

# Solid-Phase Growth of Ge from Evaporated Al Layer\*

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Solid Al was used as a medium from which to grow Ge onto a substrate of crystalline Ge. Evidence for growth was obtained from MeV He<sup>+</sup> backscattering, which showed both Ge dissolution and growth can occur at the Ge/Al interface. Backscattering experiments also indicated transport from evaporated Ge through the Al medium to a crystalline Ge substrate. Diodes formed by temperature cycling a structure of *n*-type Ge/Al showed hole injection into the substrate during reverse-recovery-time measurements, confirming the expectation that Ge growth is present and is heavily *p* type from incorporation of the Al solvent during growth.

The substantial solubility and diffusivity of Si and Ge in some solid metals offer attractive possibilities for solid-phase growth of these semiconductors. In the present experiments, two methods were studied for obtaining such growths on a crystal substrate from overlying evaporated layers: (i) temperature cycling of a Ge crystal/evaporated Al structure, Ge/Al, and (ii) lengthy heating of a doubly evaporated structure, Ge/Al/Ge. These structures were analyzed by backscattering of MeV He<sup>+</sup> ions and by reverse-recovery-time measurements. The results indicate that Ge grows out of the solid Al metallization onto the crystal substrate and that the growth is a *p*-type layer.

Ge wafers, *n* type and of  $\sim 5\text{-}\Omega\text{ cm}$  resistivity, were obtained from the Eagle-Picher Co. The mirror-polish surface of this material was used for all experiments except reverse recovery time. For that experiment the additional surface preparation described in the preceding paper<sup>1</sup> was applied before Al evaporation.

For the temperature-cycling experiment, an Al layer  $\sim 6000\text{ \AA}$  thick was evaporated onto cleaned Ge dice about 1 cm square and 0.1 cm thick, which were cleaved from the wafers. The dice were heated in dry nitrogen at temperatures between 120 and 400 °C for times varying between 15 min and 2 h and then quenched to room temperature. The treated dice were analyzed by backscattering with 1.8-MeV He<sup>+</sup> ions. Particles scattering from the Ge substrate lose energy in their double passage through the overlying Al layer. This causes the spectrum arising from the Ge substrate to be shifted to lower energy, isolating the Ge-in-Al signal so that Ge concentrations of less than 0.1% can be detected.<sup>2</sup> The Ge-in-Al signal appears in Fig. 1 between  $\sim 1.2$  and 1.5 MeV. The resultant Ge concentration (e.g., 0.18% at 250 °C, 0.78% at 350 °C) agreed with the reported<sup>3</sup> equilibrium solid solubility of Ge in Al. This agreement indicates that the Ge measured in this experiment is in solid solution in the Al.

With Ge in solid solution, a question arises as to how responsive the solution equilibrium is to temperature change. To answer this question, a die originally treated at 350 °C was reheated at 250 °C for 1 h. As indicated by the filled circles in Fig. 1, the Ge concentration observed after this treatment coincided for the most part with the dashed line representing the average Ge concentration of a die which had *only* been treated at 250 °C. This indicates reversibility of the solution reaction for these temperatures and times.

The regrown Ge evidently resides primarily in the substrate. However, Fig. 1 does indicate a secondary location for the excess Ge, namely, a surface peak at  $\sim 1.45$  MeV which accounts for  $\sim 5\%$  of the Ge which came into supersaturation during cooling from 350 to 250 °C. Thus the surface as well as the substrate can act as a growth center for supersaturated Ge. Incidentally, some limitation to the reversibility of the solution reaction occurs at lower temperatures, since a die originally treated at 200 °C could not be induced to show a lower Ge concentration in the metallization by treatments of as much as  $2\frac{1}{2}$  h at 150 °C.

A reversible solution reaction similar to that described here has been observed<sup>4</sup> in the Si-Al system using a quite different analytical tool, the electron microprobe. In that system as in the present system, the solution reaction evidently can maintain equilibrium, given times of  $\sim 1$  h and metallization thicknesses of the order of 1  $\mu$ , at temperatures as much as  $\sim 200$  °C under the

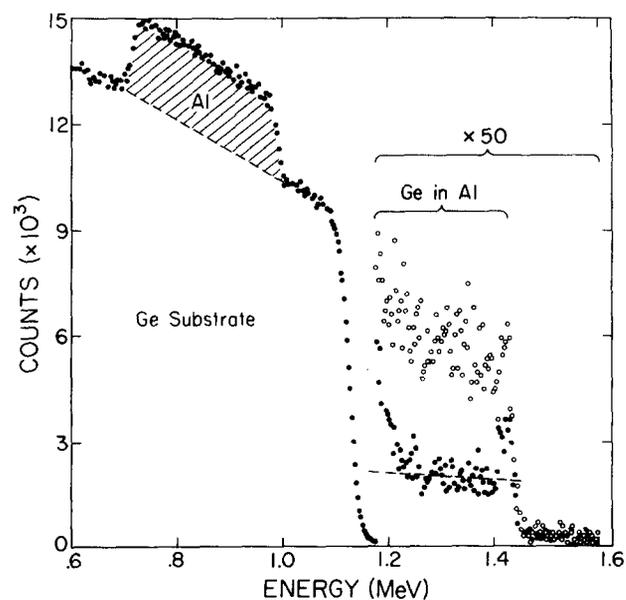


FIG. 1. Backscattering spectrum of 1.8-MeV He<sup>+</sup> on a specimen of Ge + 6400 Å of Al. The spectrum below 1.20 MeV is independent of heat treatment. Open circles: after 350 °C treatment for 15 min. Filled circles: after subsequent treatment at 250 °C for 1 h. For comparison purposes, the dashed line shows Ge concentration in a similar specimen which was *only* treated at 250 °C.

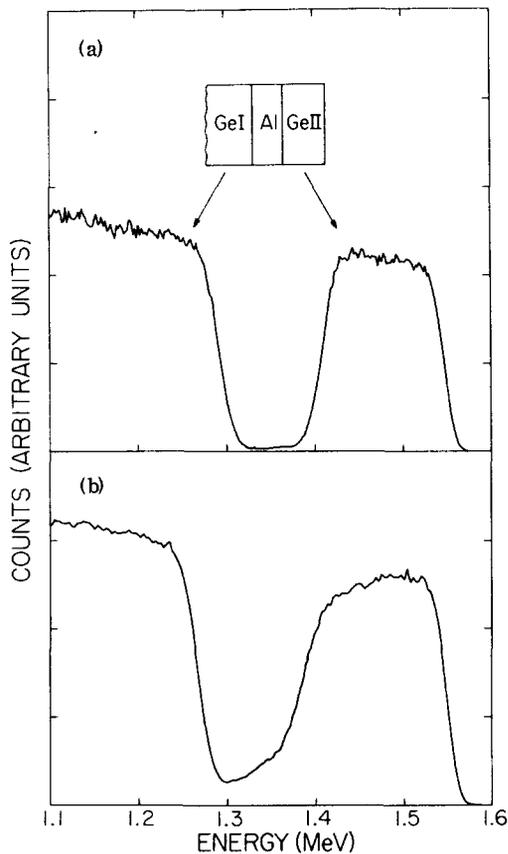


FIG. 2. Backscattering spectra of 2.0-MeV  $\text{He}^+$  on Ge/Al/Ge structure. Ge I is substrate crystal; Ge II is evaporated Ge; Al peak is at too low an energy to appear in the figure. (a) As evaporated (b), after  $12\frac{1}{2}$  h at  $128^\circ\text{C}$ .

eutectic temperature. In both systems, growth and dissolution occur primarily on the substrate crystal.

The Ge/Al/Ge sandwich structure was studied to learn whether energetic differences between crystalline and evaporated Ge would be sufficient to cause growth on the substrate. Al and Ge were evaporated sequentially to a thickness of  $\sim 2000 \text{ \AA}$  each, giving the backscattering spectrum shown in Fig. 2(a). The specimen was then heated for  $12\frac{1}{2}$  h at  $128^\circ\text{C}$  in dry argon, giving the modified spectrum of Fig. 2(b). The original sharp separation between spectrum segments arising from the crystalline Ge I and evaporated Ge II in Fig. 2(a) is due to the intervening layer of Al. After heat treatment this separation no longer occurs, instead a Ge concentration

$\geq 10\%$  is present in regions formerly occupied only by Al. In contrast to the solid solubility behavior observed in the Ge/Al structure, the addition of a Ge evaporated layer causes the Ge concentration to increase approximately two orders of magnitude over the equilibrium value<sup>3</sup> for the metallization layer.

Diodes were fabricated by heat treatment of Ge/Al structures. Al was evaporated through a mask to produce 0.3-cm-diam 2500- $\text{\AA}$ -thick metallizations on a Ge wafer. The wafer, with In smeared onto the reverse side, was placed on a quartz platform and immediately heated to  $300^\circ\text{C}$  in dry flowing nitrogen. After holding at temperature for 15 min, the wafer was cooled at  $\sim 2^\circ\text{C}/\text{min}$  to room temperature. The metallized areas were then each mesa etched. Reverse-recovery-time measurements, indicating a carrier lifetime of  $\sim 3$  to 5  $\mu\text{sec}$ , clearly showed hole injection into the bulk  $n$ -type Ge. This result along with the double-injection results<sup>1</sup> strongly suggests the presence of  $p^+$  Ge on the  $n$ -type substrate.

We conclude from these experiments that Ge can easily grow from a solid metal solvent onto a crystalline Ge substrate. Ge grown from the solid solvent Al evidently takes on the heavily  $p^+$  character that one expects from the reported<sup>3</sup>  $\sim 0.2\%$  or more solid solubility of Al in Ge at these temperatures. Such solid-phase growths should prove useful in semiconductor technology in view of the low temperatures required and the submicron-size-growth dimensions.

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