$\times 10^{-12}$ m/V, while in GaAs and ZnS, $r_{41} \sim 2\times 10^{-12}$ m/V.

The effective charge e_c^* is related to the Szigeti effective charge e_s^* by $e_c^* = [(\epsilon_\infty + 2)/3\epsilon_\infty] e_s^*$. The value of e_c^*/e varies from 0.2 to 0.4 and seems to be independent of the number of valence electrons. The calculated values of r_{ijk}^{ion} using (17) and (18) are shown in Table I as r_{ionic}. The pure electronic contribution is entered as r_{elec}. It is obtained directly from the experimentally determined second-harmonic-generation coefficient by $r_{lk} = -4d_{lk}/\epsilon^2$. For most of the cyrstals in Table I, r_{ionic} is positive and r_{elec} is negative. Therefore, the predicted electro-optic coefficients, $r_{\mathrm{sum}}^{\mathrm{theo}} = r_{\mathrm{ionic}} + r_{\mathrm{elec}}$, involve the algebraic addition or cancellation of two numbers of comparable values. The only exception is CuCl. Because of the unfilled shell in Cu, the sense of bond polarization in CuCl is different from that in other crystals.[7] The signs of r_{ionic} and r_{elec} of CuCl are thus different from others. However, the magnitude of r_{ionic} is larger than that of r_{elec} in CuCl. We still obtain a negative electro-optic coefficient for CuCl. The predicted values in Table I are in good agreement with experiment. The worst case is GaP. It is interesting to note that the electronic contribution is about double the ionic contribution. This is in excellent agreement with the experimental observation.[8]

We intend to extend this model to complex crystals with different point-group symmetries. The generalization of the bond parameters used above to multibond crystals has already been considered. The one parameter which will need added thought is e_s^*, the effective ionic charge. It was found empirically to be equal to $C/\hbar\omega_p$ in diatomic crystals.[9] If this relation and $e_c^* = [(\epsilon_\infty + 2)/3\epsilon_\infty] e_s^*$ are valid in the more complex crystals, then our model can be applied to these cases. Calculations now in progress on KH_2PO_4, $LiNbO_3$, $LiTaO_3$, and ternary chalcopyrite crystals will be reported separately.

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Interfacial Reaction and Schottky Barrier in Metal-Silicon Systems

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Electronic states at the metal-silicon interface have previously been postulated in order to explain the pinning of the Fermi level, and the origin of these states has been a matter of some dispute. We propose here that in a reactive interface, such as the interface between Si and transition metals, physical properties of the interface are related to an interfacial layer, and that the relationship is manifest through the correlation between Schottky barrier height and eutectic temperature.

The theory of the Schottky barrier is an important subject concerning solid interfaces and is relevant to applications in microelectronics.[1,2] The classical theory of Schottky assumes that at the interface between a metal and a semiconductor the Fermi levels should match up. This produces

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a potential difference (the Schottky barrier height) which is equal to the difference between the metal work function and the semiconductor electronic affinity. We note that in this classical theory no chemical interaction between the solids has been taken into account and the interface is regarded as chemically abrupt. The theory has been found to agree well with experiments performed on nonreactive interfaces, e.g., metallic contacts on ionic crystals where the assumption of no chemical reaction seems to hold.[3] However, the theory is not capable of explaining metallic contacts made on semiconductors,[3] especially those which form oxides. For metals on Si covered with a native oxide, the Schottky barrier height has been measured to be at about $\frac{2}{3}$ of the band gap of Si. Bardeen[4] suggested the existence of surface states in the gap which pin the Fermi level and, consequently, determine the Schottky barrier, which is independent of the metal used. Subsequently, Heine[5] postulated that the states in the gap are due to the tails of the metallic wave function penetrating into the semiconductor. Inkson[6] had a slightly different approach from the above and proposed that the pinning of the Fermi level is due to the narrowing of the band gap at the interface rather than the surface states. Recently, a theoretical calculation[7] of the Schottky-barrier problem assumes a model in which the semiconductor has a surface atomic structure obtained by simply terminating a perfect bulk crystal and the metal is jelliumlike. The calculation obtained the values of density of states in the gap and their decay length. All these theories have emphasized the important role of electronic states at the interface but have paid much less attention to chemical or metallurgical reactions that could occur at the interface and to their effects on the electronic properties of the interface. The native oxide is but one of the reaction products that can affect the Schottky barrier.

Recently, it has been found that the native oxide on Si surfaces can be broken by the formation of transition-metal silicide,[2,8] and hence the pinning due to the oxide is removed. In fact, the Schottky barrier height of silicides varies from 0.93 (IrSi, Refs. 9 and 10) to 0.55 eV ($ZrSi_2$).[11] Andrews and Phillips[11] have analyzed the barrier heights of silicides on the basis of the nature of their chemical bonds and found that they vary linearly with the heat of formation of silicides. Nevertheless, we have an uneasy feeling about the correlation since it relates an interfacial property to a bulk property. Besides, there are two noticeable exceptions, i.e., PtSi and IrSi.[9]

In this Letter, we postulate that in a reactive interface such as silicide-Si interfaces there is an interfacial layer which tends to dominate the Schottky-barrier height, and we will show a new correlation between Schottky-barrier height and another interfacial property to support it. Our model is similar to the oxide model except that the interfacial layer is not a native oxide but a reacted layer of the two solids in contact. We cannot yet define in general terms the extent of the reacted layer, nor the structure and composition of the layer, but the existence of such a layer can be based on the requirment of minimizing the free energy of the interface, like a diffused interface.[12] Since it is a reactive interface, the existence is also supported by a kinetic reasoning. The reaction to form near-noble metal silicides on Si occurs around 200 °C (Refs. 2 and 8); it is difficult to explain the breaking of Si covalent bonds at such a temperature without the help of a low-temperature kinetic process. It has been postulated[13] that interstitial diffusion of near-noble metals into Si can convert the covalent bonds to metallic bonds and by the utilizing of such a bond-weakening mechanism the low-temperature reaction can proceed. Here, the interfacial region containing the interstitials can be regarded as the proposed interfacial layer. Walser and Bene[14] have also postulated the existence of an interfacial layer which is amorphous and has a composition near the lowest eutectic point in the binary system. We should point out that our picture of the interfacial layer is much more general and it does not have to be amorphous nor contain interstitials. It may differ from the two solids in contact in either structure or composition or both.

If the postulation of an interfacial layer in a reactive interface is correct, the layer should control not only the Schottky-barrier height, but other interfacial properties as well. Then the question is what are the other interfacial properties that can be examined. An obvious one is interfacial free energy, but unfortunately, we know very little about it. In fact no measurements of silicide-Si interfacial energy has ever been made. Another one which is not so obvious but is readily available is the eutectic temperature of binary systems. We can regard eutectic temperature as an interfacial property for the following reason: Consider the interface between a layer of Au and a layer of Si; melting occurs at the interface but not in the bulk of the Au nor

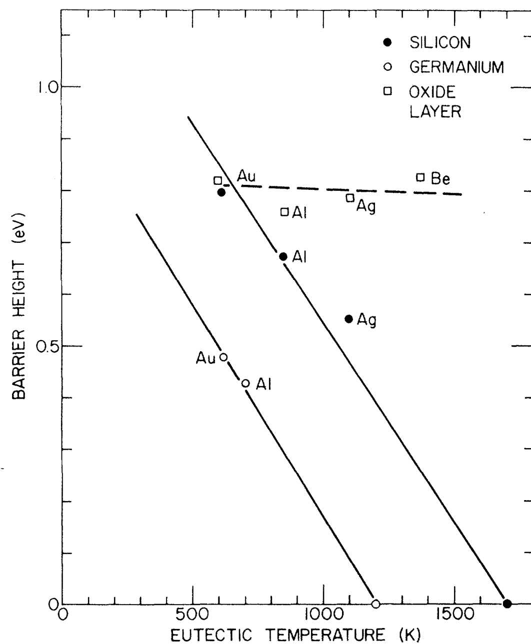

FIG. 1. A plot of Schottky-barrier height against eutectic temperature for metal-Si systems which possess a simple eutectic phase diagram. A similar plot for metal-Ge is also shown.

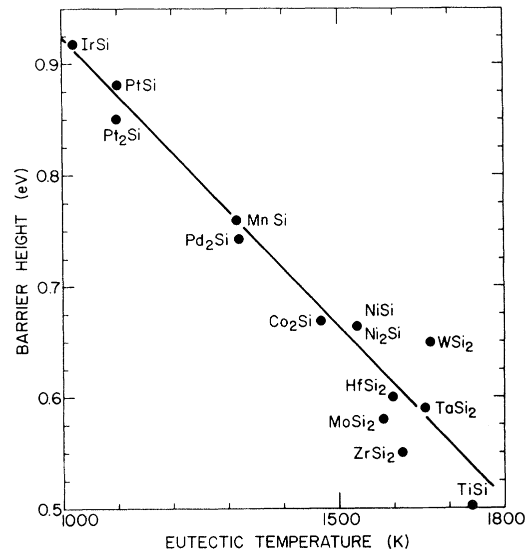

FIG. 2. A plot of Schottky-barrier height against eutectic temperature for transition-metal-silicide–Si systems. The eutectic temperature selected follows the rule described in the text.

Si when the temperature reaches the eutectic. Furthermore, a eutectic point is defined by both temperature and composition. In other words, an interfacial layer of the eutectic composition has to exist (though a kinetic process) before it melts. On the other hand, the reaction at an Au-Si interface below its eutectic temperature has also been demonstrated[15] by the observation that a 90-nm Au film deposited on Si wafers can induce Si oxide formation on top of the Au surface at temperatures ranging from 25 to 200 °C. Again, the release of Si atoms from its lattice may require Au interstitials.

In Fig. 1, we have plotted the Schottky-barrier height versus the eutectic temperature of Si-metal (Ag, Al, Au, and Be)[1] systems which are known to possess a simple eutectic phase diagram.[16] We have also plotted in Fig. 1 a datum at the melting point of Si with zero barrier height to represent an intrinsic Si-Si interface. A trend of increasing barrier height with decreasing eutectic temperature is seen and shown by the solid line. We note that there is a large scattering of the measured values of barrier height of these metals on Si.[1] We have selected those measurements in which both p- and n-type Si were used and the sum of their barrier heights equals the Si band gap. Even so, the data still show a small scattering and do not fall right on the curve. We suspect that this is due to the effect of annealing on the reactive interface, and hence it should be of interest to find out their dependence on annealing conditions. We also show in Fig. 1 those measurements which indicate that the barrier height is independent of the metals. This may be due to the oxide effect. If our prediction is correct, the height for Be on n-type Si would be about 0.3 eV. A similar solid curve for Ge is also shown in Fig. 1 based on the available data.

In extending the correlation between Schottky-barrier height and eutectic temperature to silicides, we need a rule for selecting the eutectic temperature since there are multiple choices. For those silicides whose growth is dominated by metallic atom diffusion,[2] the interfacial layer will be enriched with metallic atoms, and hence we shall use the closest eutectic on the metal side. For those silicides dominated by Si diffusion,[2] the interfacial layer will be enriched with Si atoms, and hence we shall use the closest eutectic on the Si side. Following this rule, we obtain a plot of Schottky-barrier height versus eutectic temperature of silicides as shown in Fig. 2. The trend of a high barrier height with a low eutectic temperature is again obtained. We note that both PtSi and IrSi no longer appear as exceptions but we should point out that the case of IrSi

is tentative since no eutectic but a eutectoid temperature is available and used. Another trend observed in the plot is that barrier heights of silicides of the same metal such as PtSi and Pt_2Si do not vary very much. The important meaning of this trend is unclear yet and requires further studies.

The most significant information revealed in the above figures is that there is a correlation between Schottky-barrier heights and eutectic temperatures. Although we cannot yet explain this correlation from the first principle, its physical meaning seems to be understandable starting from the Si-to-Si contact; as the interfacial layer becomes metallic, its melting point decreases while its barrier height increases. Finally, we speculate that the same interfacial layer dependence will also play a role on other covalent semiconductors such as GaAs.

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Nonradiative Recombination at Dislocations in III-V Compound Semiconductors

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A study of the nonradiative carrier recombination at individual interfacial dislocations between $Ga_{1-x}Al_xAs_{1-y}P_y$ epitaxial films provides new information on the dislocation core structure. New analytical techniques allow to correlate the nonradiative and recombination properties of dislocations with their fine crystallographic configuration. The edge sessile dislocation is found to be electrically neutral. The absence of carrier recombination leads to a reconstructed core model with no dangling bonds.

The carrier-recombination properties of dislocations in semiconductors and their effects on devices are now well-established facts. To account for such properties, Read[1] and later Hornstra[2] have proposed a dangling-bond model for the core of the clean dislocation. Recent studies of the dislocation electronic properties with use of EPR,[3] deep-level transient spectroscopy (DLTS),[4,5] and Hall-conductivity measurements[6] indicate that the density of electrically active sites along a clean dislocation core is indeed much smaller than the number of atomic sites along the core suggesting some reconstruction of the dislocation core.

Furthermore, the now well-documented dislocation dissociation in semiconductors[7-9] suggests that the electronic properties of dislocations may be intimately related to their fine crystallographic structure. This Letter reports on the recombination behavior of glide-induced "clean" dislocations in $Ga_{1-x}Al_xAs_{1-y}P_y$ heterostructures. It is found that carrier-recombination studies at individual dislocations provide useful information for understanding the core

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