

Solid-state growth of Si to produce planar surfaces*

R. L. Boatright and J. O. McCaldin

California Institute of Technology, Pasadena, California 91125
(Received 15 December 1975)

Paralleling the sophisticated control of Si and GaAs growth from fluid media, we demonstrate control of Si growth using a *solid* growth medium. Faceted dissolution pits were first produced in a Si substrate using standard photolithographic techniques and Al metallization. Si was then evaporated onto the cold structure, depositing as amorphous material. Upon heating, the amorphous Si migrated through the solid Al and grew rapidly in the faceted pits, typically refilling them flush with the surrounding substrate. Evidence that the rapid growth occurs only while the amorphous Si is dissolving into the Al is presented.

PACS numbers: 68.50.+j, 66.30.Kv, 73.40.Ns

Semiconductor growth out of fluid media has evolved into a rather sophisticated technology. Large-area uniform growths are extensively employed. Also, by suitable choice of substrate geometry and orientation, growth can fill holes in, or protrude above, a substrate of Si¹ or GaAs.^{2,3}

We demonstrate here that similar control of growth occurring out of a solid medium is possible. Starting with the faceted dissolution pits in (111) Si described previously,⁴ we have used the reactions at Si/Al interfaces to grow Si back into the dissolution pits to just exactly fill the pits. Indeed these pits are commonly filled flush enough with the surrounding planar surface so that one can distinguish them only by resorting to the special technique of voltage contrast in the scanning electron microscope (SEM).

The solid phase growth reported evidently occurs rapidly. Evidence is presented that, unlike the near-equilibrium growth commonly occurring out of fluid media, the growth reported here occurs under the special conditions obtained while dissolution of amorphous Si occurs in close proximity to the growth site.

Experiments were performed with *n*-Si wafers of $\sim 4 \Omega \text{ cm}$ resistivity whose surfaces were within 1° of a (111) plane. Processing to produce faceted dissolution pits has been described previously.⁴ Briefly, windows of various sizes and shapes were opened photolithographically in thermally grown oxide $\sim 4000 \text{ \AA}$ thick. After standard cleaning procedures,⁵ 1μ of Al was evaporated, followed by heating of the wafer at $500\text{--}550^\circ\text{C}$ for 10 or 20 min, then cooling in vacuum. [These procedures yield the structure shown in Fig. 1(b) of Ref. 4.]

Further processing in the present experiments began with evaporation of $900\text{--}5000 \text{ \AA}$ of Si onto the wafer held at temperatures $\leq 70^\circ\text{C}$ to produce the structure shown schematically in Fig. 1(a). The wafer was then heated at $475\text{--}525^\circ\text{C}$ for 10 or 20 min, causing the evaporated Si to react with the underlying Al with the result shown schematically in Fig. 1(b). After cooling, the wafer was removed from the vacuum system. Note that all the above processing occurred without breaking vacuum.

The Al plus Si inclusions were removed chemically with aqueous 1% HF solution. Mechanical scrubbing with a cotton swab aided the removal of Si precipitates from the oxide surface; those specimens on which more than

2000 \AA of Si was evaporated required the use of jeweler's rouge to loosen the more tenacious residue. Standard photolithographic procedures were used to remove

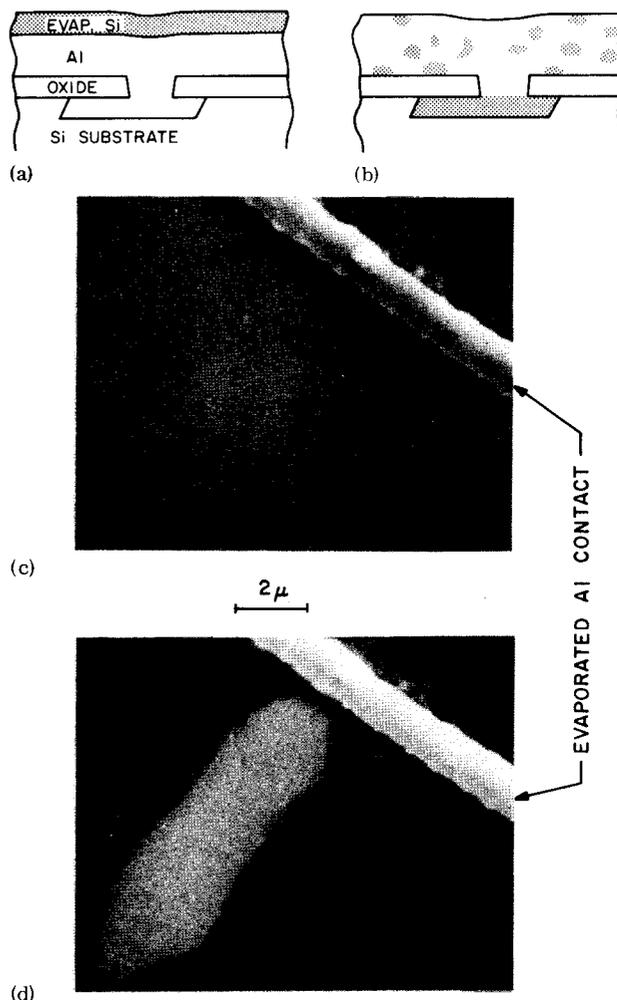


FIG. 1. Typical *p*-type growth region in an *n*-Si substrate, as displayed by voltage contrast in the SEM. Schematics illustrate the processing: (a) dissolution pit is established and amorphous Si layer has been laid down, (b) after heat treatment, evaporated Si has been redistributed, so as to fill the dissolution pit exactly. After removal of oxide and Al and Si inclusions, the specimen appears featureless in the SEM at (c), where a metal contact line has been added but is grounded to the *n*-Si substrate. When a negative bias of 6 V is applied to the metal line in (d), however, the *p*-Si growth becomes evident. *p*-Si has a relatively low electrical barrier against the metal contact and follows it into reverse bias against the *n*-Si substrate.

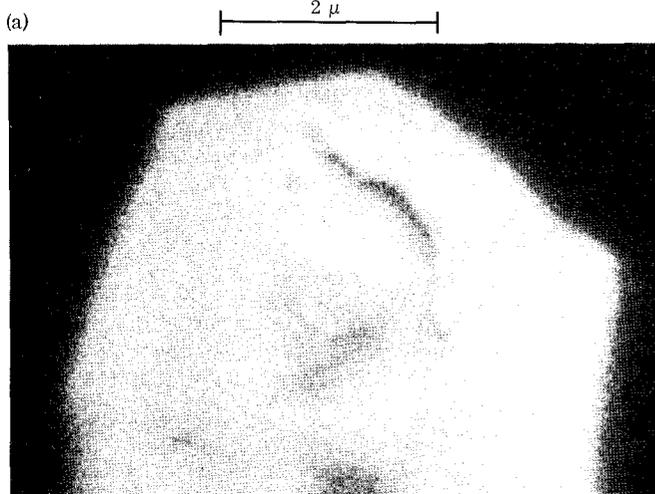


FIG. 2. *p*-type growth with surface irregularities. Same conditions as in Fig. 1, except Al contact not shown and higher magnification used here. (a) No bias; (b) -5 V bias. Note the fuzzier appearance of the *p-n* junction at higher magnification.

all oxide from the vicinity of the dissolution-growth sites and to provide Al lines for electrical contacts to the larger sites.

Figures 1(c) and 1(d) illustrate the growth morphology most commonly observed. The dissolution pit produced in the earlier stages of processing has been so smoothly filled in the later processing that ordinary SEM observations do not reveal the site of those events. However, the substrate is *n* type and the growth out of Al solution is *p* type; hence, the application of a reverse bias in the SEM distinguishes substrate from growth.

The depth of the *p*-Si growth was studied by chemically etching one end of a grown region and then examining in the SEM under reverse bias. Quantitative analysis was not possible but the depth and geometry appeared consistent with those observed in typical dissolution pits.

The Al incorporated into the *p*-Si growth was searched for by electron microprobe. No Al could be detected, which indicates that the Al concentration is less than $\sim 5 \times 10^{18} \text{ cm}^{-3}$.

Occasionally imperfect growths were encountered and these suggest some of the kinetic factors involved. Figure 2 shows the irregular growth surface commonly observed at both ends of long thin rectangular windows. This irregularity does not occur in that part of the specimen under an overhanging oxide,⁶ but only in the open area of the oxide window itself. Another anomaly observed was incomplete dissolution in the center of oxide windows more than 2μ wide, i. e., the floor of the pit was not planar and irregular islands of undissolved Si resulted.

The incomplete growth of Fig. 3 shows clearly the

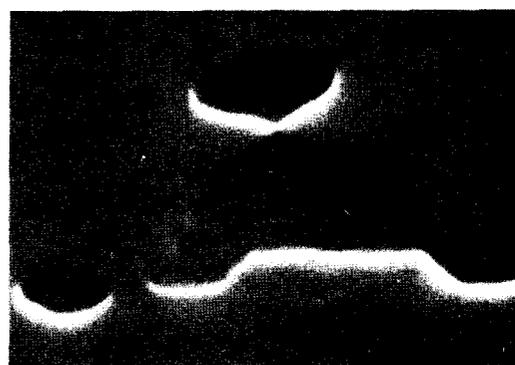
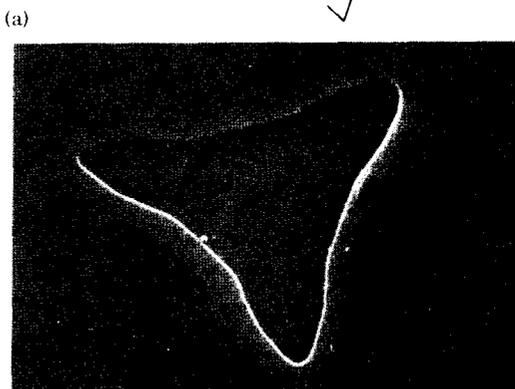
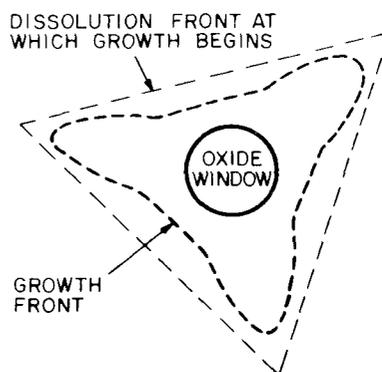


FIG. 3. Incomplete *p*-type growth, refilling only a portion of the dissolution pit. (a) Top view of a triangular dissolution front and the circular oxide window through which diffusing Si passes during both dissolution and growth. (b) An early stage of growth, showing that more rapid growth occurs at positions closest to the oxide window. (c) An extreme example, where the centrally located fast growths have cut off nutrient to the apices of the triangle, leaving pockets of Al at the apices.

surfaces on which growth is favored. As was observed in the dissolution reaction,⁴ the inclined {111} planes constituting the periphery of the structure dominate over the basal plane. This preference for lateral growth in filling pits is reminiscent of earlier reports.⁷

In other respects, however, the growth of Fig. 3 differs sharply from the dissolution reaction. In the latter, faceting and hence the interface dissolution itself were always observed to be dominant. In Fig. 3, however, transport of Si to the growth site tends to govern growth morphology. Figure 3(b) exhibits both influences: rapid growth at the more centrally located portions of the growth front, where the diffusion path for the nutrient Si is shorter, and some persisting tendencies toward faceting. In Fig. 3(c), however, the influence of short diffusion paths has become quite dominant. The additional requirement that self-diffusion remove Al from the growth site is particularly evident in Fig. 3(c).

We interpret Fig. 3 as indicating that Si growth occurs considerably more rapidly than the Si dissolution observed earlier. During dissolution the gradients in Si concentration within the dissolution pit must be small⁸ to permit faceting to dominate so completely; small concentration gradients imply a small Si flux, according to Fick's law. By contrast, Fig. 3 shows growth velocities varying inversely with distance from the oxide window, thus implying substantial Si concentration gradients within the pit. These large concentration gradients, and hence large fluxes of Si, originate from the dissolution of amorphous Si, which super-saturates the Al with Si.⁹

A further related point deserves some mention. This is the likelihood that enhanced vacancy concentrations are generated while the top layer of evaporated Si is dissolving into the Al metallization, in analogy to the well-known "emitter push" effect in bipolar transistor fabrication. There is a large volume decrease¹⁰ of each Si atom when it dissolves into solid Al, and this could easily generate excess individual vacancies. The vacancies would migrate to the substrate and be consumed by the volume increase of Si atoms coming out of solid

solution there, thus facilitating the Si growth reaction. When dissolution of amorphous Si was completed, the remaining excess vacancies would be annihilated at the free surface of Al or consumed in a last increment of rapid growth in the pit. The significance of this hypothesis is that rapid growth would be facilitated only *while* the amorphous Si is actually dissolving.

In summary, we have shown that solid-state growth of Si can fill in recesses in a Si substrate to produce a planar structure. Such growth evidently occurs quite rapidly and, we propose, is facilitated by phenomena associated with the nearby dissolution of an evaporated Si layer.

The authors wish to thank J. Devaney and K. Evans for SEM photography, T. C. McGill for valuable discussions, and D. Lawson of JPL for providing Si wafers.

*Work supported in part by the Office of Naval Research and by NASA through the Jet Propulsion Laboratory.

¹See, for example, Don M. Jackson, Jr., *Trans. Metall. Soc. AIME* **233**, 596 (1965); H. J. Kim, *J. Electrochem. Soc.* **119**, 1394 (1972).

²Don W. Shaw, *J. Electrochem. Soc.* **113**, 904 (1966).

³I. Samid, C. P. Lee, A. Gover, and A. Yariv, *Appl. Phys. Lett.* **27**, 405 (1975).

⁴John S. Best and J. O. McCaldin, *J. Appl. Phys.* **46**, 4071 (1975).

⁵Most cleaning procedures included a light 5% HF etch, but in some cases the H₂O₂-based solutions described by Werner Kern and David A. Puotinen [*RCA Rev.* **31**, 187 (1970)] were used in lieu of HF. Results were not affected by such substitutions.

⁶See Fig. 1 of Ref. 4 for sketch of the specimen geometry involved.

⁷See Fig. 8 of Ref. 2.

⁸In principle, the initial Si dissolution should occur with large gradients in Si concentration, but this regime was not observable. Only the later, slower dissolution process was observed in Ref. 4.

⁹G. Ottaviani, D. Sigurd, V. Marrello, J. W. Mayer, and J. O. McCaldin, *J. Appl. Phys.* **45**, 1730 (1974).

¹⁰When a Si atom leaves a crystal of Si and dissolves into solid Al, its volume decreases ~27%. The volume decrease when amorphous Si dissolves into Al is probably somewhat greater.