

# Atom movements occurring at solid metal–semiconductor interfaces\*

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Solid metal–semiconductor interfaces often undergo chemical reaction at rather low temperatures, in some cases not much above room temperature. After some general discussion of these reactions, more detailed consideration is given to simple noncompound-forming systems, and, in particular, to the Si–Al, Ge–Al, and Si–Au systems. Diffusive transport of Si or Ge in these solid metallizations is very rapid, though the converse process, diffusion of metal in solid Si or Ge, is usually so slow as to be negligible. The interface reaction itself is less well understood but is becoming controllable in intrinsically favorable cases like Ge–Al and in other cases by more sophisticated means.

## I. INTRODUCTION

Solid metal–semiconductor interfaces are usually envisaged as quite abrupt transitions from the pure metal into intact semiconductor crystal. Indeed, this description is what is usually implied in the phrase, "Schottky diode." According to this idealized model, a profile across the interface would show no intermediate values of chemical composition or lattice spacing. Even so, the calculation of electronic properties of the interface, e.g., the Schottky barrier height, is a substantial undertaking, as one realizes from earlier papers presented at this conference.

In practice most metal–semiconductor interfaces produced in device fabrication differ significantly from the idealized model. Indeed the original transistor, though it consisted of metal contacts pressed against a Ge crystal, probably did not operate according to the idealized model, which usually permits very little carrier injection. Furthermore, a contact "forming" treatment, which carried the metal–Ge interfaces through a temperature cycle, improved the injection efficiency of this transistor substantially. This last result is consistent with recent experiments on solid-phase growth at such interfaces, as will be discussed. Although the early "forming" process just mentioned may not have been entirely a solid state process, those to be treated further in this paper are solid state processes only. The interfaces to be discussed are always kept at temperatures well below those at which any liquid forms.

A more contemporary example of non-ideal contact behavior is afforded by Au contacts, both on Si and on GaAs. These contacts often age at room temperature with electronic parameters like the barrier height drifting noticeably over time periods as short as weeks or even days. Such electronic changes in Au contacts have been known for many years, but direct evidence for atom movements at the Au–Si interface has been presented only more recently.<sup>1</sup>

Other metal contacts to Si often do not exhibit drift only because chemical changes at the interface have *already* occurred in the course of ordinary device fabrication. For example, recent Auger measurements<sup>2</sup> on Pd–Si interfaces indicated compound formation had already occurred at the interface prior to a one-minute heat treatment at 248°C. Similarly, chemical reaction at Hf–Si interfaces appears to be preventable only with substantial care<sup>3</sup> to prevent heating during metal deposition. A similar situation obtains for Al contacts applied to Ge, as will be discussed in Sec. IV.

Low temperature changes due to an interface need not be localized to the interface. For example, the crystallization of an evaporated, amorphous semiconductor film can be profoundly influenced by a metal contact. An early demonstration of this phenomenon by Gilles and van Cakenberghe<sup>4</sup> showed that the crystallization temperature of evaporated CdS films is appreciably lowered if the CdS film is contacted by certain metals. Subsequently, the same phenomenon was demonstrated for ZnS films.<sup>5</sup> The phenomenon occurs even more strikingly in Ge and especially in Si films. Figure 1 shows the approximate temperatures at which an evaporated Si film crystallizes when standing alone and when in contact with metal. In the latter case, the absolute temperature of crystallization is seen to be approximately one-half that of a contact-free Si film. The two sets<sup>6,7</sup> of experimental data represent rather different experimental conditions and yet the magnitude of the effect is quite substantial in both cases.

To begin to elucidate such phenomena, it is perhaps best to limit oneself, as we do here, to simple cases. We do so by allowing that, in addition to electron charge carriers moving at the interface, atoms also move at the interface, i.e., chemical reaction occurs there. Otherwise stated, the usual assumption that atoms move within solids only at very high temperatures is to be abandoned. As we shall see, there is ample evidence that

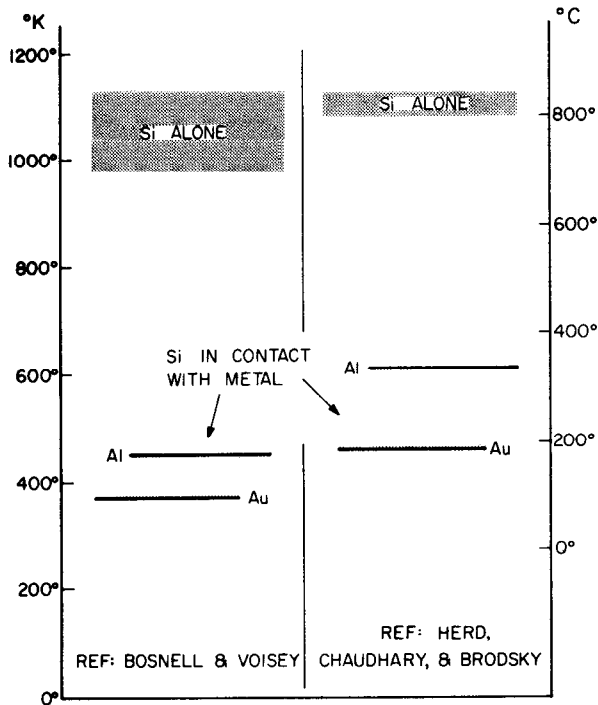


FIG. 1. The crystallization temperature of an evaporated Si film when standing alone and when in contact with an Al or a Au film, according to two different investigations as mentioned in the text.

atom movement within some solids of interest occurs at surprisingly low temperatures.

A primary consideration in chemical reactions at the interface is whether or not compounds form between metal and semiconductor. Figure 2 indicates the situation *at equilibrium* for metal-Si systems.<sup>8</sup> Silicides are formed by a majority of the metals, including all of the transition metals. Not forming silicides, however, are Be and a group of metals occupying a portion of the periodic chart near Si. Those materials which do not form compounds afford a solid solubility to Si varying from up to 100% in the case of Ge down to immeasurably small values, e.g., in Tl and Pb.

In addition to equilibrium considerations, kinetics of the reactions are important for both classes of metals. In a recent review on silicide formation, Mayer and Tu<sup>9</sup> state that "The typical silicide which is formed . . . is the phase which is most rich in Si. . . . It is surprising that more phases do not appear. . . ."; the latter statement is in view of the fact that 3, 4, or even 6 intermetallic phases are often present in the equilibrium diagrams while only one phase is usually detected at the contact between Si and a metal. Thus kinetic considerations serve to delimit substantially the possibilities indicated in the equilibrium diagrams for Si contacted by the compound-forming metals.

For the metals which do not form compounds, i.e., the eutectic systems, kinetic considerations are simpler and will be discussed shortly. First, we mention in passing the likely importance of kinetics at the borderline between the two classes of metals. The group I-B elements are divided, Cu belonging with the compound formers and Ag and Au with the eutectic systems. The

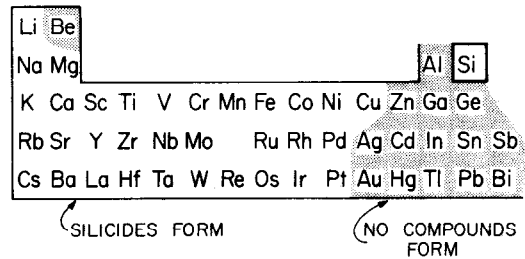


FIG. 2. Metals of the periodic chart and their reactions with Si. In the clear portion of the chart, metal-Si compounds form; in the shaded regions, no compound forms.

Au-Si system, though eutectic at equilibrium, is known to have several metastable phases that are rather persistent. For example, the Au-Si compound designated the  $\delta$ -phase is reported<sup>10</sup> to remain stable at room temperature for as long as one year, although the eutectic temperature in this system is only 370°C. On the other hand, the thermodynamically stable Cu-silicides exist only at relatively low temperatures compared to transition-metal silicides. Thus the I-B elements, taken as a group, tend to be intermediate between the two classes of metals, and the equilibrium distinctions in Fig. 2 between the two classes should be taken less seriously for this group.

## II. ATOM KINETICS NEAR INTERFACES IN METAL-SI (OR Ge) EUTECTIC SYSTEMS

Kinetics of the chemical reactions at and near the interfaces in these systems are, at least in principle, simpler than for the compound formers. Provided the system is kept close to equilibrium, only two phases are present. In principle, then, the only kinetics to be studied are the interfacial reaction and transport within the two phases. First, we consider atom transport.

The diffusivity of Si atoms in solid Al is shown in Fig. 3. A range of diffusivities is given,<sup>11</sup> the lower values for macroscopic Al specimens and the higher values for evaporated thin film Al. On the scale of Fig. 3, however,

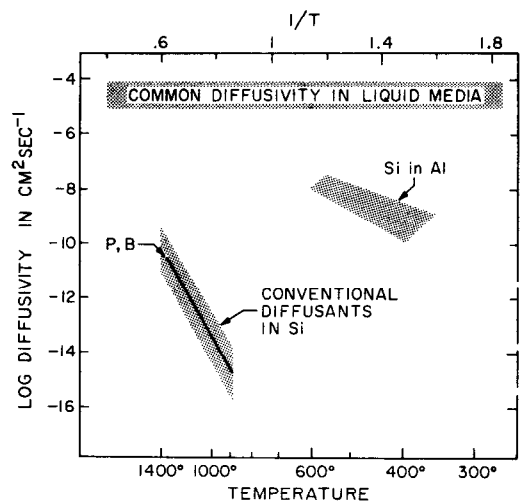


FIG. 3. The diffusivity of Si in solid Al, compared to the diffusivities of common dopants in solid Si and to the usual diffusivities in liquids.

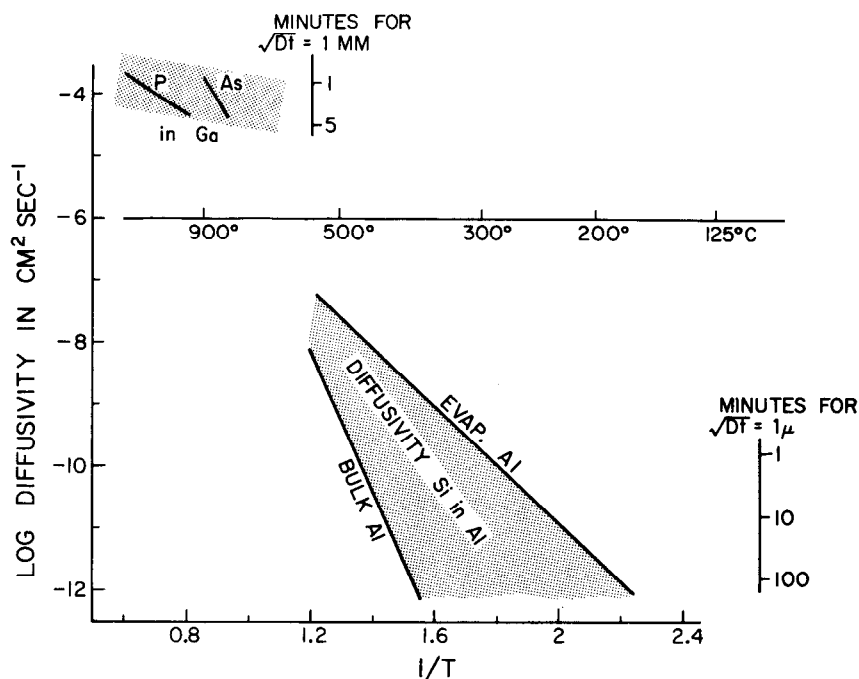


FIG. 4. Some diffusivities typical of liquid phase epitaxy vs diffusivity of Si in solid Al.

the distinction is minor. Also shown in Fig. 3 are the diffusivities in solid Si of the conventional dopants, including Al. Clearly diffusion rates differ enormously in the two solid media. Indeed at lower temperatures, e.g., 600°C or less, diffusion within solid Si is so slow that it can usually be neglected in comparison to diffusion within solid Al.

Also shown in Fig. 3 are diffusivity values common to liquid media, of the order of  $10^{-3}$  to  $10^{-4}$  cm<sup>2</sup>/sec. The comparisons given in the figure indicate that at lower temperatures Si diffusion in solid Al is closer akin to diffusion in a liquid medium than to conventional diffusion in a solid Si medium. Measurements in progress<sup>12</sup> on the diffusivity of Si in solid Au indicate a value even closer to that in liquid media than in the example just discussed.

The comparison to diffusion in liquid media is shown in more detail in Fig. 4. The diffusivities for P<sup>13</sup> and for As<sup>14</sup> in liquid Ga are representative of liquid phase epitaxy technology. The characteristic dimensions over which diffusion must occur in this technology vary from ~1 mm to 1 cm and lead to characteristic times of, at least, minutes as indicated in the figure. The corresponding dimensions for the solid phase epitaxy process are microns, leading to similar characteristic times for the two processes. Note that on the scale of Fig. 4 the enhanced diffusivity provided by evaporated Al films, as contrasted with bulk Al, is quite significant.

Overall, the import of Figs. 3 and 4 is that, at the temperatures to which metal–Si interfaces are usually heated, diffusion on the Si side of the interface can usually be ignored, but diffusion within the metal can be very rapid. Thus consideration of transport kinetics often amounts to dealing with this fast diffusion process in the metal.

The kinetics of the interfacial reaction in eutectic

systems have been less studied, at least in any quantitative way. Many qualitative observations have been made, for example, regarding approximate threshold temperatures for reaction, below which reaction evidently ceases completely. Such observations probably relate to the cleanliness of the interface, however, rather than to kinetics of the interface reaction proper. Another aspect of the interfacial reaction which has often been described qualitatively is its uniformity, or lack thereof, but here again these observations probably reflect mostly the cleanliness of the interface. Occasionally the interfaces take on a faceted geometry, both when the semiconductor is dissolving at the interface and when it is growing there, and these observations suggest that the interfacial reaction proper dominates more than do "dirt effects" in such cases.

Further discussion of chemical reactions at interfaces in eutectic systems may be more usefully accomplished by treating specific systems. The three systems chosen for discussion are among the better studied systems and illustrate the wide range of physical conditions encountered.

### III. THE Si–Al INTERFACE

This is probably the most familiar metal–semiconductor interface, being widely used in integrated-circuit fabrication. The chemical reactions that occur at the interface during fabrication are also rather well known. The simple as-evaporated metal–semiconductor structure evidently conforms to the idealized model noted in Sec. I, but upon heating, Si dissolves at the interface and goes into solution in the solid Al metallization. The dissolution usually occurs nonuniformly in the form of pits in the Si substrate which are quite obvious under the microscope, particularly the scanning electron mi-

roscope. At this point, the electrical character of the interface will not have changed from that of the idealized model. On cooling, however, the Si dissolved in the solid Al metallization comes out of solution and will deposit at suitable locations, particularly at interfaces. The deposited Si is crystalline and can be epitaxial with the original Si substrate. In any case the deposited Si is *p*-type, Al having been incorporated into the growing crystal. As such, it makes a *p-n* junction with an *n*-Si substrate, which can have great effect on the electrical properties of the contact.

The simple process just described puts the interfacial reaction, i.e., the dissolution-growth reaction, in series with a transport process, the diffusion of Si in an evaporated Al film. As was discussed in Sec. II, the transport process is very rapid and hence usually not rate-limiting over small dimensions such as the thickness of the Al metallization (typically about one micron). When Si must diffuse laterally, as occurs in the photolithographic patterned metallization of integrated circuits, the diffusion distances can be large, of the order of a hundred microns, and diffusion will then often be the rate-limiting process. Indeed, this latter situation has been put to advantage in measuring<sup>11</sup> the diffusivity of Si in Al metallizations.

The reaction at the interface has only been studied qualitatively, with particular attention being given to the nonuniformity so evident in most growth or dissolution at this interface. For example, Fig. 5 shows typical growth structures produced on a simple Si substrate (i.e., with no oxide pattern present). Rather than a uniform growth on the substrate, the growth occurs in discrete mesas suggestive of a nucleated process.

By using an oxide pattern with small diameter openings to expose the Si substrate only in selected areas, the mesa-like growth structures can be made to occur in desired locations. Figure 6 shows such a mesa-like structure which grew to fill the opening at the selected area in the oxide. The mesa in Fig. 6 was grown by a

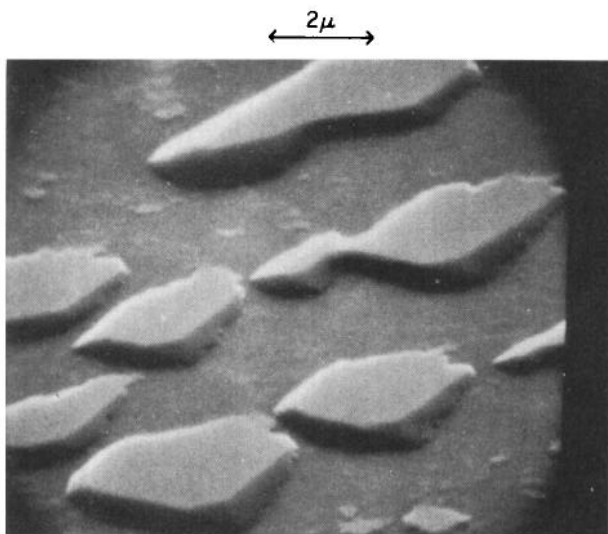


FIG. 5. Typical Si growth mesas produced on a Si substrate heated to ~500°C, as viewed by scanning electron microscopy. (View as if illuminated from above.)

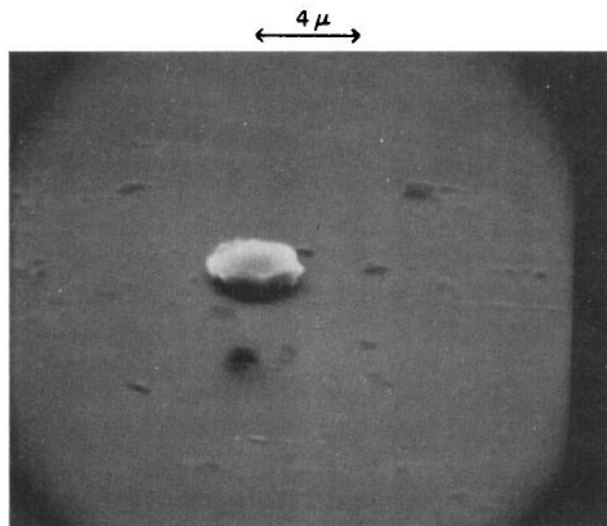


FIG. 6. Si growth which filled a cut in an oxide layer overlying Si substrate. Oxide was removed before photography, but was slightly less thick than the Si mesa growth.

variation of the simple heating-cooling cycle described earlier. The variation is depicted in Fig. 7, where the evaporated Al layer is overlaid by an evaporated Si layer. Thus the nutrient Si available to feed a growth process at the Si substrate need not have all originated from the substrate by a dissolution process. Instead, some or all of the nutrient Si is provided by the evaporated Si layer.

This alternative means of providing Si for the growth reaction at the substrate raises an interesting question as to the driving force causing growth to occur at the substrate in preference to other locations. In the example just cited the driving force is the extra free energy associated with an amorphous substance as compared to a crystalline substance. However, yet other driving forces can be used. For example, hydrostatic pressure has been employed<sup>15</sup> to control the growth-dissolution reaction, dissolution being facilitated in regions of high pressure because of the volume decrease associated with the dissolution process. In other regions of the same specimen, where the pressure is lower, growth occurs in preference to dissolution. This is a driving force unique to solid-phase growth processes since the fluid media

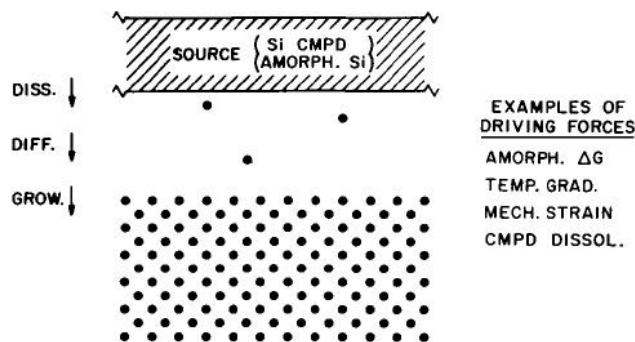


FIG. 7. Scheme for growing Si on a Si substrate. A source of Si to feed the growth process is provided as part of the evaporation schedule, which includes first a metal evaporation (e.g., Al) followed by a Si evaporation.

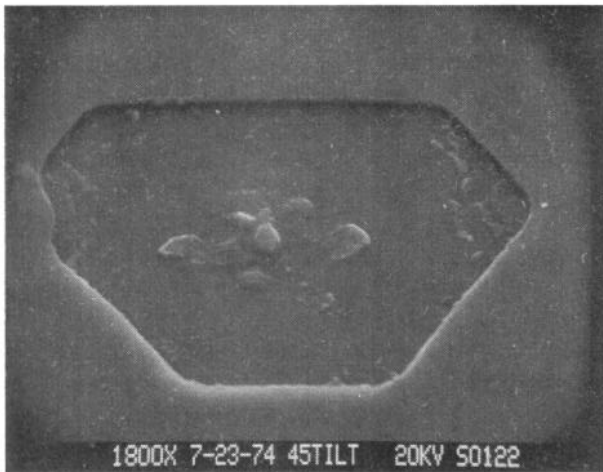


FIG. 8. Example of a fairly uniform dissolution of Si substrate, facilitated by  $\sim 100 \text{ \AA}$  of Ti evaporated on substrate just before Al evaporation. Substrate is in the (111) orientation. Cut in oxide was a square about one-half the area of above depression, which is  $\sim 50 \mu$  across at maximum diameter.

usually used in crystal growth cannot sustain a differential hydrostatic pressure as occurs with the solid medium.

In spite of the growing repertoire of driving forces and related techniques, a major problem remains in the understanding and control of the interface reaction. One possibility which is being actively pursued at the present time is the use of getters to clean up this interface. For example, Fig. 8 shows the uniformity attained in the dissolution process by interposing a thin Ti evaporated layer between the Si substrate and the Al evaporated layer. As contrasted with the pitting usual to the dissolution process, what occurs here is fairly well developed facets. Furthermore, the dissolution rate has been more rapid on the inclined (111) planes than on the horizontal (111) planes approximately parallel to the substrate surface.

#### IV. THE Ge–Al INTERFACE

Compared to the Si–Al interface just discussed, this interface is more conducive to uniform reaction. It is likely that such behavior results from the fact that Ge binds interface impurities more weakly than does Si, so that the Al metallization can more readily reduce such bonds in the Ge case.

As for the transport processes in this system, they appear not to differ much from the Si–Al case. The available data on Ge diffusivity in bulk Al indicates a value<sup>16</sup> within experimental uncertainties of that for Si in bulk Al; no data is available on enhancement of the Ge diffusivity when the Al is in the form of an evaporated metallization. The diffusivity<sup>17</sup> of Al in solid Ge is very much smaller than the diffusivity in the metal and can usually be neglected.

The interface reaction in Ge–Al has been studied by a wide variety of methods. Particularly sensitive are electronic measurements of the ability of the interface to inject minority carriers into an *n*-Ge substrate. When the ideal metal–semiconductor interface described in the

Introduction is forward biased, it does not inject, but rather extracts carriers, in this case electrons or majority carriers. This results from the pinning of the Fermi level well within the Ge bandgap at the interface due to surface states. Such ideal behavior in Ge–Al contacts is indeed observed<sup>18,19</sup> when particular care is taken that the substrate not be heated when Al is evaporated thereon. Upon heating and then cooling such a structure, however, it becomes a good injector of minority carriers, with injection efficiencies as high as 95% having been measured.<sup>18</sup> This behavior is characteristic of a *p*–*n* junction in which the *p*-region is much more heavily doped than the *n*-type substrate. The heating–cooling cycle causes a *p*-region to grow just as was discussed in the previous section for Si–Al.

Confirmation of this picture has been obtained by Mayer and colleagues<sup>19,20</sup> in several experiments. Hall specimens in the van der Pauw configuration have been prepared to measure carrier concentration and mobility in the grown *p*-regions, yielding parameters similar to those of bulk Ge saturated with Al. Further analysis<sup>19,20</sup> by backscattering of MeV He ions, by electron microscope, and by rather sophisticated particle detector devices confirm the above picture.

Implicit in most of these experiments is the ability to produce continuous, if not perfectly uniform, growths. This is in contrast to the isolated mesa-like growths encountered in Si–Al; the latter structures are not suitable for Hall-effect measurement (or indeed for carrier injection when in parallel with a Schottky barrier).

A further indication of the tractability of Ge–Al interfaces comes from measurements of the fraction of an evaporated, amorphous Ge layer, in a structure like that of Fig. 7, which can be caused to grow on a Ge substrate. In early work,<sup>21</sup> some 10% of the evaporated layer diffused through the intervening Al and grew upon the substrate. Recently the efficiency of this process has been increased<sup>22</sup> to the rather impressive figure of 81%!

#### V. THE Si–Au INTERFACE

Lest one conclude that reactions in the eutectic metal–semiconductor systems are very well understood, we consider this system. At first glance, it would appear an example *par excellence* for eutectic systems. The interface reaction itself evidently proceeds at temperatures at least as low as in the other metal–Si and metal–Ge systems. Furthermore, the transport of Si through a solid Au metallization is exceedingly rapid, at the very least as rapid<sup>12</sup> as Si through Al.

Yet there are very real difficulties in a simple view of this behavior. First, the solubility of Si in Au is evidently much less than the solubilities in analogous systems: Ge in Au, Ge in Al, and Si in Al. Recent attempts to measure the solid solubility of Si in Au only indicate an upper limit to the solubility of  $\sim 0.02 \text{ at.}\%$ .<sup>12</sup> There are, of course, other systems in which a guest atom is afforded rapid diffusivity, but very low solubility. Such is typical of the very small atoms, H and He, in many

substances where they enter interstitially. But interstitial behavior does not seem likely for Si in Au, since in the analogous systems, Ge-Au, Ge-Al, and Si-Al, the semiconductor enters the metal lattice substitutionally with approximately the same atom volume as the host metal atom has.

A second difficulty in understanding Si-Au interfaces is that the transport of Si through Au apparently does not occur homogeneously throughout the Au, but instead only in a network of preferred regions somewhat resembling grain boundaries. However, the density of the network appears to depend strongly on the orientation of the Si substrate, as well as the use of getters at the Si-Au interface. Thus simple grain boundary diffusion does not appear a sufficient explanation. Possibly the metastable compounds present in this system may play a role in this behavior.

## VI. SUMMARY

Several examples were given to point out the relatively great chemical reactivity that occurs at metal-semiconductor interfaces. Of the many combinations of metal and semiconductor that one could study, some of the very simplest, the Si and Ge eutectic systems, were considered in more detail. Two kinetic processes are important: (i) diffusion, which occurs almost entirely in the metal phase, is very rapid and rather well-characterized and (ii) the interfacial reaction itself, which is very sensitive to the presence of impurities. Specific systems were discussed to illustrate characteristics, Ge-Al because it is relatively easy to control, Si-Al because of its importance in industry, and Si-Au because it is an unusual system which is as yet poorly understood.

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