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Epitaxial Growth of Silicon

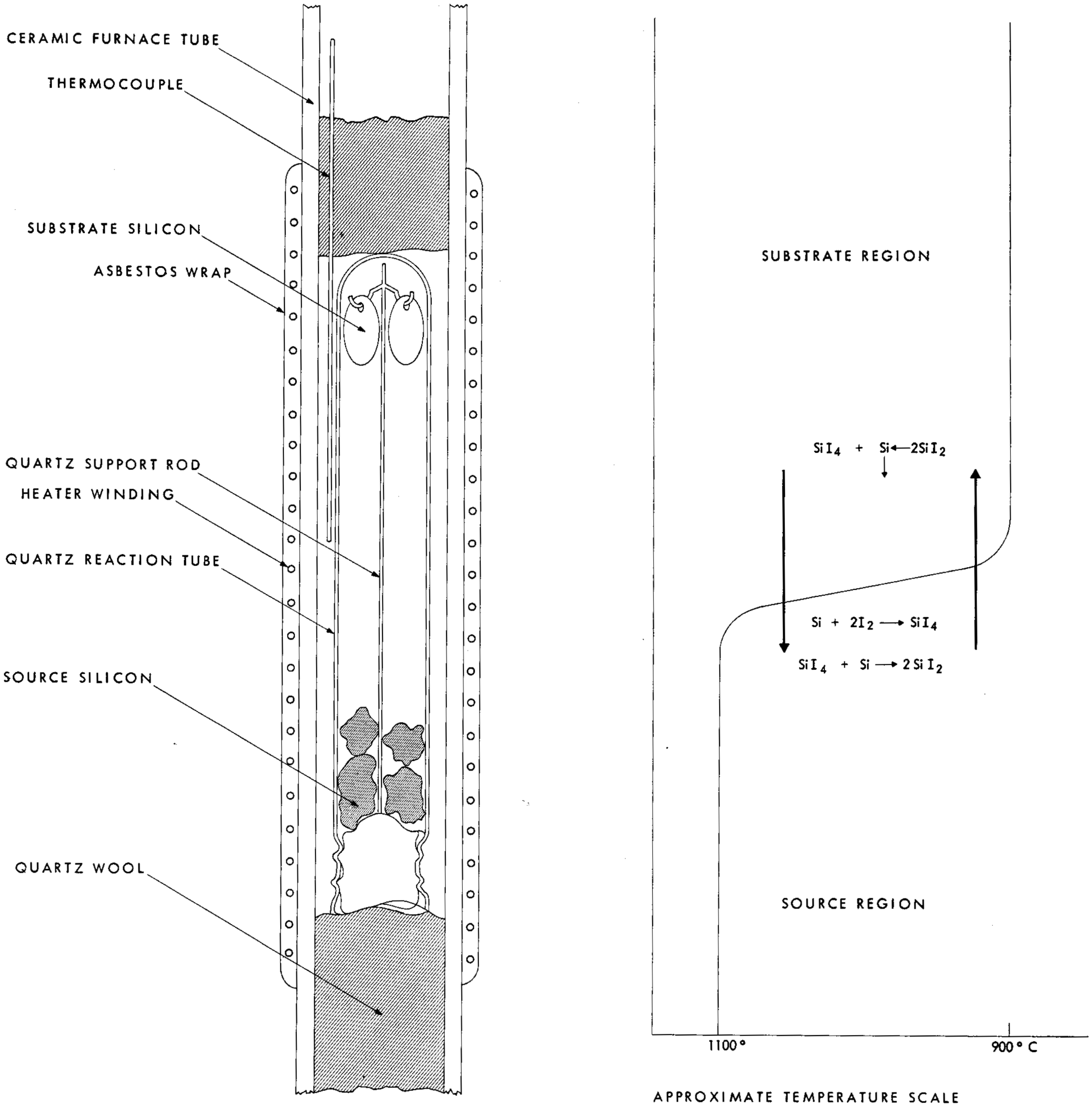


Figure 1 **Experimental reaction tube.**

The increasing interest of the electronics industry in silicon devices has prompted intensive studies on the properties of and techniques for preparing single crystals of silicon. This note describes one such study on the epitaxial growth of silicon layers on a silicon substrate from the vapor phase in which there is a chemical disproportionating reaction in the silicon iodide system.

This method permits epitaxial growth of silicon crystals at temperatures as low as 800°C and allows for the growth of extended thin layers that can be impurity-doped to form large-area electrical *p-n* junctions.[1]

Two distinct stages can be defined during crystal growth from the vapor phase. First, there is transport of the vapor from the source zone to the crystal surface and second, there is the nucleation and growth of a new layer on the substrate surface.

Transport

The disproportionation of SiI_2 has been used to transport silicon from a high-temperature source zone to a lower temperature substrate zone:

$$2\,SiI_2 \rightleftarrows SiI_4 + Si \qquad (1)$$

Experimentally, the reaction (1) is carried out in a sealed, evacuated quartz tube 2.5 cm in diameter and 18 cm long, placed in a two-zone furnace as shown in Fig. 1. The substrates, supported by small quartz hooks, are held at a fixed distance from the source silicon by a 3-mm diameter quartz rod resting on a seal-off plug and extending to the other end of the reaction tube.

From our measurements of thermochemical data on this system, we have calculated the equilibrium constant for the reaction (Fig. 2) and the results are in good agreement with the work of Schäfer and Morcher.[2] With decreasing temperature, the equilibrium of the reaction is shifted towards the formation of silicon. An extension of Schäfer and Morcher's work on the variation of SiI_2 concentration with total pressure in the reaction tube, into higher pressure regions, showed that suitable quantities of SiI_2 can be generated at source temperatures above 1000°C. The substrate temperatures can range to very low values for simple Si transport but to achieve uniform crystalline growth, the substrates should be slightly below the effective disproportionation temperature of the SiI_2. Since Eq. (1) is a reversible reaction, the quantity of iodine in the reaction tube must be sufficient to create a total pressure in excess of the critical disproportionation pressure, which in turn is temperature dependent. The Si transport from the source to substrate zone is controlled by diffusion and convection mechanisms, and consequently the reaction tube geometry and position will greatly influence the rate of transport and the macroscopic uniformity of the deposit. A large diameter reaction tube mounted in a vertical position minimized turbulence and gave a more uniform concentration of SiI_2 in the substrate region.

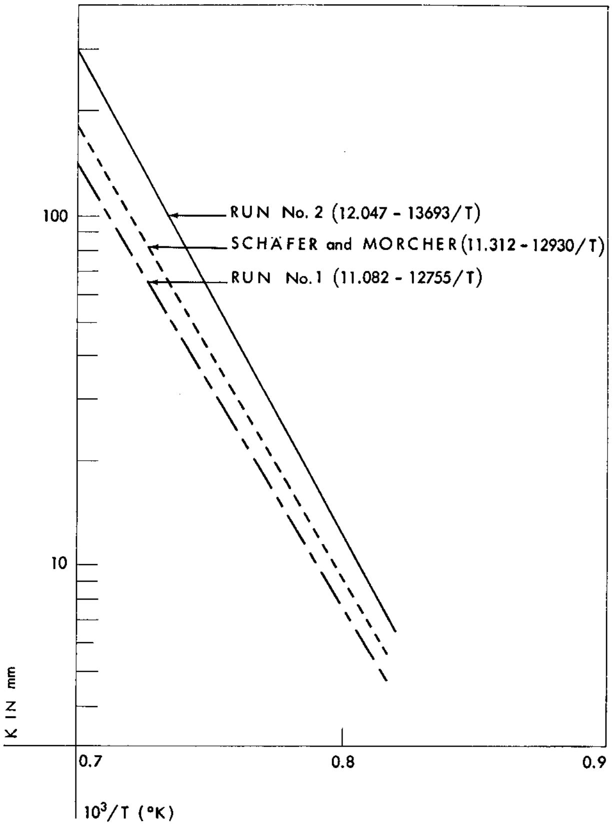


Figure 2 **Temperature variation of the equilibrium constant of the silicon-iodine reaction. (Numbers in parentheses show the range of variation of log *K*.)**

Nucleation and growth

Uniform nucleation and consequently good epitaxial growth is influenced by the substrate surface condition, crystallographic orientation, and by the deposit growth rate. Since the oxides of silicon are extremely stable and form readily in the presence of oxygen and water vapor at elevated temperatures, great difficulty was encountered in achieving a substrate surface free from oxide films. Condensed silicon oxides substantially impair uniform nucleation and may act as additional centers of crystallization which promote the formation of numerous fine silicon crystals. Moreover, oxides which crystallize simultaneously with silicon interfere with the growth of silicon crystals and impair their symmetry. Figure 3 shows a typical prismatic growth formed by silicon growing through pin holes in an oxide layer on a silicon substrate. This phenomenon occurs when the reaction tube is not sufficiently evacuated or when the substrate wafers are not adequately cleaned and dried. Chemical etches composed of nitric and hydrofluoric acid mixtures will usually leave an oxide layer about 10 angstroms thick.[3] We have found that silicon substrates chemically

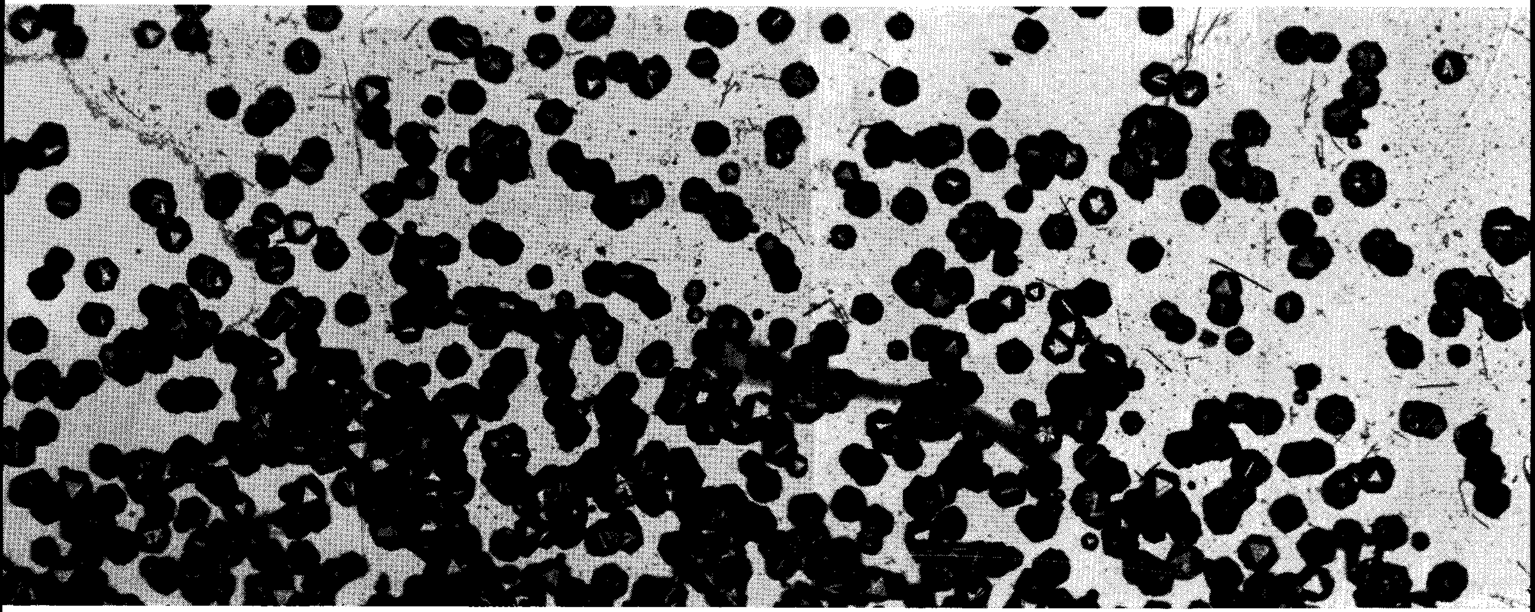


Figure 3 **Prismatic growth of silicon through pin holes in the substrate surface oxide. (80X)**

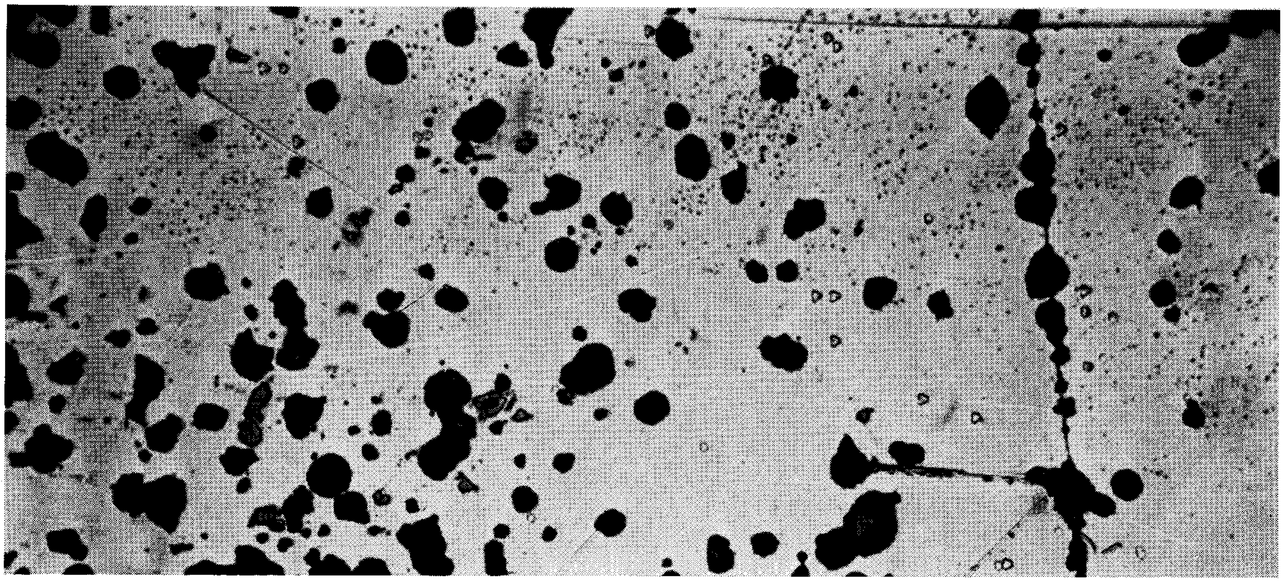


Figure 4a **Erosion of substrate during reverse deposition. (325X)**

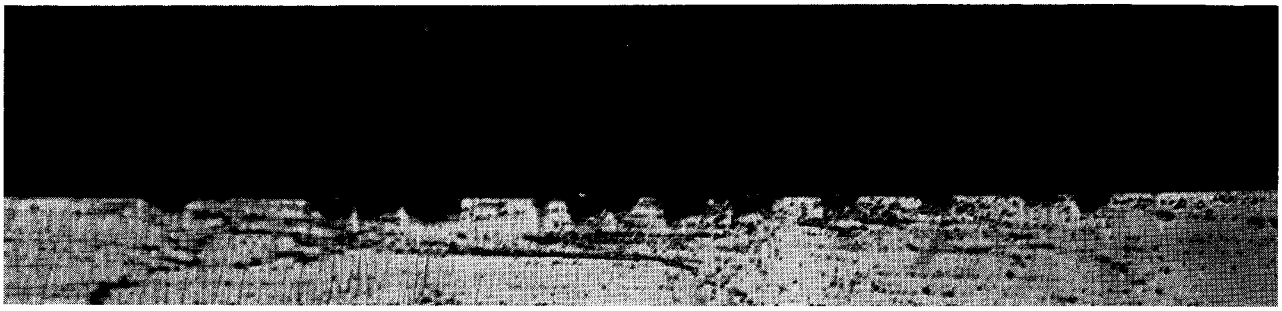


Figure 4b **Edge view of eroded pits. (325X)**

etched in a mixture of 5:1 nitric to hydrofluoric acid followed by ultrasonic cleaning in hydrofluoric acid and methyl alcohol would produce a sufficiently clean surface with a minimum impurity film. Since clean surfaces exhibit a high affinity for chemically active gases such as oxygen, the take-up rate is very high in the freshly cleaned condition but falls rapidly as the gas (or oxide) layer forms.[4]

Efforts to achieve a clean substrate surface by reverse deposition, i.e., by adjusting conditions for reaction (1) to transport silicon from the substrate to the source zone, produced an eroded surface as shown in Fig. 4a. Apparently, the silicon reacted at places where the oxide had pin holes and left the remaining oxide layer untouched. Figure 4b shows the depth of the erosions as viewed from a sectioned edge.

Forward deposition onto (111) oriented substrates, which had been initially treated by reverse deposition, filled the eroded holes in the substrates and then continued from these points. Figure 4c shows an edge view which has been lightly etched to show the interface between the growth and the substrate. Figure 4d is a photograph of the final surface growth and shows a characteristic (111) growth which eventually would grow laterally over the entire surface and include the oxide layer in the interface region.

Typical epitaxial growths, ranging in thickness from 25 to 800 microns, deposited on the (111) and (100) surfaces of silicon substrates are shown in Fig. 5. The (111) growths nucleate in many different forms. The epitaxial silicon growth starting at crazes in the oxide layer on the substrate and continuing to form a type of "lacework" is shown in Fig. 6. These vein-like regions tend to grow sidewise with time and eventually coalesce into the typical three-fold symmetrical pyramids that are characteristic of (111) growths.

This experiment was performed in a horizontal furnace with the substrates suspended vertically. In such a physical configuration, there exists a large vertical concentration gradient of SiI_2 in the substrate region, created by turbulence and convection currents. Since the growth rate is dependent on the SiI_2 concentration, the

Figure 4c **Edge view of deposited silicon growth from eroded pits. (325X)**

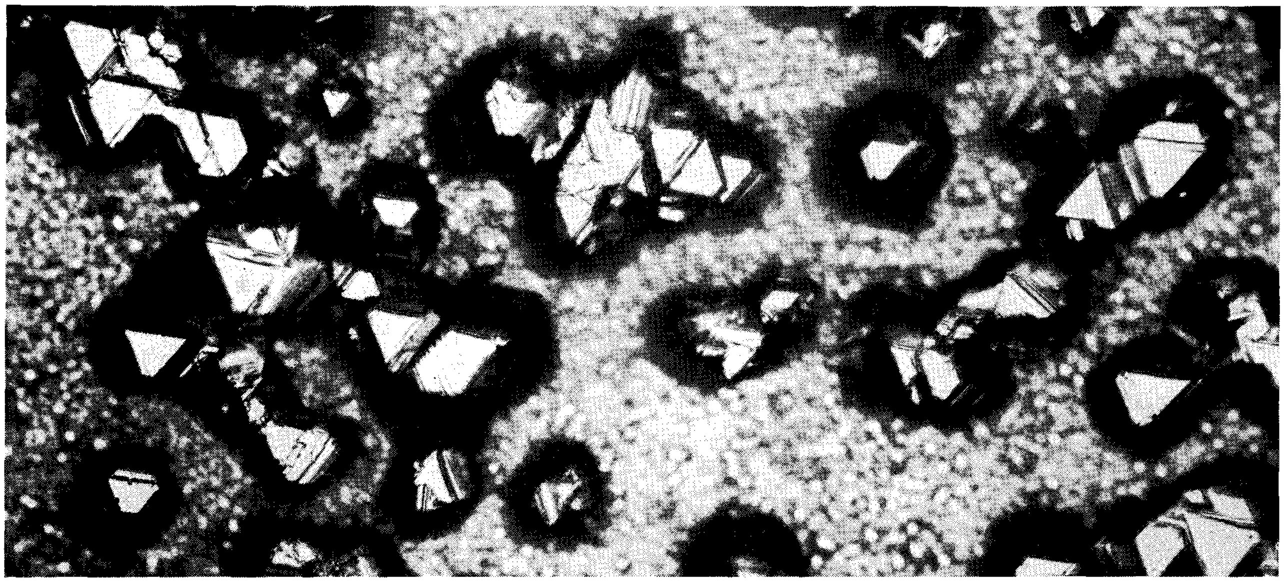


Figure 4d **Surface growth spreading laterally over oxide layer. (325X)**

upper portion of the sample grew more rapidly than the lower part.

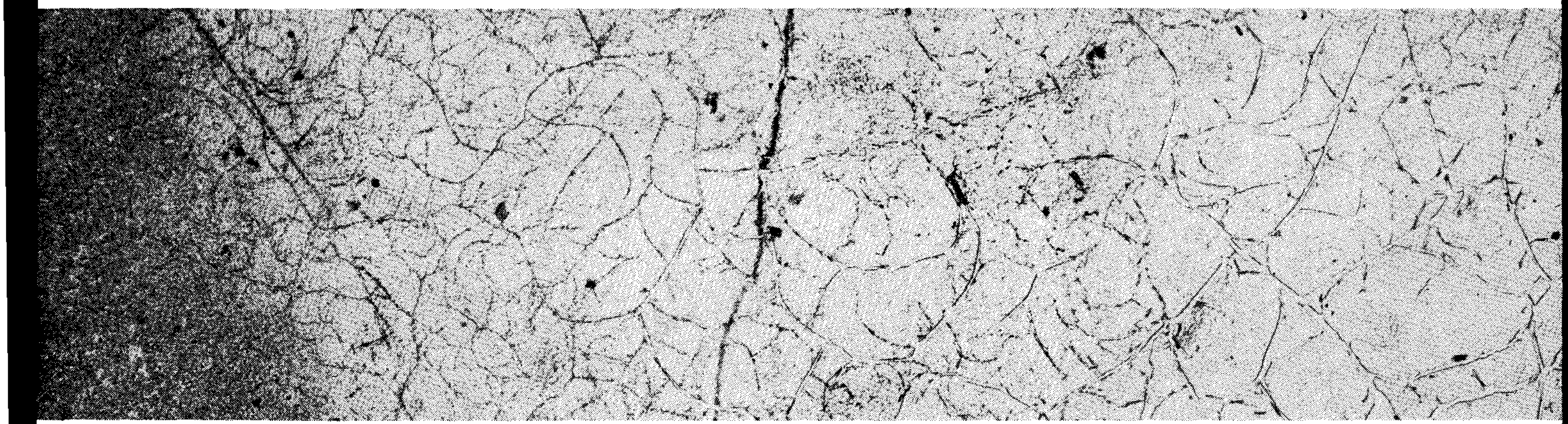
Both microsectioning and fracturing techniques were used to examine the interface between the substrate and deposit. This examination revealed that the interface contained entrapped impurities and voids and that the deposit bond to the substrate was poor except in those regions where growth was initiated.

A portion of such a deposit is illustrated in Fig. 7a. Fracture techniques were applied to this specimen.

In contrast to this poor quality bond, Fig. 7b shows an interface region of good adherence which was ob-

Figure 5a **Typical epitaxial growth on the (111) silicon substrate. (200X)**

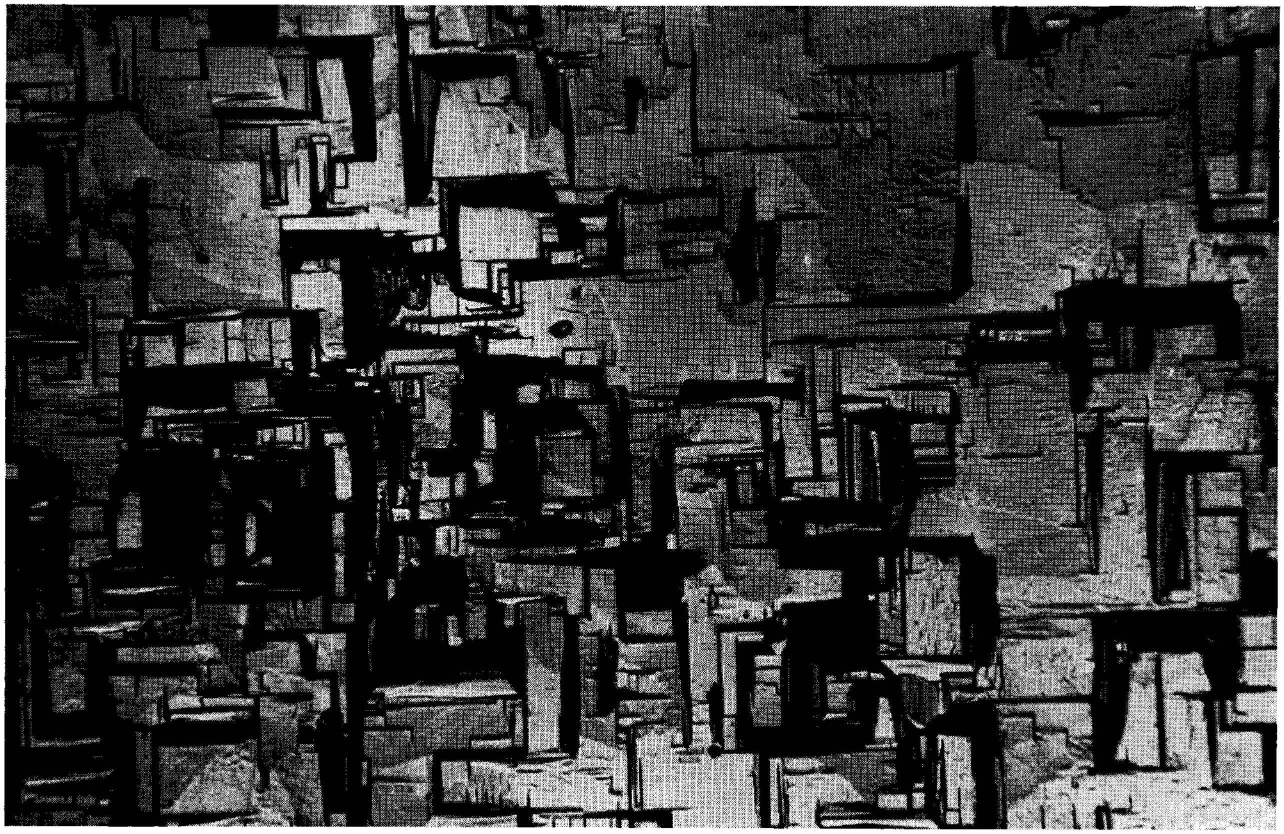
Figure 6 **Nucleation and crystal growth at crazes in the surface oxide. (30X)**



tained by carrying out the deposition process in a hydrogen ambient. For this run, a predetermined amount of hydrogen was introduced into the reaction tube along with the silicon and iodine reaction constituents before sealing off the tube.

The deposit surface roughness varied with crystallographic orientation and growth conditions. Deposits grown on (111) oriented wafers showed a decrease in surface roughness for slower growth rates. Moreover, variation in deposition thickness over the substrate area was a function of the position of the substrate in the reaction tube. Average growth rates, calculated from de-

Figure 5b **Typical epitaxial growth on the (100) silicon substrate. (200X)**



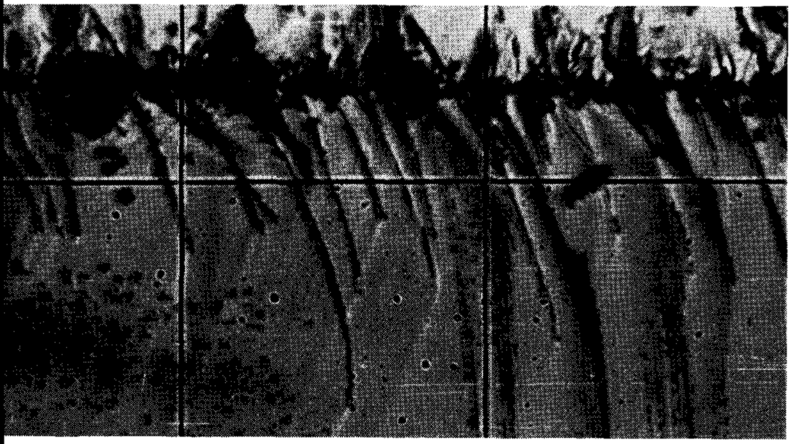


Figure 7a **Substrate and deposit interface containing entrapped impurities and voids. (880X)**

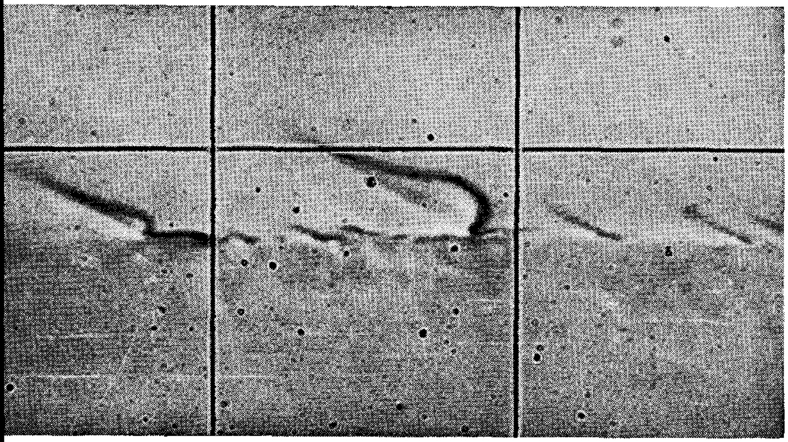


Figure 7b **Interface forming a good bond between substrate and silicon deposit. (880X)**

position time and thickness of deposit, ranged from a few microns per hour in some experiments to 15 microns per hour in other experiments entirely dependent on prevailing growth conditions.

Another mode of nucleation on the (111) surface with growth conditions similar to those described in Fig. 6 is shown in Fig. 8. Here the growth started in a very peculiar manner with the formation of small, highly elongated and oriented pyramids. The final deposit appeared a dull grey and the surface roughness was smaller than the deposits described previously. The growth rate was also much lower than those of the deposits reported above.

Chemical impurities left on the substrates will prohibit nucleations. Figure 9 shows growth that took place over the entire wafer except in rings where a chemical residue remained as a result of an improperly rinsed and dried substrate. Silicon substrates properly rinsed and dried after etching do not produce this ringlike cavity.

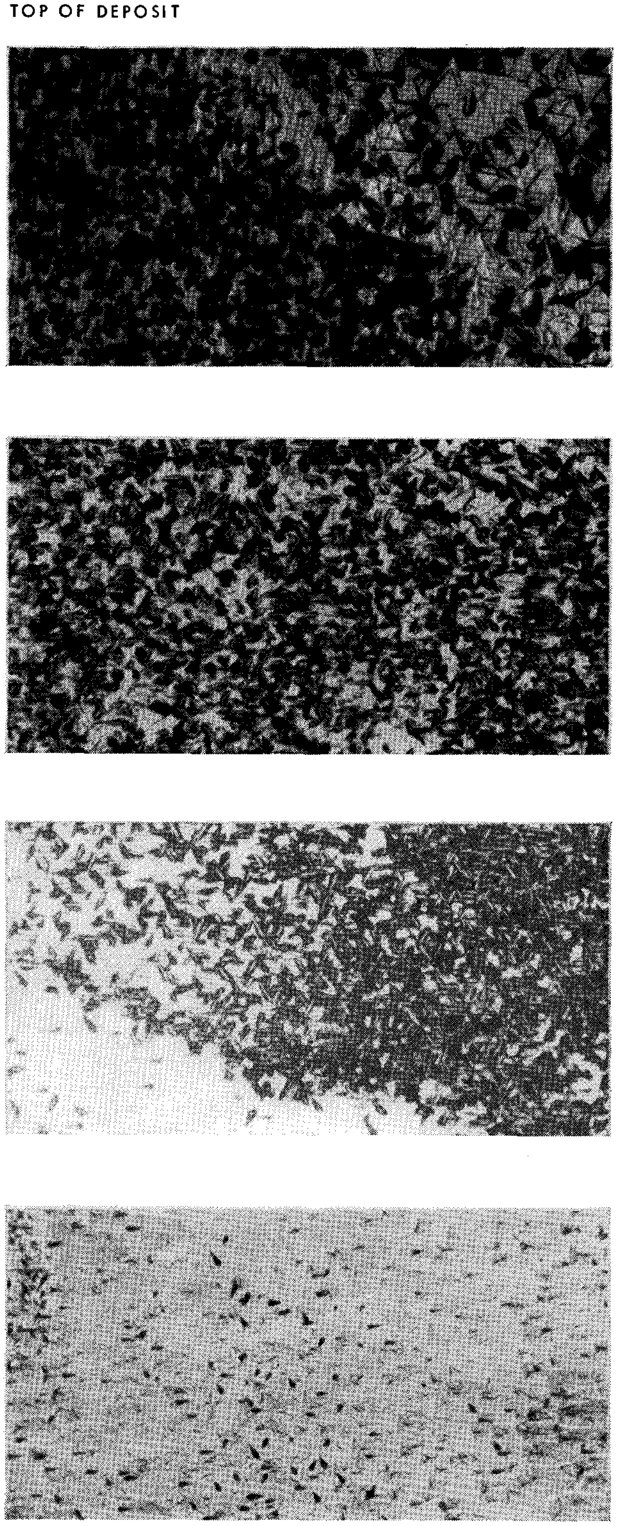


Figure 8 **Nucleation and crystal growth of the deposit on (111) substrates. The sequence of micrographs shows a progression of the crystal growth. (85X)**

Figure 9 **Chemical impurities on substrate surface impeding nucleation and subsequent crystal growth. (65X)**

An x-ray examination of the vapor-deposited specimens indicated that the deposits were essentially monocrystalline with the same orientation as the parent substrates. X-ray patterns of a typical sample showed only the expected 3-fold symmetry of the (111) oriented substrate. Evidence of polycrystallinity, such as Debye-Scherer rings and multiple superimposed single crystal patterns, was not observed. X-ray patterns of several different areas from the same sample were identical with respect to the single-crystal nature and orientation of the sample. This analysis does not preclude the possibility of crystal grains larger than the x-ray beam diameter or of nearly perfectly aligned mosaic structures, although none of these imperfections have been observed to date.

Further analysis of the deposits, using electron reflection diffraction, showed Kikuchi lines which are indicative of the single-crystalline nature of the silicon deposit. Furthermore, when the sample was moved beneath the electron beam for a distance of about 5 mm, no shift of the Kikuchi pattern was observed.

Conclusions

The thickness and structure of the deposited silicon films depends on the duration of the crystallization process, temperature, concentration of silicon vapors and the content of impurities in the system. A detailed study of these growth variables has not been made. However, an empirical approach in setting the operating conditions used in this study, has led to establishing the feasibility of epitaxially growing silicon layers on silicon substrates by the disproportionation of silicon di-iodide.

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