Role of Virtual Gap States and Defects in Metal-Semiconductor Contacts

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Chemical trends of barrier heights reported for metal- and silicide-silicon contacts are analyzed. The data are easily explained when both virtual gap states of the complex band structure of the semiconductor and electronic levels of defects created in the semiconductor close to the interface during its formation are considered. The virtual gap states determine the barrier heights when either the defect density is low or the defects are completely charged or all neutral.

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The rectifying properties of metal-semiconductor contacts, which were discovered by Braun,[1] are caused by depletion layers on the semiconductor side of the interface, as was first shown by Schottky.[2] The fundamental parameter which characterizes such a junction is its barrier height, i.e., the energy distance from the Fermi level to the bottom of the conduction band at the interface when the semiconductor is doped n type. A basic understanding of Schottky contacts thus needs a model which explains the chemical trends of the barrier heights observed with different metal-semiconductor pairs.

Schottky[3] and Mott[4] proposed the barrier height to equal the difference of the work function of the metal and the electron affinity of the semiconductor. Although for a given semiconductor the barrier heights are generally found to increase when the work function of the metal in contact becomes larger, the simple Schottky-Mott rule is not obeyed by the experimental data. Bardeen[5] attributed this discrepancy to the presence of interface states. They could accommodate charge which is transferred between the metal and the semiconductor because of their generally different electronegativities. This means that a dipole layer exists at the interface. Since the work function of metals and their electronegativities were found to be linearly related, such interface states intuitively explain that the barrier heights are increased by metals with larger work functions but do not follow the Schottky-Mott rule. Two basically different models on the physical nature of such interface states have been suggested. In the following, they will be briefly reviewed.

The first model, which was introduced by Heine,[6] assumes that within the band gap of the semiconductor the wave functions of the metal electrons are tailing into the virtual gap states (VGS) of the complex band structure of the semiconductor. Since the virtual gap states are split off from the valence and the conduction band, their character varies across the gap from mostly donor type close to the top of the valence band to mostly acceptor type close to the bottom of the conduction band. The charge transferred between the metal and the semiconductor then pins the Fermi level above, at, or below the charge-neutrality level E_0 of the virtual gap states when the electronegativity of the metal is smaller, equal to, and larger than, respectively, the one of the semiconductor. In the following, three different and independent results will be presented which support the VGS model of Schottky contacts.

For the column-IV elemental and the III-V compound semiconductors Tersoff[7] has calculated the charge-neutrality levels of the VGS. He has obtained good agreement between $(E_{cs}-E_0)$ and the barrier heights Φ_{Bn} experimentally determined with gold Schottky contacts on samples doped n type. This finding is supporting the VGS model since the electronegativities of gold and of the semiconductors only differ slightly. Second, the adsorption of cesium[8] and of chlorine[9] was found to pin the Fermi level above and below, respectively, the charge-neutrality level of the VGS at cleaved GaAs(110) surfaces. Since the electronegativities of cesium and of chlorine are smaller and larger, respectively, by almost the same amount than the value of gallium arsenide the results mentioned are again in support of the VGS model.

The third indication is represented by the data plotted in Fig. 1. When interface states are assumed to be present in a metal-semiconductor junction the barrier height Φ_{Bn} increases proportionally to the work function Φ_M of the metal.[13,14] The slope parameter $S=d\Phi_{Bn}/d\Phi_M$ only depends on the product of the density of states $D_{vs}(E_0)$ around the charge-neutrality level of the interface states and the width δ of the related dipole layer as

$$S=[1+e_0^2 D_{vs}(E_0)\delta/\varepsilon_0]^{-1}. \quad (1)$$

In the VGS model, this product $D_{vs}\delta$ is determined by the average band-gap energy of the semiconductor which, on the other hand, is related to the electronic polarizability $(\varepsilon_\infty-1)$ of the semiconductor.[12] Although in some cases the experimental slope parameters are not well defined,[10,11] the S values of nineteen different semiconductors follow a pronounced chemical trend[12] when $(1/S-1)$ is plotted over $(\varepsilon_\infty-1)$ as shown in Fig. 1. A least-squares fit to the data yields

$$(1/S-1)=0.1(\varepsilon_\infty-1)^2 \quad (2)$$

and a regression coefficient $r=0.91$. This result again

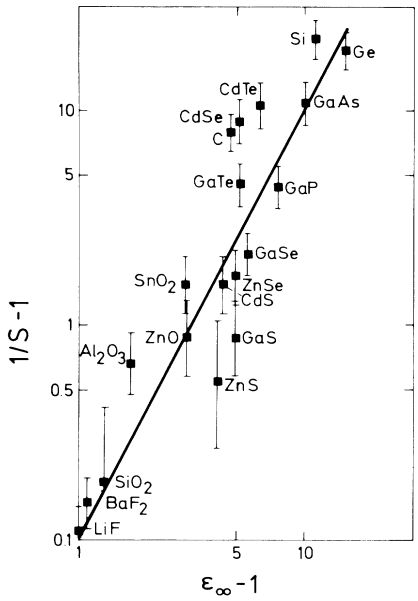

FIG. 1. Slopes $S = d\Phi_{Bn}/d\Phi_M$ plotted vs the electronic contribution ε_∞ of the dielectric constant of the semiconductor. The data were taken from Refs. 10 and 11 in the manner of Ref. 12.

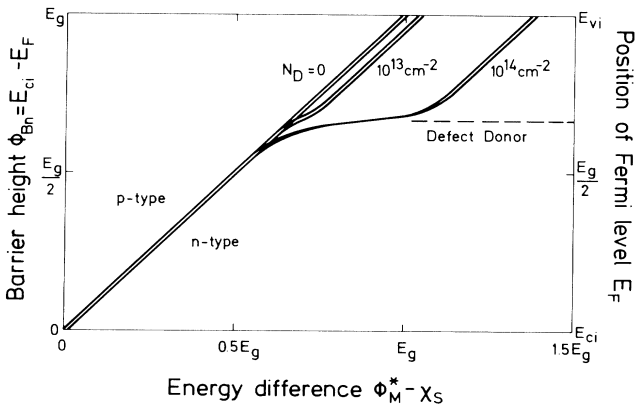

FIG. 2. Barrier height as a function of the difference between the internal part of the metal work function Φ_M^* and the electron affinity X_s of the semiconductor for three different densities of defects (shown schematically in the manner of Refs. 21 and 22).

strongly supports the VGS model of metal-semiconductor contacts.

The second model which was proposed by Wieder[15] and Spicer *et al.*[16] identifies the interface states in Schottky contacts as electronic states of native defects which are created during the formation of the junctions (see Mönch[17] for a review). The defect model was motivated by the observations that Schottky barriers on III-V compound semiconductors were found to be insensitive to within 0.2 eV to the metals used and to follow no apparent chemical trend. Up until now, no spectroscopic evidence has emerged for any defect such as vacancies or antisite defects which have been discussed theoretically.[18,19] This might indeed prove to be difficult since in many cases chemical reactions and intermixing were observed.[20] Therefore, interfaces between most metals and III-V compound semiconductors are difficult to characterize with respect to local variations in chemical composition.

The influence of defect levels on the barrier height of metal-semiconductor junctions was theoretically studied by Zur, McGill, and Smith[21] and by Duke and Mailhiot.[22] They placed defects 5–10 Å apart from the interface into the semiconductor. The metals were described by a jellium model. The results of these calculations are schematically explained in Fig. 2. When the area density N_D of defects is kept below 10^{13} cm^{-2} the position of the Fermi level moves across the energy gap of the semiconductor to the same extent as the internal work function Φ_M^* of the jellium metal is increased. For larger defect densities, the Fermi level gets transitionally pinned at the defect level, until the defects are all charged, and then further moves towards the top of the valence band at the interface as a function of metal work function.

These models have been developed in parallel to many experimental studies of metal-semiconductor junctions which have provided a huge body of data on electronic, structural, and chemical properties of such interfaces. In the following, the analysis of experimental results and the search for chemical trends shall be restricted to metal-silicon contacts for the following reason. The interfaces of Schottky contacts on III-V compound semiconductors were found to be intermixed in many cases[20] and they are thus difficult to characterize chemically. Metal-silicon junction, on the other hand, can be prepared with quite abrupt interfaces since the controlled formation of silicides, which are mostly metallic, is a well-established technique.[23] Cross-sectional pictures obtained with high-resolution transmission-electron microscopy have proven that, for example, epitaxial films of $NiSi_2$, NiSi, and Pd_2Si may be grown on silicon substrates (see, e.g., the work of Liehr *et al.*[24] and Ho[25]).

In searching for chemical trends of the barrier heights measured now with metal-silicon contacts, the main difficulty arises with the ordering of the metals. The first choice, which was motivated by the early Schottky-Mott rule, has still remained the metal work function which, however, contains an internal part plus a surface dipole contribution. The internal part of the work function, which is of interest in interfaces, may be approximated by the electronegativity of the metal. Here, the most popular scale has been the one developed by Pauling.[26] He has designed his set of values to describe the partly ionic character of covalent bonds, and it is this field where Pauling's electronegativities have their merits in semiconductor bulk and surface physics, too (see, e.g., the work of Mönch[27]). In metal-semiconductor con-

tacts, on the other hand, the ionicity of metallic bonds comes into play. Chemical trends in the properties of metal alloys and intermetallic compounds have been successfully described by another set of electronegativities which were derived by Miedema, el Châtel, and de Boer.[28] In the present paper, the further analysis will use the electronegativities proposed by Miedema.

In Fig. 3 barrier heights measured with metal- and with silicide-silicon junctions are plotted over electronegativities based on the Miedema scale. For silicides M_mSi_n, the geometric mean $(X_M^m X_{Si}^n)^{1/(m+n)}$ of the metal and the silicon electronegativities were taken.[26,31] In this respect the plot differs from a similar one by Schmid[29] who has introduced Miedema's electronegativities in the discussion of metal-silicon junctions but has plotted Φ_{Bn} vs X_M only. In Fig. 3, the data points are obviously arranged in two groups. The straight line drawn in full is a least-squares fit to fifteen data points and is given by

$$\Phi_{Bn} = 0.17\langle X_M \rangle - 0.04 \text{ eV},$$

with a regression coefficient $r = 0.98$. The marked data point labeled CNL represents the charge-neutrality level of the virtual gap states of the complex band structure in silicon ($X_{Si} = 4.7$ eV) as calculated by Tersoff.[7] Obviously, the charge-neutrality level of the VGS fits exactly into that straight line. This finding implies that those barrier heights, which define that straight line in Fig. 3, are determined by the VGS of silicon. The broken line connecting another eighteen data points resembles the shape of the curve shown in Fig. 2 which was obtained for heavily defected metal-semiconductor contacts.

Considering the VGS and the defect model of metal-semiconductor junctions as outlined above, the data plotted in Fig. 3 suggest the following explanation. Those metal-silicon junctions, the barrier heights of which are found close to the straight-line fit, are exhibiting a density of defects below approximately 10^{13} cm^{-2} and their barrier heights are thus determined by the tailing of the metal electron wave functions into the virtual gap states of the silicon bond structure. The other silicon Schottky contacts contain a large defect density of approximately 10^{14} cm^{-2}. As the inflection of the dashed line indicates, one defect level is located at approximately 0.62 eV below the bottom of the conduction band. That defect level was already concluded by Schmid[29] from his Φ_{Bn}-vs-X_M plot for the silicide-silicon junctions. For barrier heights less than about 0.6 eV the dashed curve is running in parallel to the straight line, which is determined by the VGS of silicon, but is shifted by 0.1 eV to lower values. This indicates the presence of another defect level at or above 1.12–0.37 eV = 0.75 eV above the top of the valence band. The explanations just given for the data plotted in Fig. 3 are strongly supported by results of a study on nickel-silicide-silicon interfaces recently published by Liehr *et al.*,[24] which will be discussed in the following.

Both groups of data points in Fig. 3 contain results

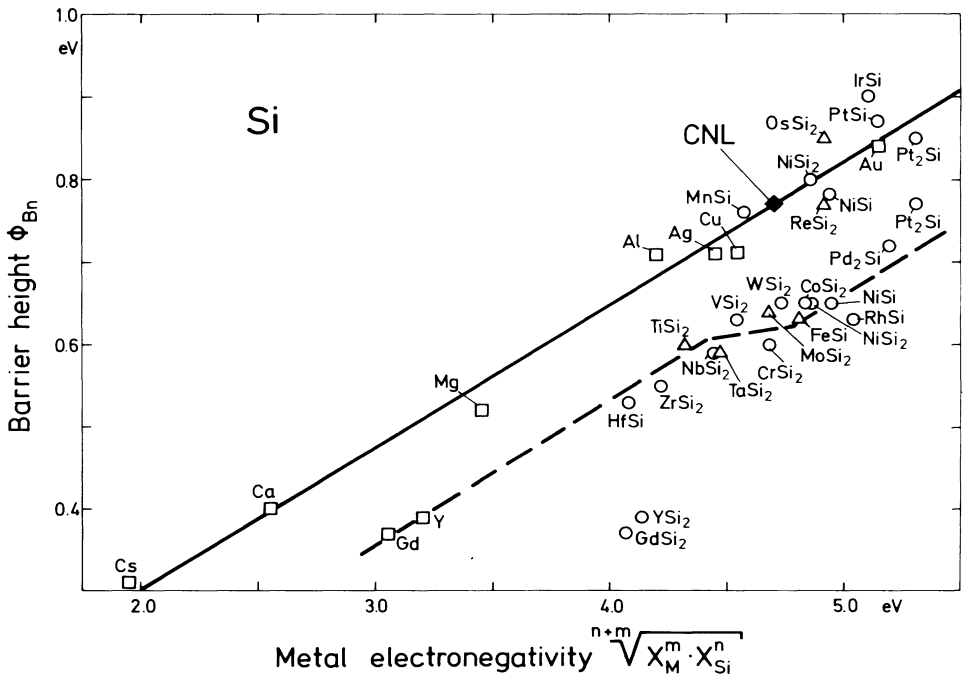

FIG. 3. Barrier heights of metal- and silicide-silicon contacts vs the effective Miedema electronegativities. The barrier heights were adopted from Refs. 24, 29, and 30.

from the study of Liehr *et al.* for $NiSi_2$ and NiSi which differ by $\Delta\Phi_{Bn} \approx 0.15$ eV. With both nickel silicides the larger values were found when epitaxial silicides were grown, which in the case of the disilicide consisted of either pure type-*A* or type-*B* interfaces. With a mixture of both types, which only differ in the stacking sequence when passing the interface, the lower value of the barrier height was observed regularly. Cross-sectional TEM pictures always revealed such interfaces exhibiting the lower Φ_{Bn} values to be less perfect, containing phase domain boundaries with faceted or stepped structures.[24] With the nickel monosilicide, large barrier heights were also observed only when the interfaces were of the same high degree of perfection as found with single-type disilicide. "The degree of perfection of the interfacial structure is more important than specific epitaxy in determining the barrier height," as was pointed out by Schmid *et al.*[32] From preliminary evaluations of further capacitance spectroscopy studies they also computed approximately 10^{12} to 10^{13} interface states per square centimeter for the single-type $NiSi_2$-Si interfaces but about 1 order of magnitude more for the mixed-type interfaces. These experimental findings by Schmid *et al.* are in excellent agreement with the explanations of the data plotted in Fig. 3 which were given above.

The results of the present paper may be summed up as follows. The analysis of the chemical trend of the barrier heights reported for 31 different metal- and silicide-silicon interfaces has revealed that both VGS and defects are needed to explain the complete set of experimental data. When, however, the experimental conditions during the preparation of Schottky contacts can be controlled such as to reduce the defect density to below approximately 10^{13} per square centimeter then the barrier height is determined by the virtual gap states of the semiconductor band structure only. In highly defected Schottky barriers the virtual gap states also determine the barrier heights when all the defects are either charged or neutral. A preliminary analysis of barrier heights observed experimentally with metal-GaAs(110) contacts show that the same concepts apply to these interfaces, too.

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