Interfacial impurities and the reaction between Si and evaporated Al†

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As commonly formed, the interface between substrate Si and evaporated Al is laden with impurities; subsequent heating causes modest dissolution of Si into solid Al, the dissolution morphology being influenced by the interface impurities. In the present experiments, the amount of Si dissolving was considerably enhanced, causing sufficient interface movement to carry most interfaces clear of the original impurities. Under these conditions, the Si/Al interface assumes, during brief heat treatment, a simple shape composed of a few{111}facets. Such Si/Al interfaces produced *in situ* should be useful for low-temperature solid-state growth of Si.

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Chemical reaction at the interface between Si and evaporated metal is strongly influenced by impurities at the interface, present either intentionally or unavoidably. For example, Si dissolution into many solid metals is hindered by SiO_2 at the interface, or conversely is facilitated when Pd is present at the interface.[1,2] A further influence on the interfacial reaction is the crystallinity of both the Si substrate and the metallization. Thus Si growths occurring out of an Al metallization may relate to crystal orientations of the various Al grains or to the orientation of the Si substrate.[3]

The present investigation sought to avoid some of the above complexity with the goal of producing a clean and geometrically simple interface between Si and solid Al. Such an interface is desirable as the starting point in studies of Si growth out of solid metal solution, the "solid phase epitaxy" process. To obtain such an interface, we caused substantial Si dissolution to occur during heating, so that the Si/Al interface moved an appreciable distance from the contaminants unavoidably present at its original location. When the interface is thus freed of contaminants, it tends to adopt a sharply faceted character constituted of the {111} crystal faces of the substrate Si. In contrast, we find that the crystallinity of the solid Al plays no role in determining the interface shape for the short-duration heat treatments reported here.[4]

Experiments were performed on *n*-Si wafers, of approximately 1 Ω cm conductivity, whose surfaces were within 1 ° of a (111) plane. The wafers were covered by thermally grown SiO_2 approximately 4000 Å thick in which contact windows of various shapes and sizes were opened photolithographically. The windows were widely spaced to enhance the amount of Si dissolution in each. Such windows present Si for reaction with an overlying metallization not only at the basal (111) plane of the substrate, but also, after some dissolution has occurred on the basal plane, at the perimeter of the window. Initially, interest was focused on circular windows, since the perimeter in that case presents a large number of crystal planes for dissolution.

Immediately prior to evaporation, wafers were cleaned sequentially in organic solvents, followed by DI water, HF diluted 10 : 1, and a final DI water rinse. Al evaporation[5] onto the wafers was performed in an oil-free ion-pumped system at ~10^{-6} Torr, films typically being about 1 μ thick. Typically, specimens were heated at 550 °C for times of 5–25 min in dry nitrogen. Results similar to those to be described were obtained for heat-treatment temperatures as low as 450 °C, but the higher treatment temperature provided larger structures suitable for detailed study. After heating, specimens were immediately dropped onto an asbestos board at room temperature.

Optical observation of the specimens proceeded as sketched in Fig. 1. An etch of 1% HF in H_2O was used to remove most of the Al, but little of the SiO_2, as shown schematically in Fig. 1(c). An actual structure appears in Fig. 2. The Al remaining in recessed parts of this structure is evident because of the high reflectivity of Al. In these regions Si, which dissolves into solid Al and diffuses therein very rapidly,[6] has been displaced by Al; thus Al indicates the maximum lateral extent of Si dissolution.

Further observations of such dissolution structures were made in the scanning electron microscope (SEM) after removing all oxide and Al from the specimen. The typical dissolution structure shown in Fig. 3 is com-

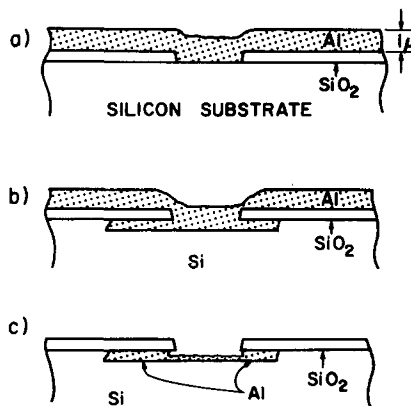

FIG. 1. Schematic of specimen preparation, shown approximately to scale. In (a) a (111) Si substrate with a patterned oxide has been metallized with Al. Heat treatment causes Si dissolution into the Al and replacement with Al as shown in (b). Finally, most of the Al is chemically removed for optical viewing, as shown in (c).

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posed of rather well-defined facets similar to those that can be observed in anisotropic chemical etching of Si at room temperature.[7] The facets constituting the short sides of the hexagon of Fig. 2 clearly represent an undercutting of the original Si surface, as is evident in Fig. 3. The facets constituting the longer sides of the hexagon have been examined by SEM at various viewing angles and appear approximately parallel to the undercut facets. Other specimens have been cleaved and cross-section views of the dissolution pits thereby obtained. The angles measured between the floor of the pit and the inclined sides are approximately those expected for (111) facets.

In the typical example just shown of an isolated circular contact window, a large number of crystal planes could, in principle, constitute the lateral boundaries of the pit. Only {111} planes do so, however. Thus dissolution must be occurring more rapidly on other crystal planes causing them to "grow out". Indeed, of the {111} facets, the undercut ones recede the more rapidly and eventually grow out, causing the hexagon of Fig. 2 to become an equilateral triangle. Also evident in Fig. 3 is that all the inclined {111} planes recede more rapidly than the basal (111) plane. In some specimens the pit diameter is twice that in Fig. 3 and the pit depth is only 1000 Å. For such a pit the inclined planes must on average recede $\approx 50\times$ faster than the basal plane. These variations in dissolution velocity are probably related to the termination of inclined {111} planes, but not the basal plane, at the Si-SiO_2 boundary, since that is the principal way in which these two groups of planes differ.

Other window geometries are possible in which the perimeter of the window is not parallel to any inclined {111} plane. This is true, for example, of a window composed of $[11\bar{2}]$ directions. For a particular $[11\bar{2}]$ segment of such a window, the Si dissolution front must lie over-all in the $[11\bar{2}]$ direction defined for it by window geometry. On a microscopic scale, however, we observe such fronts to break up into "hill and valley" structures[8] composed of {111} facets. The evolution of hill and valley structures appears complex and is a subject we are continuing to study.

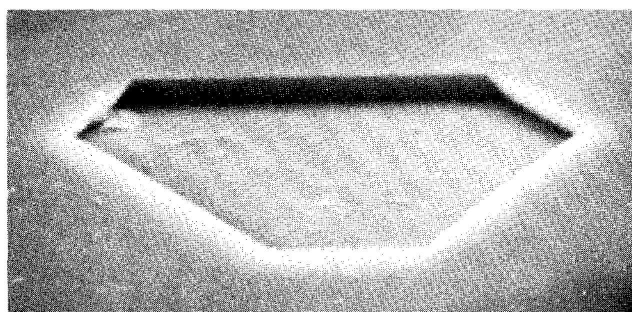

FIG. 3. Same structure as Fig. 2, but with all oxide and Al removed, as viewed in the SEM. Tilt: 65°. The dissolution pit has been rotated from its position in Fig. 2 so as to better exhibit inclinations of some of the facets. Maximum lateral extent of the structure is 9 μ.

Also being studied further are various experimental parameters influencing the relative dissolution velocities in the lateral and vertical directions. The results already obtained, however, indicate how a contaminant-free simple surface may be produced for use in solid-state growth of Si, in analogy to the etch-back step which precedes crystal growth from fluid media, e.g., in chemical vapor deposition or liquid-phase epitaxy.

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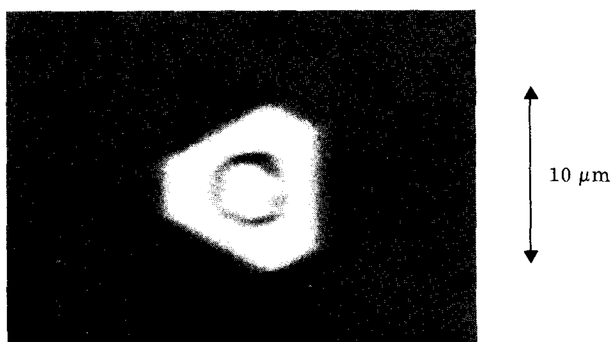

FIG. 2. Optical micrograph of structure sketched in Fig. 1(c) as seen from above. The brightly reflecting regions are areas where Al is still present. The circular region near the center of the structure is the original window in the oxide. The larger hexagonal region shows the maximum lateral extent of Si dissolution.

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[4]For longer heating times, a more complex situation develops in which Al grain structure plays a role.
[5]Al metallizations containing Cu concentration up to 4.5 wt% were also studied and gave generally similar results, in spite of the ternary eutectic in Cu-Al-Si at 524°C.
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[7]See, for example, Fig. 7 of R.M. Finne and D.L. Klein, J. Electrochem. Soc. 114, 965 (1967).
[8]See, for example, B. Bennema in *Crystal Growth; an Introduction*, edited by P. Hartman (North-Holland, Amsterdam, 1973), Chap. 12.

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