Nature of the Schottky Term in the Schottky Barrier

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We studied the Schottky barrier for several metal-semiconductor interfaces using both deposition sequences: metal on semiconductor and semiconductor on metal. The interface morphology was found to depend on the deposition sequence, whereas both sequences produced the same interface chemical species and the same Schottky-barrier dependence on the metal electronegativity. These results clarify the nature of the Schottky term in the barrier height, supporting the effective-work-function theory of Freeouf and Woodall.

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The nature of the Schottky barrier at metal-semiconductor interfaces has been a fundamental and controversial problem in solid-state science for over fifty years.[1] In the past two decades, substantial progress has been made with the extensive use of surface-sensitive experimental techniques and of advanced theoretical methods. Yet, the problem is still largely unresolved.

Roughly speaking, there are two kinds of contributions to the Schottky barrier: the Schottky term and a Fermi-level-pinning term.[2-4] The Schottky term—usually the only one discussed in textbooks—is proportional to the difference between the metal and semiconductor electronegativities,[2-4] $\Delta\chi$, and can be written as $S\Delta\chi$. Here S is known as the "pinning strength parameter." The Fermi-level-pinning term is caused by the presence of localized states at the interface.[2-4] In turn, such states can have different causes: Most authors agree that interface defects[5] and metal-induced gap states[6] are the leading ones. In turn, the metal-induced gap states are produced by the tailing of the metal wave functions into the semiconductor's gap.[6]

The Schottky-barrier height of each interface is determined by the interplay of these different terms.[2-4] In the extreme Schottky case, there is no pinning at all and the barrier height is determined by the Schottky term.[7] When pinning occurs, the Schottky term still produces a dependence on the electronegativity difference.[2-4] Such a dependence is more or less pronounced depending on the value of the S parameter.

We present experimental data which lead to a substantial clarification of the nature of the S parameter. The crucial point in our work is the comparison of interfaces obtained by depositing metal overlayers on semiconductor substrates with interfaces obtained by depositing Si or Ge overlayers on single-crystal metal substrates.[8] We systematically investigated the Si-Au, Si-Cu, Si-Ni, Si-Al, Si-Ag, Ge-Cu, and Ge-Au interfaces with this approach, using photoemission spectroscopy with synchrotron radiation.

The comparison of the two deposition sequences revealed substantial differences in the local interface morphology; e.g., the Si-Cu interface is much narrower when Si is deposited on Cu than when Cu is deposited on Si. On the other hand, we found that the S parameter is *in-*

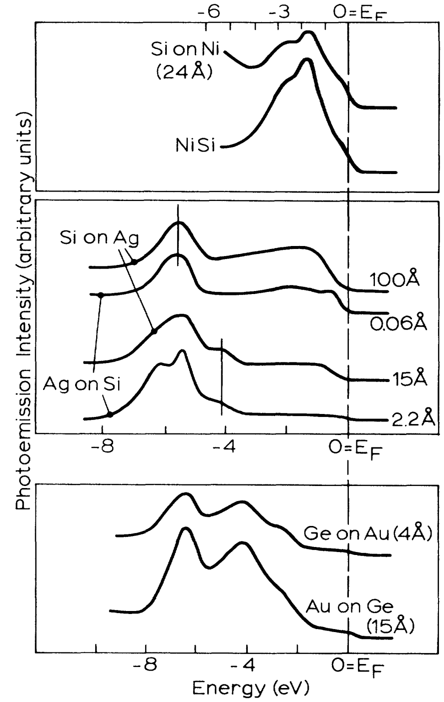

FIG. 1. Top: Valence-band photoemission spectra taken for Si on polycrystalline Ni and on NiSi (Ref. 10); the nominal thickness of the Si overlayer is shown in parentheses. The photon energy was $h\nu=40$ eV for Si on Ni and 50 eV for NiSi. Middle: Valence-band photoemission spectra for Ag on Si(100) (Ref. 11, $h\nu=55$ eV) and Si on Ag(111) [$h\nu=40$ eV; the data for Si on Ag(100), not shown here, are very similar to those of Si on Ag(111)]. The vertical lines mark the features discussed in the text. Bottom: Valence-band photoemission spectra ($h\nu=60$ eV) for Ge on polycrystalline Au (our data and Ref. 12) and Au on polycrystalline Ge (Ref. 12).

dependent of the deposition sequence. We also found that the same interface chemical species are formed for the two deposition sequences. These results can be easily explained within the framework of the effective-work-function model of Freeouf and Woodall.[9] In essence, the model replaces the metal work function (and in a broader sense its electronegativity) with that of interface compounds involving metal and semiconductor. Our results, on the other hand, cannot be easily reconciled with other hypotheses on the nature of the Schottky term.[2-4]

Figures 1-3 show some of the experimental evidence for our conclusions. Figures 1 and 2 show photoemission or Auger spectra taken with the two deposition sequences, which reveal the formation of similar chemical species. In Fig. 1 (top), we see that an interface photoemission spectrum of Si on Ni reveals the formation of NiSi; this is the same compound which is formed when Ni is deposited on Si.[10] In Fig. 1 (middle), we see the comparison of valence-band photoemission spectra for Ag on Si[11] and Si on Ag. The two top curves correspond to a few Ag adatoms on Si and to Ag atoms outdiffusing from the Ag substrate into the Si overlayer; in both cases, the spectra correspond to the same chemical environment (probably, very small Ag clusters). The other two curves correspond to intermediate stages of interface formation; in both curves, we observe a feature 4-4.2 eV below the Fermi level, E_F. This feature and the overall similarity of the spectra indicate that the same species is formed. In Fig. 1 (bottom), we see the similarity between the interface valence-band photoemission spectra of Au on Ge and of Ge on Au.[12] Ruckman *et al.* (Ref. 12) have explained these spectral features as fingerprints of the formation of an interface Au_3Ge phase.

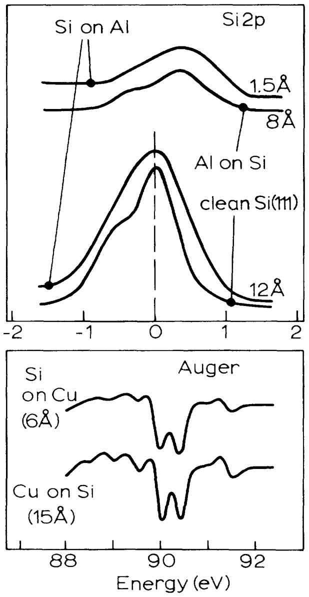

FIG. 2. Top: Si-2*p* core-level photoemission spectra for Si on Al(111) [$h\nu = 150$ eV; data for Si on Al(110) are very similar] and for Al on Si(111) ($h\nu = 130$ eV, Ref. 13). Bottom: Auger spectra for Si on Cu(111) and for Cu on Si(111) (from Ref. 14).

Evidence for similar chemical species can also be extracted from core-level photoemission and Auger spectra, as seen in Fig. 2. In Fig. 2 (top), we see the close resemblance of the interface Si-2*p* photoemission spectra of Si on Al and of Al on Si.[13] In Fig. 2 (bottom), we see that the interface Auger spectra are virtually identical for Cu on Si[14] and for Si on Cu; the Cu-on-Si features have been interpreted as evidence for an interface Cu_3Si species.[14]

In the course of our experiments, we found extensive additional evidence supporting the conclusion that similar chemical species are formed for both deposition sequences: Figs. 1 and 2 show only a few examples. Such an invariance is revealed by entire sequences of spectra taken at different overlayer thicknesses. Furthermore, it is observed for other interfaces besides those represented in Figs. 1 and 2. These results suggest that bulk chemistry overrides surface kinetics in determining the chemical structure of the interface.

The similarity of the interface chemical species is in sharp contrast with marked changes in the interface morphology, also revealed by our experiments. Such changes are clearly visible for at least three interfaces: Si-Ag, Si-Cu, and Ge-Au. In the first case, we found evidence of an extended interface for Si on Ag,[15] whereas most authors report very sharp interfaces for Ag on Si.[16] For Cu on Si, the spectral features related to the interface species are visible[14] at least up to 100-Å overlayer coverage; on the contrary, such features disappear for ≈ 9 Å of Si on Cu. The spectra of Au on Ge(111) and Au on amorphous Ge demonstrate that these interfaces are much more extended than Ge on Au: The features due to interface species are visible after coverages of the order of 100 Å,[12] whereas 10 Å of Ge on Au are sufficient to remove them. Additional evidence for morphology changes is provided by the detailed study of the intensity of photoemission features as a function of the nominal overlayer thickness.[16]

The third fundamental result of our study is that the S parameter is essentially independent of the deposition sequence. Consider the plots of Fig. 3, which show the distance at the interface between E_F and the top of the valence band, E_v (this distance is equivalent to the p-type Schottky-barrier height). The distance is plotted versus the Miedema electronegativity[3,17] of the metal, and the slope corresponds to the S parameter. The full circles are our data points, obtained with well-known photoemission methods[18] in the case of semiconductor-on-metal interfaces. The open circles are data derived from Refs. 3 and 19 for the other deposition sequence.

In the case of Si interfaces, we estimated the S parameter with the least-squares code MINUIT, obtaining 0.22

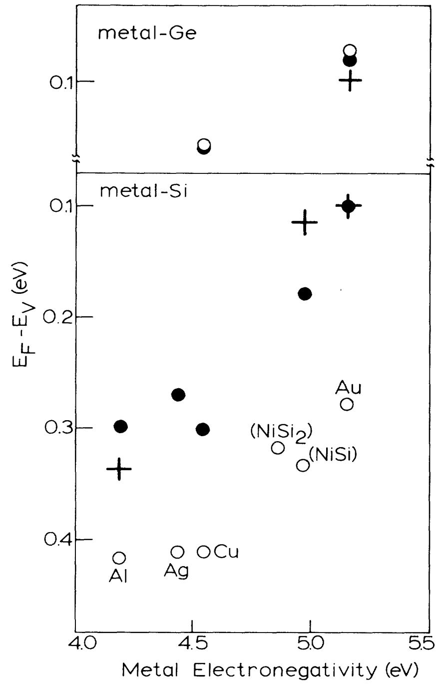

FIG. 3. Plots of the energy distance between E_F and the top of the valence band (corresponding to the p-type Schottky-barrier height) vs the Miedema electronegativity of the metal (Refs. 3 and 17). The full circles are our photoemission data for Si or Ge on metal substrates. The open circles are transport data for metals on Si (Ref. 3) or Ge (Ref. 19). The crosses are data from Ref. 20 for metals on amorphous Si (normalized to the full circle of Si on Au) or amorphous Ge.

± 0.04 for the full circles, and 0.16 ± 0.04 for the open circles. Thus, both sets of data are consistent with an average value $S = 0.19$ within the experimental uncertainty; this value is also consistent with the estimate of Mönch.[3] The limited data on Ge interfaces (Fig. 3, top) support the conclusion that S is independent of the deposition sequence.

Note that the interfaces corresponding to full circles and open circles are different in the long-range order besides being different in the deposition sequence and local morphology. In fact, photoemission spectra indicate that thick Si and Ge overlayers on Al, Ag, Cu, and Au are amorphous, and a thick Si overlayer on Ni produces a polycrystalline phase. The long-range order affects the band gap, and could influence the local polarizability and other interface properties, potentially relevant to our conclusion that the S parameter is independent of the deposition sequence. Therefore, we included in our analysis data obtained for metals on amorphous Si or Ge substrates.[20] These data, shown as crosses in Fig. 3, fully confirm our conclusions on the S parameter.

In Fig. 3, the absolute values of the full circles and open circles for metal-Si interfaces are shifted by 0.1–0.15 eV with respect to each other. This shift could be due to a systematic difference between photoemission and transport results, but neither set of data is sufficient to clarify this point. Alternatively, it could be due to a real effect such as a systematic difference in the pinning position (caused, for example, by differences in the local defects or in the long-range order). The shift, however, does not affect the S parameter, which is the central point of our present discussion.

Several authors have explained the S parameter in terms of the dielectric constant and of the local density of states.[2-4,21] In turn, the dielectric constant is related to the magnitude of the semiconductor's gap. Strictly speaking, the use of the dielectric constant is a (relatively crude) approximation *in lieu* of a detailed treatment of the local polarizability. This approximation is necessary since the treatment of local polarizability is a very difficult quantum-mechanical problem.

On the other hand, our results cannot be easily justified with an explanation based on local density of states and local polarizability. The invariance of the S parameter would imply the invariance of the combined effects of density of states and polarizability, and this is difficult to reconcile with drastic changes in the local interface morphology and crystallinity, like those discovered in our study. We estimate that the corresponding effects on the polarizability would in some case modify the S parameter beyond the experimental uncertainty.[22]

The effective-work-function model[9] provides instead a simple explanation for our data, by considering the bare interface dipole caused by the electronegativity difference of local chemical species. We conclude, therefore, that our data support the notion of effective work functions for the Schottky term of the metal-semiconductor barrier.

Note that our conclusion only concerns the Schottky term: Our results do not support, rule out, or clarify the Fermi-level-pinning term.[2-4] Based on existing experimental data from many authors, it appears that such a term is determined by the interplay between defects and metal-induced gap states.[2-4] This is a very interesting problem, whose solution is necessary to completely clarify the nature of the Schottky barrier. The partial but fundamentally important clarification provided by our present results should pave the way for a definite solution of this long-standing problem.

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