights reported in Fig. 1 were measured [31] by the photoresponse technique and by fitting the current-voltage curve with a model including image force barrier lowering, series resistance and parallel conductance. For low barrier junctions, measurements were also performed on p-type substrates. For Ni and Pd, similar measurements were made on samples prepared in ultra-high vacuum conditions [32].

The analysis of the I–V characteristic provides the most trustworthy determination of the barrier height: Artifacts such as series resistance and edge leakage are easily detected and accounted for, and the value of the ideality factor n [31] increases when the barrier height is not uniform across the junction area or when large concentrations of recombination centers are present in the depletion layer. Also, I–V measurements are not overly sensitive [33] to the inhomogeneous depletion layer doping that may result from the fabrication process [34, 35, 36]. The photoresponse technique also gives unambiguous results, provided the barrier height is uniform across the junction area and provisions are made to minimize contributions from the back contact. The model commonly used [31] to deduce the barrier height from the capacitance dependence on junction bias is too simple to account for the complex depletion layer field geometry caused by inhomogeneous doping, charged interfacial defect distributions or non planar interfaces with steps or facettes, and the behavior of the C–V characteristic does not give clear clues when such complications are present.

Barrier heights for silicides of gadolinium [37], yttrium [38], hafnium [39, 40], titanium [41, 42], tantalum [25], vanadium [43, 37], manganese [40], chromium [25, 44], tungsten [25, 45], iron [46], cobalt [25, 47, 48], rhenium [49], osmium [49] and iridium [50] were taken from the literature. Note that the gadolinium value is representative of other rare earths [37]. More references can be found in a review by Murarka [51]. Published values of the barrier height sometimes show a considerable scatter. In such cases, the preference was given to
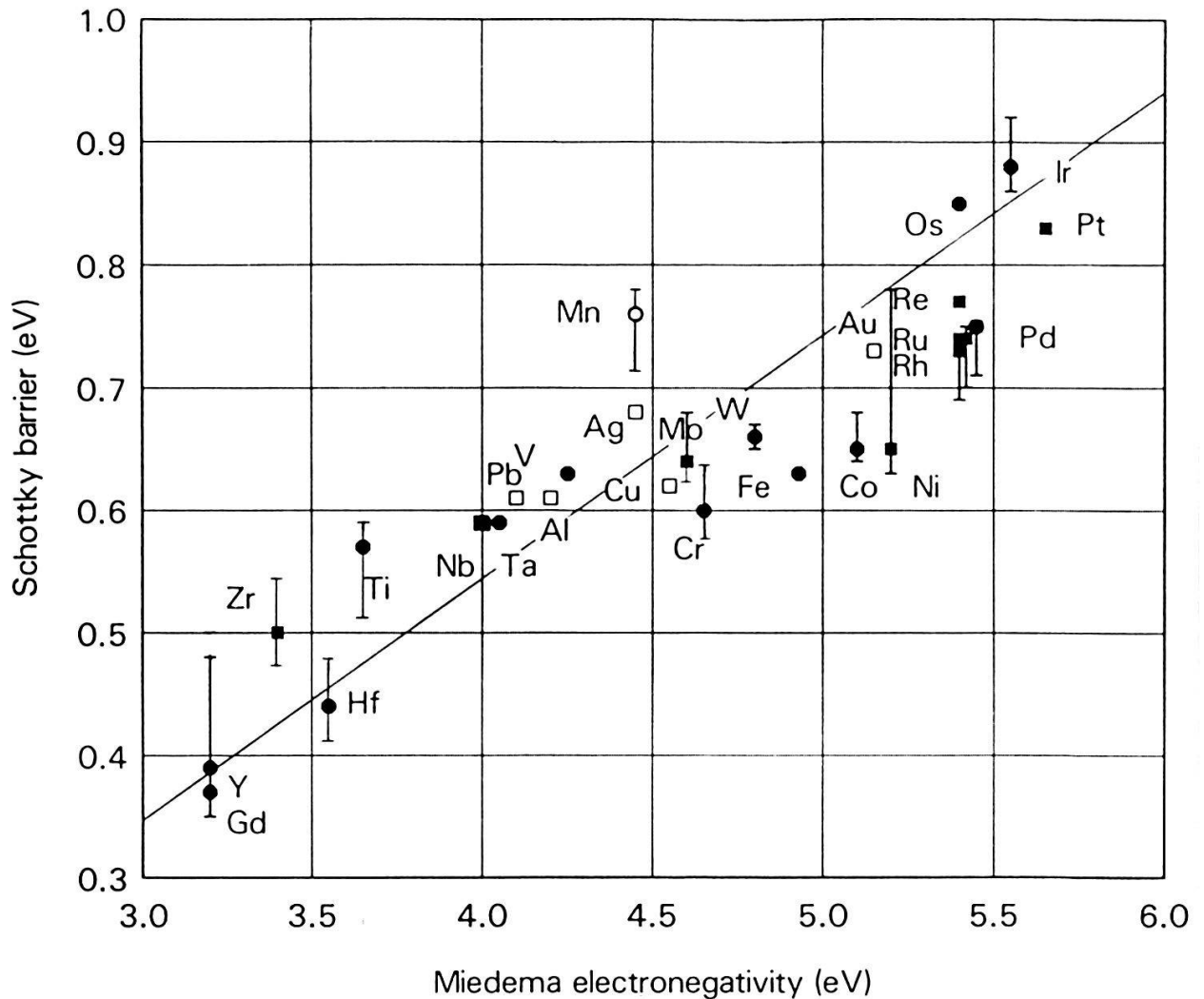
Figure 1
Barrier height of transition metal silicides and nonreacting metal Schottky barriers on n-type silicon. Solid circles and squares: silicides; open squares: nonreacting metals; solid circles: data from the literature (see text).

values supported by two measurement techniques. Data on Nb, Ta, Cr, Co and Mn are particularly scarce. In such cases, error bars are difficult to estimate.

Because of its small gap, silicon should be a prototype of semiconductors where the MIGS extend well into the semiconductor and the improved linear model has a chance to hold true, in spite of the strong interactions taking place at the interface. We have tried to correlate the change in barrier height with the change in chemical potential of the silicide. The chemical potential was evaluated with the stoichiometry-weighted average proposed by Freeouf [52]. Using either the work function or the Miedema scale, as first suggested by Andrews and Phillips [25], gave unsatisfactory results. One source of difficulty is that in many cases the composition of the silicide at the interface is not known, even if the bulk of the metallization has transformed to a well defined compound. For Os and Re, no bulk silicide formation was reported, but is conjectured that an interfacial reaction may well have occurred [49]. In other cases (Ni, Pt, Ir) a change in the stoichiometry of the bulk of the silicide hardly affects the barrier height [32, 50, 53]. A much more convincing correlation is found when the barrier height

is plotted against the Miedema electronegativity of the metal atom, without regard to the stoichiometry of the silicide (Fig. 1).

In Fig. 1 are also included the barrier heights obtained by Thanailakis [54] on ultra-high vacuum cleaved substrates for metals which do not form silicides. The barrier heights used in the figure correspond to the results of both photoresponse and current-voltage analysis.

3.2. Discussion

The first conclusion that can be drawn from Fig. 1 is that there is a definite correlation between Miedema's electronegativity for the transition metal and the Schottky barrier height. The only point that really stands out is due to Mn, for which, unfortunately, few data are available. If, in the spirit of the linear model, one fits the data with a straight line, one finds for S, the derivative of the barrier height with respect to the electronegativity, a value of 0.2. (In a plot the barrier height versus a calculated silicide electronegativity, S reaches a value close to 0.5.) The span of barrier heights is centered around 0.62 eV from the conduction band and covers a good 50% of the silicon gap. The reasonable fit of the data with a straight line would tend to support the general picture of the linear model where the movement of the barrier height is damped by MIGS, and non-linear effects would have to account for deviation in the barrier height of at most 0.1 eV.

On closer examination, it is easy to see that there is a systematic deviation from the straight line: This deviation is roughly symmetrical with respect to a barrier height of 0.62 eV and an electronegativity of 4.6 eV (The electronegativity of Si is 4.7 eV on the Miedema scale). Outside the 4.0 to 5.0 eV range, the slope is markedly larger than 0.2. For electronegativities between 4.0 and 5.0.eV, the value of the slope appears to be smaller, possibly much less than 0.2.

Such a behavior could be explained if the density of gap states had a maximum at an energy 0.62 eV below the conduction band. According to one author [9], the density of MIGS has no extremum, and according to another [11], there is a minimum at 0.76 eV below the conduction band. The most serious weakness of the MIGS model is the absence of calculations showing the relationship between the electron occupation of the MIGS and the magnitude of the induced interface dipole, in particular when the Fermi level approaches the band edges. There is actually a suggestion [55] that MIGS might give rise to a dipole no larger than 0.02 eV. The high slopes observed for extreme values of the electronegativity indicate that MIGS may well not be the dominant factor controlling the height of silicon Schottky barriers.

The enhanced Fermi level pinning observed in the intermediate electronegativity range can be evidence for a distribution of interface states centered around 0.62 eV, spreading over some 50 meV and able to give electrons to or accept electron from the metal. Figure 2 shows how a simple linear dependence of barrier height on electronegativity is modified by such a distribution of defects. For intermediate values of the electronegativity, the defect states exchange charge with the metal in proportion with the change in electronegativity. For extreme values of the electronegativity, the defect states are completely filled (or empty): They contribute an electric dipole of fixed magnitude. Increasing the number of defects per unit area broadens the span of electronegativity for which the barrier height remains nearly constant. Increasing the energy spread of the defect states
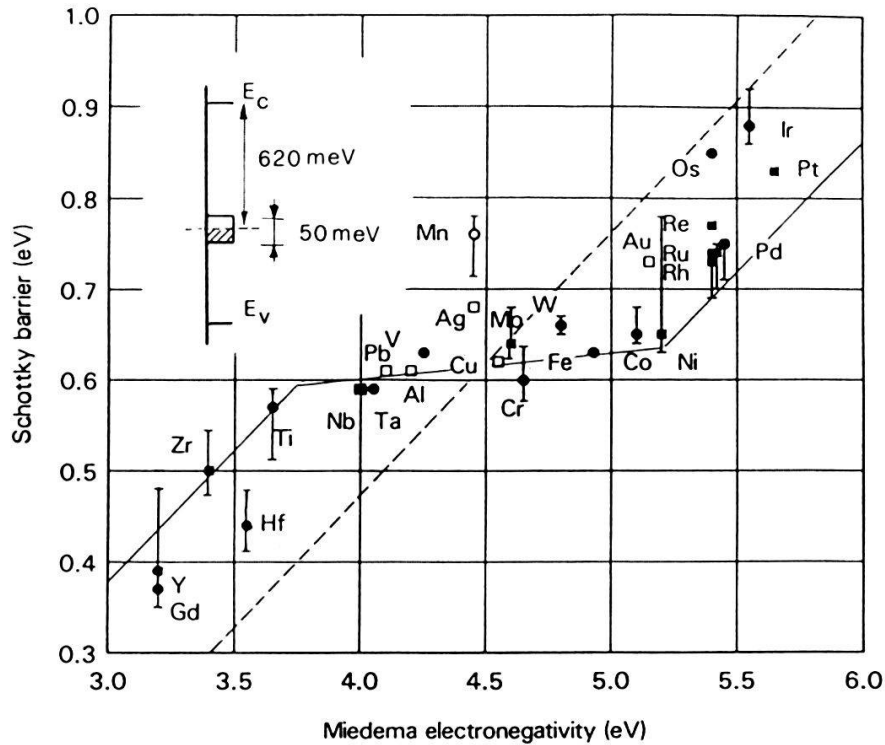
Figure 2
Linear dependence of Schottky barrier height on metal electronegativity (dashed line) modified by the defect density of states shown in the inset (solid line).

would decrease the degree of pinning of the barrier height. Implicit in the analysis is the assumption that the energy position of the defect states is not strongly dependent on the transition metal, and that their energy is defined with respect to the silicon band edges. The model proposed by Sankey [56] of half-filled Si dangling bonds sheltered by interface vacancies could satisfy these requirements.

In contrast with the extrinsic defects mentioned earlier, these defects could be intrinsic in nature: they may be a side product of the atomic displacements that occur during silicide formation. They may also be induced by the lattice mismatch at the interface. Using the estimates given in [10] and [24] for the dipole length and the electronic screening at the interface, the concentration of these defect states should be in the range of $2 \cdot 10^{13}$ to $1 \cdot 10^{14}$ states per cm^2.

If one is dealing with defect states, it should be possible to modify their number while observing the change in barrier height, for instance by hydrogen annealing. The effect of hydrogen annealing on the electronic structure of the Pd/Si interface has been demonstrated [18]. Recent results on the NiSi$_2$/Si (111) interfaces suggest that manipulation of the defect state population can be accomplished by a careful control of the silicide growth parameters. Schottky junctions of Nickel silicides fabricated by standard technology have barriers heights of about 0.65 eV, independent of stoichiometry or substrate orientation. Similar values are usually obtained with ultra-high vacuum techniques [57, 32]. Tung [58] has shown how NiSi$_2$ could be grown on Si (111) with a high degree of epitaxial perfection and control on the relative orientation of the silicide and substrate lattices. (The lattices are parallel in *A*-type interfaces and rotated by 180 degrees around the interface normal in *B*-type interfaces.) *A*-type interfaces showed the

usual barrier of 0.65 eV while pure *B*-type interfaces revealed a barrier of 0.78 eV [59, 48]. This surprisingly high barrier value on epitaxial interfaces has been reproduced [60]. It is proposed that this value is representative of a defect free interface. The value of 0.65 eV then corresponds to junctions with the same canonical interface defects that explain the central plateau of Fig. 2. It is noteworthy that with a barrier height of 0.78 eV, Ni compares much better with the other noble and near-noble metals (Fig. 1). It may also be feasible to improve the structural perfection of the Co and Pd silicide epitaxial interfaces and to observe an increase in barrier height. The present interpretation of the barrier height of epitaxial NiSi$_2$ differs from Tung's proposal that the barrier height difference between *A*-type and *B*-type interfaces is an intrinsic interfacial property: If such is the case, the barrier height depends on minute details of the interface geometry. It makes it consequently hard to understand how the barrier height can be independent on stoichiometry.

The small dependence of barrier height on silicide stoichiometry is supported by direct evidence when several silicides can be formed with the same transition metal [32, 53, 50], and indirectly by the better correlation of the barrier height with the metal electronegativity rather than with the bulk silicide electronegativity. It is doubtful that more refined models of the chemical potential of compounds would conclude to the independence of the chemical potential on silicide stoichiometry. Interface defects may well explain the slow decrease of the barrier height when going from Ni-rich to Si-rich silicide by heat treatments at increasingly high temperatures [32], but not more. It could be argued that the interface has a constant composition, no matter what the stoichiometry of the bulk. There is no experimental evidence that this is so, unless the region with this special stoichiometry is so thin that it extends over only 2 or 3 atomic layers, and furthermore, that this interfacial composition is approximately the same for all silicides, as proposed by Freeouf [61].

A more likely explanation is that the barrier height is defined by interfacial rather than by bulk properties of the junction. Such an interfacial model differs from the linear model discussed earlier by the nature of the driving force that sets the barrier height. In the conventional MIGS model, the driving force is the chemical potential difference between the two bulks. It causes the formation of an interface dipole by means of a charge transfer that defines the position of the bands with respect to the Fermi level, and hence the barrier height. In the truly local interface model, the driving force is the interaction between the semiconductor and the metal atoms of the silicide. It defines the energy and occupancy of the interface states.

The mechanism of the interface model implied by the experimental results can be described as follows. For the sake of argument, let us consider separately the local density of electron states (LDOS) in three distinct regions: in the metal bulk, at the interface and in the MIGS region of the semiconductor. The key assumption is that at the interface, the LDOS about the Fermi level consists essentially of states bonding the interfacial silicon atoms of the semiconductor to interfacial metal atoms of the silicide. This large interfacial LDOS then determines the energy of the Fermi level at the interface by the requirement of charge neutrality. If the covalent character of the interface bonds is sufficiently pronounced, it is quite conceivable that the interfacial LDOS remains essentially unaffected by changes in the stoichiometry of the silicide: the number of interface

bonds per unit area is given by the number of silicon atoms at the semiconductor surface; the energy of the bonds is determined primarily by the nearest-neighbor interaction between a metal atom on one side and a silicon atom of the semiconductor surface on the other side. Experimentally, a large density of states in the vicinity of the Fermi level has been detected at the Pd_2Si-Si interface [15]. In specific studies at low coverage, the pinning of the Fermi level at the interface has been attributed to interfacial metal–silicon bonds [62, 63].

Let us consider now the effect of replacing the silicide of metal A by a silicide of the more electropositive metal B. In the bulk of the silicide, the Fermi level rises as the chemical potential changes from μ_A to μ_B. At the interface, the bonding states now probe the metal B atoms and their energy rises by an amount that can be scaled, in first approximation, to a fraction α of the Miedema electronegativity difference $X_B - X_A$, At this point, the Fermi level is different in each of the three regions. Equilibrium is reached by charge exchanges and the building of electric potential steps [8]. The transfer of a small amount of charge $d\sigma$ from the silicide to the interface produces a small change of the interface Fermi level dE_{Fi}:

$$dE_{Fi} = -4\pi e\delta \cdot d\sigma - \frac{d\sigma}{eD_i(E_{Fi})} \qquad (2)$$

where δ is the effective length of the dipole, that is, the true length divided by the appropriate dielectric constant, and $D_i(E_{Fi})$ is the interfacial density of states per unit of area and energy at the interface. The first term of (2) is the electric dipole energy and the second accounts for the occupation change of the interfacial LDOS. If, in agreement with our assumption, the interfacial LDOS at the Fermi level is high enough, the second term of (2) can be neglected. The electric dipole resulting from the charge transfer moves the LDOS of both the interface and the semiconductor until the interface Fermi level matches the silicide Fermi level. The change in barrier height will be the response of the MIGS region to the remaining Fermi level mismatch at the interface, namely $\alpha (X_B - X_A)$. It can be noted that α directly affects the slope S in equation (1). Since α is clearly less than 1, the role of MIGS in explaining the small value of S is deemphasized.

On the contrary, if the interfacial LDOS is small, say less than 10^{14} $(eV)^{-1} cm^{-2}$, the first term of (2) can be neglected: The charge transferred from the silicide to the interface fills the interface LDOS until its Fermi level matches the silicide Fermi level, but leaves the LDOS in the semiconductor unaffected. The change of barrier height would now be the response of the MIGS to $\mu_B - \mu_A$, the change of Fermi energy in the silicide. This is in effect the linearized Schottky model, which would apply when the interface bonding does not satisfy the requirements mentioned earlier.

The interface bond model can thus explain why the change in barrier height correlates with a property of the metal atom rather than with a property of the silicide. It points out that chemical contaminants may strongly affect the barrier height by disrupting the interface bonding. It also explains the correlation in the change of Fermi level observed for small metal coverage and for bulk interfaces. Interface bonds may exist even at silicon interfaces with metals that do not form silicides. However, since such interfaces are not buried under the original semiconductor surface, they are likely to be affected by extrinsic defects.

4. Conclusions

The analysis of a large number of silicide–silicon Schottky barriers gives support to a model that emphasizes the role of the interface electronic structure. Eventhough strong interactions are usually involved, the details of the interface geometry and chemical bonding do not seem very critical. The effects of interface defects can be identified. There is a clear correlation between the barrier height and a property of the metal atoms involved: Miedema's electronegativity. The Fermi level is pinned at the interface with respect to the metal atom concentration, but it varies systematically with a simple chemical property of the metal atom. The results will hopefully encourage the development of a quantitative interface model of Schottky barriers.

Acknowledgments

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