Rapid growth of Si by solid-phase epitaxy, including comparisons to conventional Si crystal growth*

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A recent development in solid-phase epitaxy is discussed, namely, that Si can be rapidly grown back into a dissolved pit in a (111) Si substrate to just exactly fill the pit, at which time growth ceases. This growth process is driven by the nearby dissolution of amorphous Si and, unlike most conventional growth processes, is *not* a near-equilibrium process. Also the solid-state growth is strongly affected by volume changes occurring during growth.

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Precipitation and growth of crystals out of solid solution is a phenomenon long studied in physical metallurgy. In the last few years such growths have been investigated at and near the semiconductor–metal interface, where it has been found possible to cause growth to occur epitaxially on a single-crystal Si substrate.[1] Processes producing such growths have been called "solid-phase epitaxy." A recent development in such studies is the fabrication of Si planar structures, in which a pit in a (111) substrate is refilled with Si growth so flush with the surrounding substrate as to be indistinguishable from it under ordinary conditions of observation. The degree of control in such solid-phase growth is similar to that obtained from fluid media.[2]

The ability to produce planar growth structures using either a solid or a fluid growth medium suggests at first glance that the physical processes involved in the two cases should be similar. However we feel, to the contrary, that the two processes differ in significant respects and take the present opportunity to point this out. After a brief description of the most recent experiments yielding planar Si structures, we make some comparisons between the two processes.

I. RAPID SOLID-PHASE GROWTH PROCESS

This process, which is described more fully elsewhere,[3] utilizes conventional lithographic structures in a (111) Si substrate. Briefly, a window is opened in thermally grown SiO_2 on the substrate, Al is evaporated, and the assembly heated. Dissolution of Si into the solid Al produces a faceted pit in the substrate as described in Ref. 4. Figure 1 shows an especially large pit formed in this manner and it will be discussed in detail later. Amorphous Si is evaporated over the specimen, which is then heated, causing the amorphous Si to dissolve into the solid Al, supersaturating it. At this point Si precipitates out of the solid Al in many locations, but particularly into the dissolution pit, filling it quite flush with the surrounding substrate. Interruption of the growth process before it succeeds in refilling the dissolution pit can be quite informative of the kinetics involved. For example, such interrupted growths show that lateral growth is almost always much faster than vertical growth in the pit. Another example

is that structures exhibit diffusion-limited growth; i.e., Si concentration gradients far from equilibrium.

II. VOLUME CHANGES DURING SOLID-STATE GROWTH

Crystal growth is accompanied by volume changes since the atomic volume of the Si in the crystal is different than Si in the surrounding medium. When the growth medium is fluid, this volume change is easily accommodated. With a solid growth medium, however, this is no longer so, and it is interesting to observe how growth is affected thereby. In an earlier study,[5] hydrostatic pressure was observed to govern whether or not Si growth would occur at a Si–Al interface. In the present report we point out how means to accommodate the volume change greatly facilitate growth in the dissolution pit.

First, we note that when the dissolution pit is formed, there is a volume *decrease* of matter in the vicinity. Figure 1 illustrates schematically a pit in which the volume change was rapid and extensive enough to cause a severe depression in the overlying Al film. A view looking down into such a cavity from above appears in Fig. 2. One cause for such a volume decrease is that each Si atom occupies approximately 28% less space when it goes into solid solution in the Al than it did when present in crystal Si.[6] A second factor is the Kirkendall effect, whereby the flux of Si diffusing outward in the Al metallization is greater than the indiffusing flux of Al to replace the lost Si. Now both these factors are expected to have the reverse effect when Si grows back into the pit. The precipitating Si atom regains its original atom volume when returning to crystal Si form; the Si atom diffusing through the metallization is still more mobile than the Al atom, producing a greater flux. Thus a positive volume change is expected when Si tries to grow back and refill the pit.

Second, we note that attempts to get Si to refill a dissolution pit without adding the evaporated, amorphous Si layer described previously are quite unsuccessful. For example, in a previous experiment[7] the coarsening of Si precipitates in a solid Al metallization was noted. During coarsening, the more energetically favored precipitates grow at the expense of those
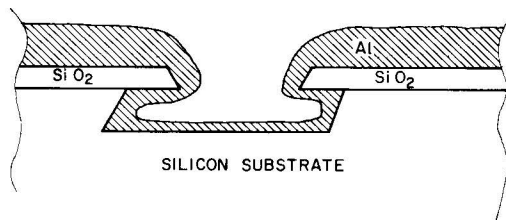
FIG. 1. Schematic of a dissolution pit formed on planar Si through an oxide window. The extent and rate of dissolution are such that a cavity forms in the Al film to accommodate the large associated volume change.

less favored, so that if a pit were energetically favored, preferential growth there would be expected. This does not occur to a significant extent.

However, under the experimental conditions described in Sec. I, i.e., with amorphous Si dissolving into the top Al surface, Si growth into the pit is rapid and indeed refills the pit with Si. Thus the pit becomes a highly favored site for growth. True, precipitates grow at various locations within the Al, but the pit is especially favored as a growth site, judging by the amount of growth that occurs there.

We suggest that the above observations indicate that the dissolving amorphous Si supersaturates the solid Al with vacancies as well as with dissolved Si. The evaporated layer of Si can be expected to generate vacancies[8] as it dissolves into the Al, due to the aforementioned 28% volume decrease. Thus the Al is bathed with the highly mobile vacancies as long as the amorphous Si is dissolving, facilitating Si growth in the relatively confined region of the pit.

In this view, the dissolution of evaporated Si into Al metallization assists the growth we have been describing in *two* ways. The free-energy changes associated with converting amorphous material into crystalline drive the reaction energetically, and secondly, dissolution of the evaporated Si generates a vacancy flux useful in accommodating volume changes.

III. NONEQUILIBRIUM CHARACTER OF THE PROCESS

The description of the solid state growth in the preceding section indicates the highly dynamic nature of the process. An irreversible dissolution of amorphous Si underway not far from the growth site provides a copious supply of Si and vacancies to accomplish the growth. It is worthwhile to contrast this situation with conventional crystal growth.

Chemical vapor deposition (CVD), for example, is usually a near-equilibrium process, with the chemical equilibrium constants playing a key role. Similarly, liquid phase epitaxy is performed fairly close to equilibrium with only a moderate
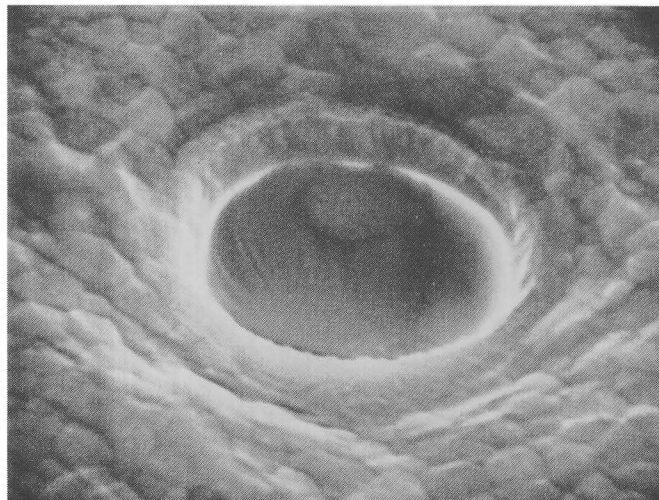

FIG. 2. SEM micrograph showing the Al-lined cavity formed by extensive dissolution through a circular oxide window, as seen from above. Diameter of oxide opening is ~5 μm.

supersaturation of nutrient materials in the liquid phase. A further example of near-equilibrium growth is the collection of solution-growth techniques described by Holden and Singer.[9]

Other processes, e.g., Czochralski growth, entail substantial irreversible processes. During Czochralski growth significant temperature gradients are maintained, with resultant large heat flows. However, these losses are not essential to the occurrence of crystal growth itself, but are used to control growth geometry, growth rate, etc.

The necessity for nearby irreversible reactions in obtaining rapid solid-phase growth in our experiments raises some interesting questions. How does the crystal perfection compare to that obtained during conventional growth? Can the experimental parameters be chosen so as to reduce the supersaturations produced and more nearly approach equilibrium conditions? These questions will need to be addressed in future investigations.

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[1]See, for example, V. Marrello, J. M. Caywood, J. W. Mayer and M-A. Nicolet, Phys. Status Solidi A 13, 531 (1972) or Ref. 7 below.
[2]See, for example, D. W. Shaw, J. Electrochem. Soc. 115, 777 (1968).
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[5]H. Sankur, J. O. McCaldin, and J. Devaney, Appl. Phys. Lett. 22, 64 (1973).
[6]H. J. Axon and W. Hume-Rothery, Proc. R. Soc. (London) Ser. A 193, 1 (1948).
[7]J. O. McCaldin and H. Sankur, Appl. Phys. Lett. 20, 171 (1972).
[8]A liquid layer dissolving into the Al, however, likely would accommodate the volume change without injecting vacancies into the solid Al.
[9]A. Holden and P. Singer, *Crystals and Crystal Growing* (Doubleday, Garden City, NY, 1960).