Solid-phase epitaxial growth of Si mesas from Al metallization*

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Si epitaxial growth from solution in solid Al onto crystal Si substrates was studied by scanning electron microscopy. Growth in reentrant corners of the substrate was found to be favored over growth onto a flat surface. For this reason, the smaller-diameter oxide cuts used in integrated-circuit fabrication, in which no portion of the exposed substrate Si is far from a reentrant corner, are favored sites for growth. Si growth readily fills in such oxide cuts forming mesa structures potentially useful in device construction. The probable cause for such preferential growth was indicated in pressure experiments which show that regions in the solid Al under relatively less compression are favored locations for growth.

Substantial evidence has recently been presented[1] to show that solid-phase growth of a semiconductor can readily occur at the semiconductor-metallization interface during commonly used heat treatments. Such growths in the Si-Al system are studied in the present work by scanning electron microscopy (SEM). A first experiment explores the variety of growth morphologies occurring in the system and indicates a preferred growth location. By utilizing the latter observation, a second experiment shows that small-diameter mesas are readily grown at desired locations. Finally, the role of mechanical stress in the growth medium is studied in a third experiment and found to be the probable cause for preferred growth.

The first experiment, exploring variety in growth morphologies, employed a prototype integrated-circuit structure[2] similar to that used in an earlier electron-microprobe study.[3] The structure provides large areas of bare substrate as well as oxide-cut boundaries where edge effects can be observed. Briefly, a Si crystal substrate, approximately in (111) orientation, was covered by thermally grown oxide, into which cuts ~50 μ wide were produced photolithographically in the pattern of a cross. The whole structure was then covered by an Al evaporation, typically 10–20 μ thick, containing sufficient Si to suppress dissolution of the substrate. The specimen was heated to 540 °C and held there 5 min, cooled at about 4 °C/min to 150 °C, then quenched to room temperature. The metallization was removed in 65 °C phosphoric acid, which left Si and SiO_2 intact for viewing.

Specimens were studied by SEM[4] and exhibited a diversity of growth structures including (i) vertical membranelike Si growths in the grain boundaries of the Al, (ii) low-profile structures resembling geological drumlins (elongated hills) with their long directions lying parallel within a given Al grain, and (iii) low-profile faceted structures. The most commonly observed growth structures, however, were those shown in Fig. 1. The mesas interspersed over the exposed substrate were occasionally as large as 25 μ in their longest dimension and were typically 1000–2000 Å high. Also, a favored site for mesa growth was the boundary of the oxide cut, as is particularly evident in the upper right-hand quadrant of Fig. 1.

A second experiment was designed to explore the favorable growth conditions at the boundaries of oxide cuts. Holes nominally 6 μ in diameter and rectangles 6×12 μ were cut in a thermal oxide about 2000 Å thick on a (111) Si substrate. The actual cuts varied in size; e.g., the holes ranged from 3 to 6 μ in diameter. Next followed the same sequence of Al-Si evaporation, heat treatment, and removal of metallization, as was just described. Observation by SEM indicated most of the smaller-diameter holes had been completely filled by Si growth. An example is shown in Fig. 2, where close observation suggests that growth proceeded somewhat beyond the height of the surrounding oxide and began to exhibit hexagonal faceting. Where such growth facets could be seen, they aligned with ⟨111⟩ directions of the substrate crystal, in agreement with the epitaxial orientation found in channeling studies for the Ge-Al system.[5]

The large-diameter holes and rectangles showed growth only at their peripheries. This result is analogous to the observation[6] that dissolution in integrated circuits

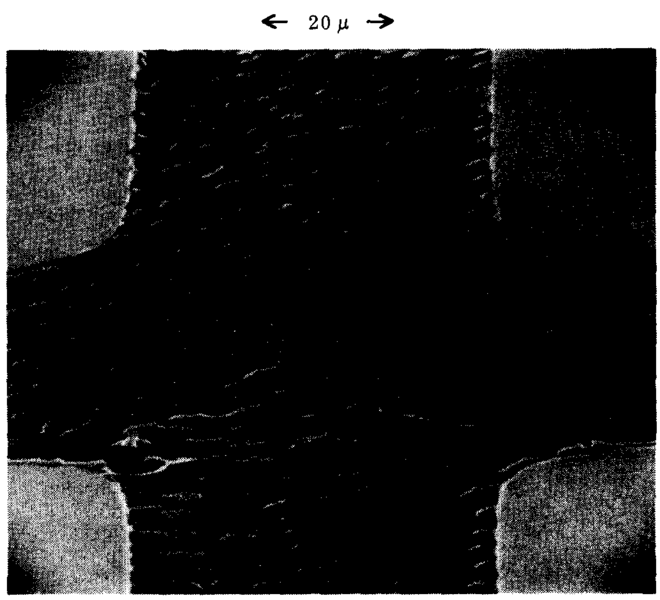

FIG. 1. Si mesas grown onto the exposed substrate Si (cross region) of the prototype integrated circuit, as exhibited by SEM after removal of the Al metallization. Tilt angle, 65°. The metallization had been provided with ~1.2% Si by coevaporation. Oxide from the photolithographic preparation is still present in the four corners.

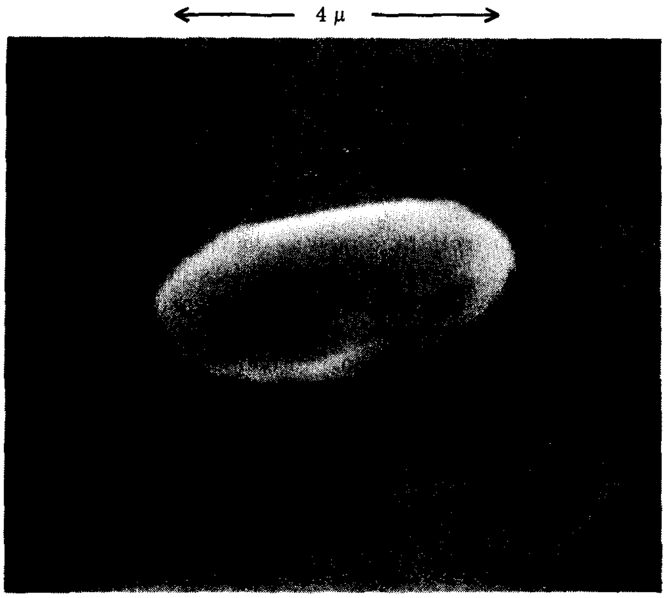

FIG. 2. Single Si mesa about 3000 Å high, grown in a circular oxide cut much smaller than the cross region of Fig. 1. The oxide was removed before the SEM picture was taken. Tilt angle, 65°.

metallized with pure Al occurs preferentially near the boundaries of oxide cuts. Such a preferred location for both dissolution and growth has a number of possible explanations; we decided to study the stress in the Al film, resulting from the relatively greater thermal expansivity of Al compared to Si. On heating, the Al film becomes compressed beyond its elastic limit; plastic flow partially relieves the compression, but less so in reentrant corners, pits, and other enclosed geometries. Similarly, on cooling, tension is less relieved in such geometries.

A third experiment was devised to explore the stress hypothesis in the simplest possible form: at constant temperature and with an externally applied force. As indicated in the schematic at the top of Fig. 3, a "waffle-iron" pressure plate, with the square regions raised, was fabricated from Si by common photolithographic procedures and thermally oxidized. The accompanying specimen consisted of a uniform Si substrate covered by a uniform ~3-μ-thick Al evaporation, without Si coevaporation. The pressure plate exerted a downward pressure averaging ~40 atm onto the specimen during a 13-h heat treatment at 540 °C. Pressure was removed and the specimen quenched in 3–4 sec. After removal of the metallization, study of the specimen under an optical microscope showed the waffle-iron pattern of the pressure plate had clearly transferred to the Si substrate. Further study by SEM, while showing a complicated topography, indicated clearly that the central portions of the square regions of the specimen were depressed. In two specimens with relatively simple topographies, the regions between squares were sharply delineated and showed a step height of 2000–5000 Å above the squares.

A clearer picture of the effect of pressure was afforded by voltage contrast in the SEM, a technique which distinguishes n and p regions. Using the Au bond shown in Fig. 3, a negative potential with respect to the bulk n-type Si was applied. Comparison of Figs. 3(b) and

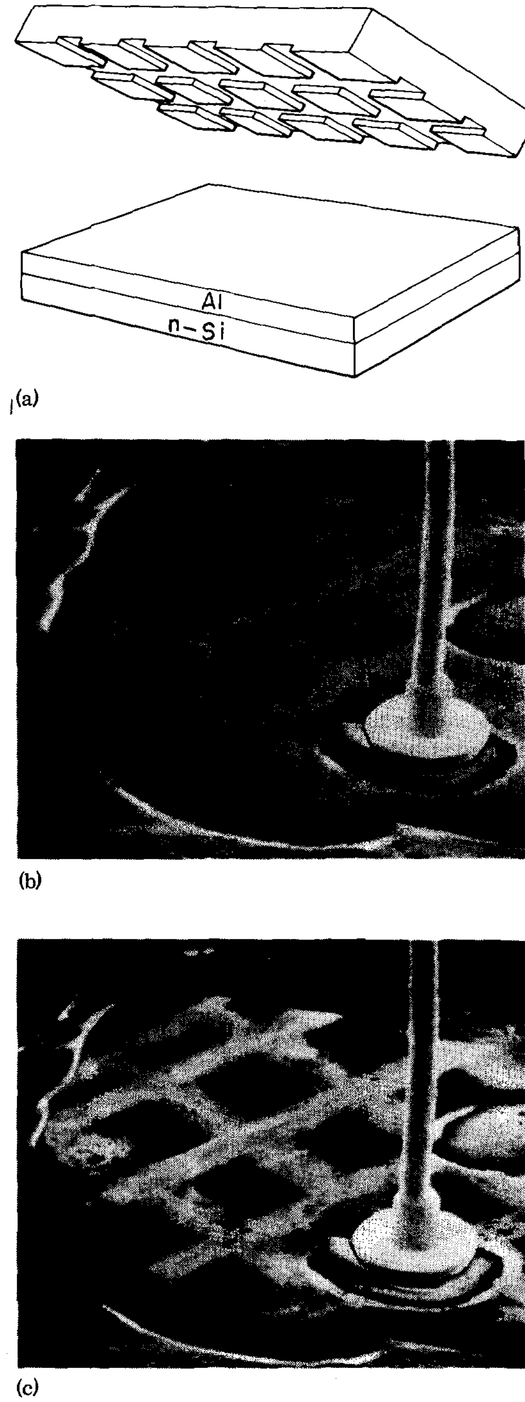

FIG. 3. Dissolution-growth patterns produced by nonuniform compression normal to the metallization. (a) Schematic of the "waffle-iron" compression plate and plain specimen (no oxide or photolithography). (b) and (c), appearance of the specimen in the SEM after combined pressure-temperature treatment: (b) no applied voltage, (c) −1.8 V on Au bond. Specimen was mesa etched to electrically isolate a relatively small area. Back contact to the bulk n-type Si was made with Ag paint. The Au bond shown, which was formed on a region of evaporated Al (dark in figure), electrically contacts the p region, but not the n region, as does a Schottky clamp in bipolar technology. Au wire is 25 μ in diameter.

3(c) shows that the central portions of the squares remained at the same potential as the bulk Si, but that the regions between squares brightened appreciably. The amount of brightening increased monotonically with applied reverse bias. Thus these regions are electrically interconnected[7] and are *p* type. One sees then that the central portions of the squares, where the Al was under the highest compression, remain *n* type, so the dissolution must have been dominant there. On the other hand, regions between the squares, where the Al was under the least compression, have become *p* type, so that growth must have been dominant there.

A qualitative interpretation of the pressure effects observed can be given in terms of the volume change associated with the growth-dissolution reaction

$$Si_{Al} \rightleftharpoons Si_{Si} \quad (1)$$

where Si_{Al} represents a Si atom dissolved in solid Al and Si_{Si} represents a Si atom in crystalline Si. The volume per Si atom for Si_{Al} and Si_{Si} was 14.4 and 20 $Å^3$, respectively. The volume of Si_{Al} (strictly speaking a partial molar volume) is derived from lattice-spacing measurements[8] and is some 28% reduced from that of Si_{Si}. In the present view, higher pressure favors the dissolution reaction, i.e., the more compact reaction product Si_{Al}. Such is the case of the square regions. Conversely, relatively lower compression favors the forward, or crystal growth, direction in (1), i.e., the more voluminous reaction product Si_{Si}. Such is the case of the regions between squares. If a pressure differential of 40 atm occurs between these two regions, the differential in pV energy would amount to 1.4×10^{-4} eV/Si atom between the two regions, a value of the approximate magnitude needed for the concentration gradients to effect the transport observed. A more quantitative analysis would require consideration of the nonhydrostatic stress field and a considerable refinement of experimental technique to ensure control of pressure on a microscopic scale.

In conclusion, our SEM studies of solid-phase epitaxy in the Si-Al system show that a variety of growth morphologies occur. A favored location for growth during cooling of a specimen is an "enclosed geometry", e.g., the reentrant corner at the boundary of an oxide cut, or the whole oxide cut itself when it is of sufficiently small diameter. These preferred locations for growth appear to be the result of a force not present in conventional crystal growth from fluid media—namely, the nonuniform stress field present in solids. A simple experiment using an externally applied, but nonuniform pressure demonstrates the role of mechanical stress in the growth-dissolution reaction. An incidental result of the study is the confirmation of the anticipated[9] *p*-type nature of Si growth out of a solid Al medium.

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[1]See, for example, J.O. McCaldin, Bull. Am. Phys. Soc. 17, 683 (1972), or Ref. 5.

[2]The present specimens differ significantly from customary integrated-circuit practice in that (a) much thicker metallization is used to produce growths high enough to be readily seen in the SEM and (b) coevaporation of Si is used to suppress substrate dissolution, so that growth structures will stand out on an otherwise flat surface.

[3]J.O. McCaldin and H. Sankur, Appl. Phys. Letters 19, 524 (1971).

[4]All SEM observations were made without the application of conductive overcoatings.

[5]V. Marrello, J.M. Caywood, J.W. Mayer, and M-A. Nicolet, Phys. Status Solidi (to be published).

[6]See, for example, A.Y.C. Yu and C.A. Mead, Solid-State Electron. 13, 97 (1970).

[7]In other specimens the regions between squares would brighten only over a limited but sharply defined *portion* of the mesa, which would indicate a discontinuity in the interconnection.

[8]H.J. Axon and W. Hume-Rothery, Proc. Roy. Soc. (London) A 193, 1 (1948).

[9]J.O. McCaldin and H. Sankur, Appl. Phys. Letters 20, 171 (1972).