

# Solid-phase crystallization of Si films in contact with Al layers\*

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Low-temperature (400–540°C) crystallization of amorphous and polycrystalline Si films deposited on SiO<sub>2</sub> and covered with an evaporated Al layer has been studied using SEM, TEM, electron diffraction, electron channeling, and MeV <sup>4</sup>He<sup>+</sup> backscattering. Silicon deposited by evaporation and chemical vapor deposition (CVD) at 640°C (both amorphous) was found to crystallize into islands of polycrystalline aggregates. Silicon deposited by CVD at 900°C (polycrystalline with ~2000-Å grains) produced relatively large (~10 μm) single-crystal islands. In both cases island size increased with annealing time, and the rate of crystallization increased with temperature. Crystallization rates were observed to be the same for both sources of amorphous Si, while 900°C CVD Si was noticeably slower, consistent with the postulate that the driving force for the reaction is the free-energy difference between initial and final states. The crystallization rate for 900°C CVD Si decreased when the Al layer thickness was reduced to a value less than the initial Si grain size. The inclusion of a native oxide layer between the deposited Si and Al layers greatly retarded the crystallization process.

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## I. INTRODUCTION

Crystallization and crystallite growth have been studied for many years in order to gain insight into the fundamental properties of solids.<sup>1</sup> Currently, much interest exists in the crystallization properties of Si.<sup>2</sup> With the incorporation of polycrystalline Si (poly-Si) in semiconducting devices<sup>3,4</sup> and with the possibility of inexpensive fabrication of solar cells from poly-Si,<sup>5–7</sup> the investigation of polycrystalline materials has gained in importance.

Thin films of amorphous Si are known to crystallize upon annealing.<sup>8</sup> The kinetics of Si crystallization is dependent upon parameters such as ambient,<sup>6</sup> substrate,<sup>9</sup> and preparation.<sup>10</sup> For example, vacuum-evaporated 5000-Å-thick Si films on fused silica substrates crystallize when annealed in pure argon at temperatures between 596 and 679°C for times ranging from 20 to 0.6 h, respectively.<sup>11</sup> Csepregi *et al.*<sup>12</sup> have found that amorphous Si layers about 4600 Å thick, formed by irradiation with 100-keV Si ions, will crystallize in vacuum epitaxially on (100) and (110) substrates when annealed at temperatures near 500°C for less than 1 h. They observe that impurities at the interface between the amorphous layer and the substrate influence the crystallization process. Films of evaporated Si approximately 600 Å thick in contact with a 150-Å layer of evaporated Al show crystalline character when annealed in vacuum at temperatures as low as 335°C.<sup>9</sup>

The fact that amorphous Si can crystallize at temperatures as low as 335°C is of interest for a number of reasons. First, by proper choice of preparation, one might devise a low-temperature, and hence economically attractive, process for producing single-crystal or large-grained polycrystalline Si from small-grained or amorphous Si. Such a process could be useful to both the semiconductor device and the solar cell industries. Second, poly-Si used in the electronics in-

dustry is usually in intimate contact with a metal such as Al. A knowledge of structural changes, such as crystallization, is of prime importance because the poly-Si must maintain its structural integrity during heat treatments while in contact with other metals.

Nakamura *et al.*<sup>13</sup> reported that Si deposited at 640°C by chemical vapor deposition (CVD) onto SiO<sub>2</sub> and covered with Al will crystallize when heated in vacuum for 30 min or less at temperatures between 400 and 560°C. They found that deposited Si dissolved, was transported, and recrystallized in the Al matrix. The objective of the present investigation is to extend their work to Si deposited by evaporation and by CVD at 900°C, allowing the relationship between Si preparation technique and crystallization to be studied. Because of their speculation that poly-Si might not crystallize in the temperature range between 400 and 560°C if the Al layer is thinner than a typical grain dimension in the deposited Si layer, crystallization from samples with Al layers ≤ 500 Å thick were also studied.

Samples investigated were similar in structure to those used by Nakamura *et al.*<sup>13</sup> and consisted of an SiO<sub>2</sub>/Si/Al trilayer structure on a Si wafer (see Fig. 1). Annealing temperatures were always maintained below the Al-Si eutectic temperature of 577°C<sup>14</sup> to limit the investigation to solid-phase processes.

## II. EXPERIMENTAL TECHNIQUES

Three analytical techniques were used to characterize the interaction of Al and Si—backscattering spectrometry (BS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Backscattering spectrometry of MeV <sup>4</sup>He<sup>+</sup> was used to measure thicknesses of Al, Si, and SiO<sub>2</sub> layers in the unannealed samples and as a quick method to determine if annealing had brought about any substantial changes in a sample. Using a 2.0-MeV <sup>4</sup>He<sup>+</sup> beam and an energy analyzer

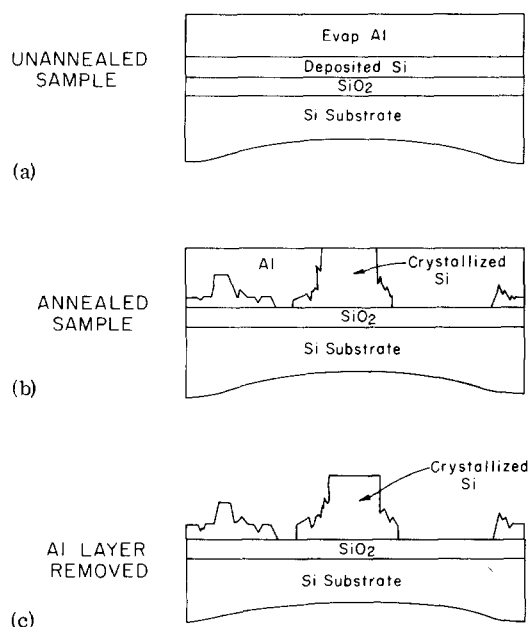


FIG. 1. Schematic representation of (a) an unannealed sample, (b) an annealed sample with the Al layer intact, and (c) an annealed sample with Al layer removed.

with a resolution of 18 keV, film thicknesses in an SiO<sub>2</sub>/Si/Al trilayer structure can be measured to an accuracy of about 10%, provided each individual layer is greater than about 300 Å and the total thickness of the structure is less than about 3 μm.<sup>15</sup>

Microstructure in unannealed samples was determined by removing the Si and Al films from the substrate followed by examination of the films in a JEOL JSEM 200 scanning transmission electron microscope. This instrument provides conventional TEM and SEM with electron energies up to 200 keV. Grain sizes in the deposited Al and Si were measured using bright-field imaging, dark-field imaging, and electron diffraction<sup>16</sup> (see Fig. 2). Those Si films for which grain sizes could not be determined by direct imaging or conventional electron diffraction were examined using micro-micro electron diffraction to determine an upper bound.<sup>17</sup>

Micro-micro diffraction patterns were produced using a focused incident electron beam whose convergence angle ranged from  $0.5 \times 10^{-4}$  to  $2 \times 10^{-4}$  deg. With a condenser aperture of 10 μm and the condenser lens set for maximum resolution, the beam spot on the sample was less than 100 Å in diameter.

The crystallinity of Si islands after annealing was investigated by electron channeling using the beam-rocking mode of the JSEM 200.<sup>18</sup> This technique involves rocking the incident electron beam in two orthogonal directions about a spot a few microns in size on the sample surface. A CRT is scanned in synchronism with the rocking beam while intensity modulation of the CRT is provided by the signal from either a secondary electron detector or a set of backscattered electron

detectors mounted above the sample. If the sampled region is a single-crystal larger than about 1 μm, a pattern will be obtained on the CRT indicative of the crystal structure and orientation. If the sampled region is composed of a number of large grains (> 1 μm), a pattern is produced for each grain. Grains with similar orientations produce patterns which may be indistinguishable due to superposition. An alternate mode of operation is to have the primary electron beam rock about a point slightly above the sample surface. In this way, a low-resolution SEM micrograph will be obtained superimposed on the channeling pattern (see Fig. 6) showing unambiguously the area on the sample being channeled.

Sample morphology before and after annealing was investigated by scanning electron microscopy using a JEOL JSEM U-3 or an Akashi-Seisakusho model MSM-2 Mini-SEM. The U-3 was equipped with an energy dispersive x-ray system<sup>19</sup> for elemental analysis.

### III. SAMPLE PREPARATION AND CHARACTERIZATION

Samples were prepared on polished substrates of <100>-oriented *n*-type 2–6-Ω cm Si wafers approximately 2 in. in diameter and 20 mil thick. Each wafer was covered with between 1000 and 1500 Å of thermally grown SiO<sub>2</sub>. Silicon was deposited on the SiO<sub>2</sub> layer by either electron-beam vacuum deposition at pressures less than  $2 \times 10^{-6}$  Torr, chemical vapor deposition (CVD) at 640°C, or CVD at 900°C. For ease of discussion these three types of deposited Si will be referred to as evaporated Si, 640° CVD Si, and 900° CVD Si, respectively.

For the TEM study, self-supporting fragments of Si film were obtained by dissolution of the SiO<sub>2</sub> layer between the Si substrate and the deposited Si layer in a solution of 1 part HF and 10 parts 1-MΩ cm deionized water. After approximately 48 h of immersion, some of the deposited Si film would float to the surface of the solution from where it could be removed and washed. Those films thicker than about 5000 Å were chemically thinned using a drop of diluted CP-4.<sup>20</sup> Films were placed on a No. 100 mesh copper TEM grid by dipping the grid into the final wash and lifting the film from the liquid.

The remainder of each wafer bearing a deposited Si layer was cleaned by sequential immersion into beakers of acetone, HF diluted 1:10 in deionized water, and ethanol, in that order. Ultrasonic agitation was used during the immersion process. The clean wafers were dried in a jet of dry nitrogen and placed on holders which were inserted into an ultrahigh-vacuum evaporator for immediate pump down. Films of Al ranging in thickness from 300 Å to 1.5 μm (depending on the experiment to be performed) were electron-beam evaporated onto the wafers at pressures less than  $2 \times 10^{-6}$  Torr.

A self-supporting Al film was taken from a wafer with 9000 Å of Al on 5000 Å of 640° CVD Si. Using a 20× binocular microscope, a pair of fine tweezers, and a sharp needle, the Al layer was scratched and a por-

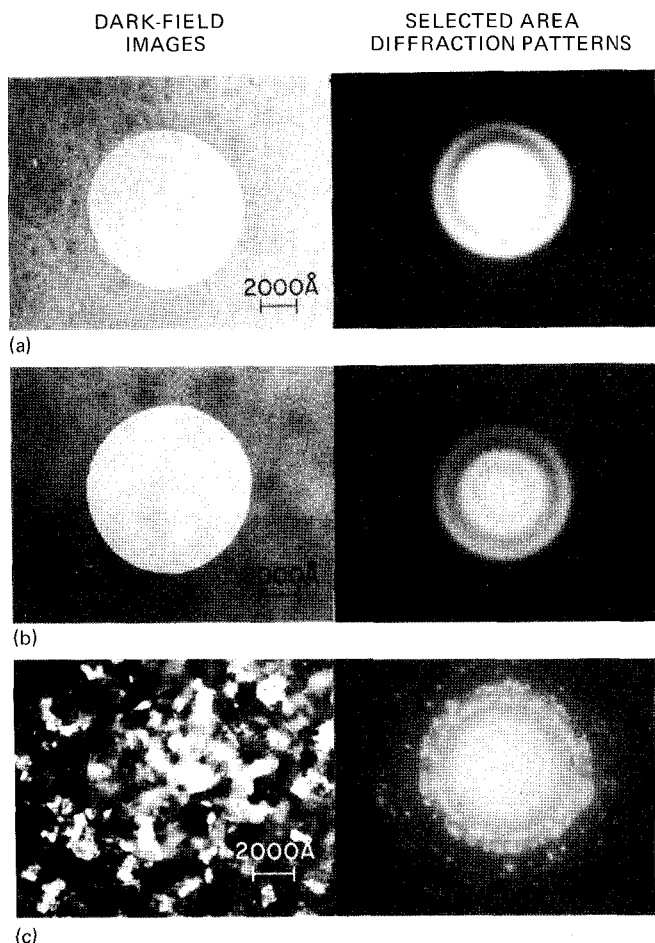


FIG. 2. Transmission electron microscope dark-field images and selected-area diffraction patterns for (a) evaporated Si, (b) 640° CVD Si, and (c) 900° CVD Si. All micrographs were taken with an electron-beam energy of 200 keV. Selected-area diffraction patterns were taken from the area within the light circles shown on the dark-field images.

tion of the film was removed from the deposited Si layer for mounting on a No. 50 copper TEM grid.

In the heat-treatment study, four 1-cm samples could be annealed simultaneously in a quartz boat ensuring nearly identical annealing conditions for a given group. Anneals were performed in a commercial furnace having a quartz tube evacuated to  $< 5 \times 10^{-6}$  Torr by a liquid-nitrogen trapped oil diffusion pump. Vacuum was also maintained in an adjacent room-temperature holding chamber. Boats were slid into the anneal furnace from the holding chamber for the anneal cycle and returned there afterwards for cooling. Furnace temperature was measured with a calibrated chromel-alumel thermocouple to an accuracy of  $\pm 5^\circ\text{C}$ . The calibration is traceable to an NBS standard thermocouple.

After annealing, samples were examined using optical microscopy, SEM, and BS. Small pieces, typically 3–5 mm square, were cut from the annealed samples for Al layer dissolution, accomplished by immersion in a solution of 1 part 12M HCl and 10 parts deionized water. Samples with the Al layer removed were re-examined by optical microscopy and SEM. X-ray analysis was used to ensure that all Al had been removed and that observed features were Si.

## IV. RESULTS

### A. Preanneal sample characteristics

A knowledge of the microstructure of the initial state is of prime importance in a study of crystallization. Both evaporated Si and 640° CVD Si had grain sizes so small that no contrast could be seen by conventional TEM imaging. Conventional electron diffraction indicated that both had grain sizes less than about 300 Å [see Figs. 2(a) and 2(b)]. Micro-micro electron diffraction indicated that the grains were less than about 50 Å.

The 900° CVD Si had grains rather uniform in size, with typical dimensions ranging between 1000 and 2000 Å. These grains were easily discernible by conventional dark-field imaging as shown in Fig. 2(c). The diffraction pattern [Fig. 2(c)] is typical of a polycrystalline film. The small flakes of Al removed from an unannealed sample could only be examined around their periphery by conventional TEM and electron diffraction because the center of the films excessively attenuated the electron beam. Most Al grains were between 1000 and 2000 Å in size, but some grains as large as 4000 Å were observed.

Examination of the Al surface of unannealed samples by SEM showed no features at magnifications up to 60 000 $\times$ . Furthermore, no interaction between the Al and the underlying Si was evident from BS spectra. Scanning electron micrographs of unannealed samples with the Al layer chemically removed also appeared featureless [see Fig. 3(a)]. Therefore, no perceptible interaction occurred between Si and Al during the Al evaporation. Moreover, the chemical etch used to remove the Al did not chemically interact with the deposited Si in any significant way.

Samples were examined to determine microstructure stability and reproducibility. It was found that Si layers

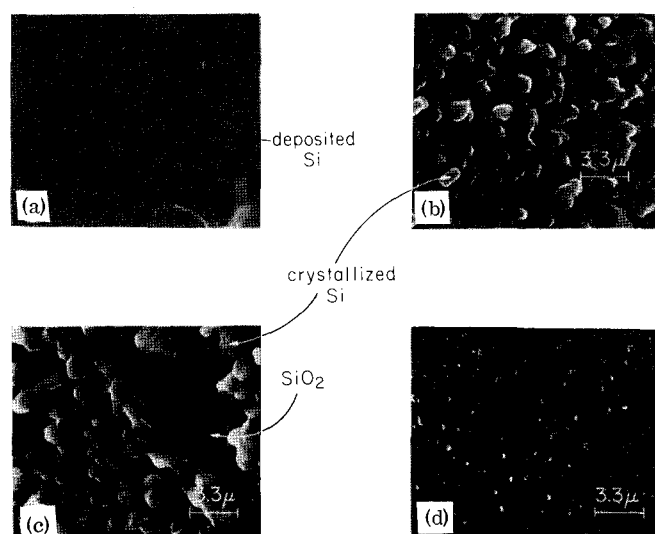


FIG. 3. Scanning electron micrographs of samples initially composed of 1  $\mu\text{m}$  of Al on (a) 3500 Å of evaporated Si—unannealed, (b) 3500 Å of evaporated Si—annealed, (c) 5000 Å of 640° CVD Si—annealed, and (d) 5400 Å of 900° CVD Si—annealed. Anneals were performed in vacuum at 440°C for 30 min. All samples are shown without the Al layer and tilted 25° with respect to the incident electron beam.

taken from wafers prepared up to six months apart had virtually identical structures. Specimens taken from wafers which had been stored in air at room temperature for up to four months were indistinguishable from those prepared only a few days prior to analysis. Furthermore, no appreciable differences could be detected between analyses performed on different areas of a given wafer. These facts indicate that the microstructure of the deposited Si layers was reproducible, relatively uniform, and stable with respect to all storage and handling procedures employed.

## B. Postanneal sample characteristics

It is important to distinguish between the two types of samples used in this investigation. Compared to both layer thickness and average grain size of the deposited Si film, the Al-layer thickness was either larger ("thick Al") or smaller ("thin Al").

### 1. Thick Al films

Deposited Si does not remain smooth and featureless upon annealing in vacuum above 400 °C when in contact with a thick Al layer. Morphological details, in general, depend on the method of Si deposition, anneal time, and anneal temperature. Deposited Si layers ranged in thickness between 3500 and 5400 Å, whereas Al layers ranged in thickness between 0.8 and 1.1 μm. No correlation was detected between layer thickness and observed morphology within these ranges.

Two samples, one with 1 μm of Al on 3500 Å of evaporated Si and the other with 1.1 μm of Al on 5000 Å of 640° CVD Si, were vacuum annealed at 440 °C for 30 min. The Si layer in both samples crystallized into aggregates from 1 to 5 μm in size. These aggregates were composed of small crystallites about 5000 Å in size [see Figs. 3(b) and 3(c)]. Aggregates shown for the evaporated Si sample can be seen to be slightly smaller and more uniformly spaced than those for the 640° CVD sample, but these subtle differences are probably not significant. Similar samples annealed at higher temperatures were almost indistinguishable.

A sample with 1 μm of Al on 5400 Å of 900° CVD Si was also annealed in vacuum at 440 °C for 30 min. The morphology of this sample differed significantly from either of the previous two samples [see Fig. 3(d)]. Only a small amount of crystallization has taken place. Most of the surface is rough and contains dissolution pits typically 5000 Å across, indicating that 900° CVD Si crystallizes more slowly at 440 °C than either evaporated Si or 640° CVD Si. These three samples were also examined prior to removal of the Al layer. The 900° CVD Si sample appeared to be essentially featureless at a magnification of 30 000×, whereas the evaporated Si and the 640° CVD Si samples had small lumps of material sparsely scattered about the Al surface. These lumps may have been Si crystallites, but this hypothesis could not be confirmed by x-ray analysis due to interference from Si in the underlying layers.

The time evolution of the crystallization process for 640° CVD Si can be traced using the series of SEM micrographs shown in Fig. 4. Samples with 8000 Å of Al

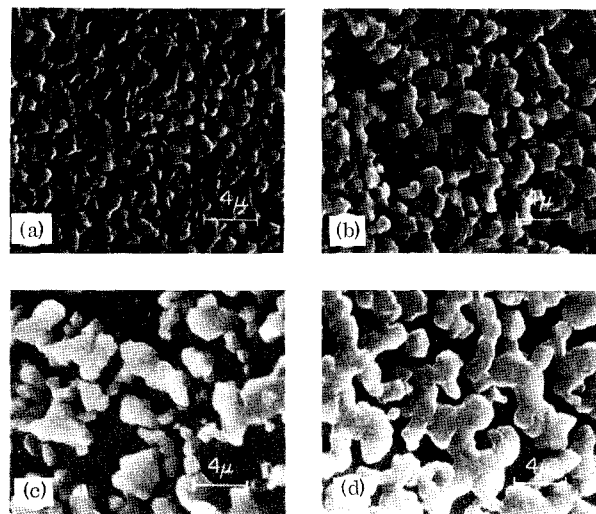


FIG. 4. Scanning electron micrographs showing a time-sequence annealing study of samples initially composed of 8000 Å of Al on 5000 Å of 640° CVD Si annealed in vacuum at 500 °C for (a) 5 min, (b) 10 min, (c) 40 min, and (d) 94 min. All samples shown without the Al layer and tilted 35° with respect to the incident electron beam.

on 5000 Å of Si were vacuum annealed at 500 °C, each for a progressively longer time. Crystallization begins with a high density of small crystallites which grow to about 0.5 μm [see Fig. 4(a)]. These small crystallites combine to form aggregates, even when the annealing time is only 5 min. As the annealing time is increased, larger aggregates form by the apparent coalescence of smaller aggregates. After 94 min, aggregates from 1 to 6 μm in size are formed [see Fig. 4(d)]. Examination of a sampling of these aggregates by TEM revealed that islands 6 μm in size typically contained about 10 randomly oriented single crystals each averaging about 1.3 μm across.

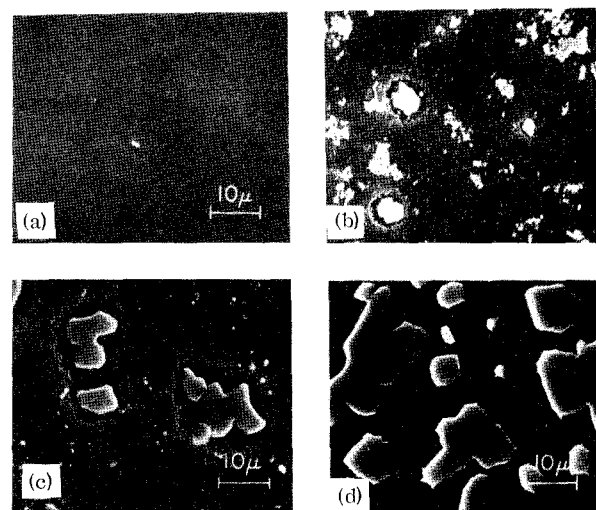


FIG. 5. Scanning electron micrographs showing a time-sequence annealing study of samples initially composed of 8000 Å of Al on 3000 Å of 900° CVD Si annealed in vacuum at 500 °C for (a) 30 min, (b) 94 min, (c) 180 min, and (d) 13 h 42 min. All samples shown without the Al layer and tilted 30° with respect to the incident electron beam.

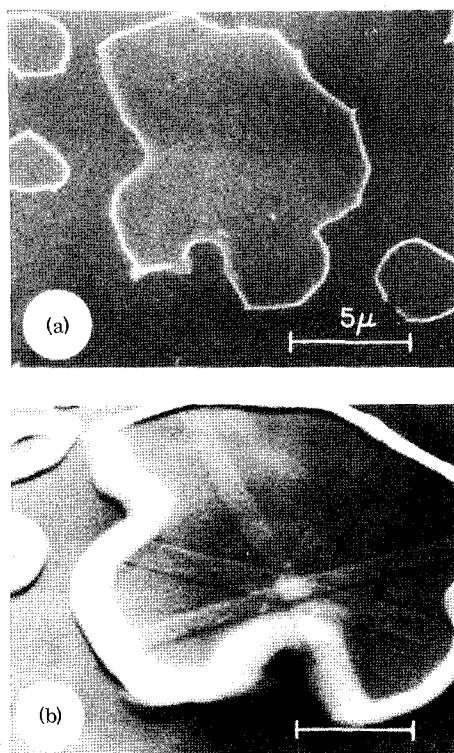


FIG. 6. Secondary electron micrographs taken on the JEOL JSEM 200 electron microscope from the same sample shown in Fig. 5(d) using (a) the scanning mode and (b) the beam-rocking mode. A low-resolution image is shown superimposed with an electron channeling pattern in (b) from the same grain shown in (a).

Figures 3(b) and 4(b) are quite similar. However, the sample in Fig. 3(b) required 30 min at 440°C to reach the same state which the sample in Fig. 4(b) reached in only 10 min at 500°C. This indicates a similar crystallization process in this temperature range, although the crystallization rate is higher at the higher temperature. Studies performed on evaporated Si gave the same results, i.e., crystallization begins by the formation of a high density of small crystallites which subsequently appear to coalesce into aggregates, and the crystallization rate is higher at 500°C than at 440°C.

The time evolution of the crystallization process for 900°C CVD Si is quite different from that of evaporated Si or 640°C CVD Si. Micrographs in Figs. 5(a)–5(d) show a time-sequence study of samples with 8000 Å of Al on 3000 Å of 900°C CVD Si annealed at 500°C. The 900°C CVD Si crystallizes with a much lower density of nucleation sites which leads to the formation of widely spaced crystallites. Furthermore, these crystallites grow as single crystals rather than as polycrystalline aggregates. Some crystallites become large enough to merge with neighboring crystallites to form large “islands”. Channeling patterns taken from islands where the contributing smaller crystallites were still distinguishable revealed that each of the smaller crystallites had a separate orientation with respect to the substrate. Channeling patterns taken from islands whose shape suggested that they also had formed from a number of smaller, though no longer distinct, crystallites

[see Figs. 6(a) and 6(b)] revealed these islands to be single crystals. A rough count showed that about one-half of the islands on the sample shown in Fig. 6 are single crystals.

Comparing two samples of 900°C CVD Si annealed for 30 min, the first at 500°C [Fig. 5(a)] and the other at 540°C [Fig. 7(a)], it is again evident that the crystallization process is faster at the higher temperature. Also, the rate of crystallization is much lower for the 900°C CVD Si than for the 640°C CVD Si. After 40 min at 500°C [see Fig. 4(c)] most of the 640°C CVD Si has crystallized into large aggregates, whereas after 30 min [see Fig. 5(a)], the 900°C CVD Si is just beginning to crystallize. This fact is also evident from a comparison of Figs. 3(c) and 3(d), where the anneal temperature is 440°C. Hence, the 900°C CVD Si crystallizes more slowly than the other two types of Si at both 440 and 500°C.

Summarizing the above results, films of Si deposited on SiO<sub>2</sub> by evaporation, CVD at 640°C or CVD at 900°C, ranging in thickness from 3000 to 6000 Å and covered with evaporated Al between 8000 Å and 1.1 μm thick will crystallize if vacuum annealed at a temperature between 440 and 540°C for a time between 5 min and 14 h. The final state of crystallization consists of single-crystal or polycrystalline islands averaging ~5 μm in size. The rate of crystallization increases with temperature regardless of Si deposition method. The Si deposited by CVD at 900°C crystallizes more slowly than either evaporated Si or 640°C CVD Si. The latter two types appear to be similar in all respects.

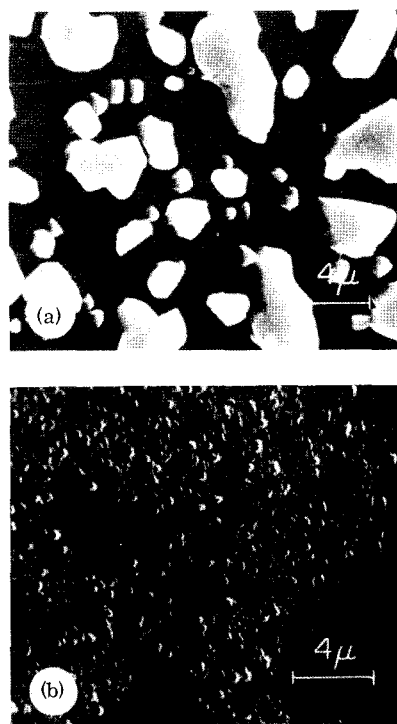


FIG. 7. Scanning electron micrographs of samples initially composed of Al on 3000 Å of 900°C CVD Si annealed in vacuum at 540°C for 30 min with (a) 1 μm of Al and (b) 360 Å of Al. Both samples are shown without the Al layer and tilted 30° with respect to the incident electron beam.

Sample cleaning prior to Al deposition was found to play a major role in the reproducibility of these observations. If the cleaning step was omitted or improperly conducted, the Si crystallization rate was retarded independent of the method of Si deposition. However, it was always possible to find a combination of time and temperature below the Al-Si eutectic where crystallization would still occur. When the cleaning step was omitted, the annealed 640° CVD Si samples had isolated Si islands and spires, the size, shape, and distribution of which varied from sample to sample. For properly cleaned samples, storage in air at room temperature for up to three months (with the Al layer intact) had no measurable effect.

The number density of Si crystallites observed on annealed samples after Al removal was not found to be reproducible. This was shown to be attributable, at least in part, to the Al etching procedure. A sample with 8000 Å of Al on 3000 Å of 900° CVD Si was annealed at 500°C for 3 h. Subsequent to etching the Al layer, the HCl solution was strained through a 0.25-μm Millipore filter. Analysis of the filtered residue revealed the presence of Si islands very similar to those observed on the sample. Unused etch solution was also analyzed in this way but no Si islands were found. Samples of 640° CVD Si annealed long enough to produce large aggregates appeared to be most susceptible to this phenomenon.

## 2. Thin Al films

In Sec. IV B 1 results were presented for samples in which the Al layer thickness was larger than both the layer thickness and the typical grain size of the deposited Si. The thin-Al study included only 900° CVD Si because it permitted Al layers to be reliably applied thinner than both the layer thickness and the typical grain size in the deposited Si layer.

Al layers as thin as 360 Å can promote crystallization. The sample shown in Fig. 7(b) had 360 Å of Al on 3000 Å of 900° CVD Si and was annealed for 30 min at 540°C. The surface has dissolution pits and small rugosities characteristic of the onset of crystallization [see Fig. 4(a)]. Also present, though, are areas of relatively little reaction, a general characteristic of samples of this type. Similar samples annealed for 60 min showed small precipitates about 400 Å in size as well as interconnected aggregates of crystallites up to 2 μm across.

Samples with 500 Å of Al on 3000 Å of 900° CVD Si showed the formation of islands up to 10 μm across after annealing for 30 min at 540°C. These islands grow laterally until they join, forming an interconnected maze of Si crystals resting on a background of very small crystallites (~500 Å in size). Nakamura *et al.*<sup>13</sup> have shown a similar structure for a sample with 2500 Å of Al on 3500 Å of polycrystalline Si annealed at 400°C for 30 min in their Fig. 4.

In addition to the difference in features between samples with thin Al and thick Al there is a striking difference in rate of crystallization. The sample shown in Fig. 7(a) differed from the one shown in Fig. 7(b) only

in Al-layer thickness (1 μm and 500 Å, respectively). After similar annealing, the sample in Fig. 7(a) shows a much greater degree of crystallization than does the sample in Fig. 7(b). Samples with 500 Å of Al likewise showed a higher rate of crystallization than did those with 360 Å when annealed for the same time at the same temperature. These general trends were all found to be consistently reproducible when experiments were repeated under similar conditions.

## V. DISCUSSION AND CONCLUSION

The detailed processes leading to crystallization in films are very complex. Results presented here are basically descriptive in nature and thus any conclusions drawn from them must remain qualitative. Moreover, any attempt to model these processes as a means of explaining our observations is necessarily speculative. However, the results do provide insight into the behavior of Si films in contact with Al layers.

Grain size determinations in deposited Si films have previously appeared. Anderson<sup>21</sup> has reported that Si films 0.9 μm thick deposited by evaporation onto SiO<sub>2</sub> substrates are "pseudoamorphous", giving only broad diffuse rings in the electron diffraction patterns. Furthermore, he found that Si layers between 0.12 and 2 μm thick deposited on SiO<sub>2</sub> by CVD at temperatures below 650°C are also pseudoamorphous. Emmanuel and Pollock<sup>22</sup> have stated that layers of CVD Si ranging from 850 to 1000 Å thick deposited below 650°C onto Si<sub>3</sub>N<sub>4</sub> or SiO<sub>2</sub> are noncrystalline with average grain sizes less than 10 Å. Nagasima and Kubota<sup>23</sup> have shown electron diffraction results for Si films 1000 and 8000 Å thick deposited on SiO<sub>2</sub> by CVD from which they concluded that with a substrate temperature below 650°C the films are amorphous. All of these observations are consistent with the findings of this study for evaporated Si and 640° CVD Si. We have shown that the 900° CVD Si used in this study has a grain size ranging from 1000 to 2000 Å. Nagasima and Kubota<sup>23</sup> have presented TEM results that indicate a grain size up to about 5000 Å for Si films 1000 and 8000 Å thick deposited on SiO<sub>2</sub> by CVD at 900°C, consistent with the findings of our study. Rai-Choudhury and Hower,<sup>24</sup> however, report that CVD Si layers less than 1 μm thick deposited onto SiO<sub>2</sub> below 950°C have grain sizes on the order of 200 Å. Anderson<sup>21</sup> states that 1.7-μm layers of polycrystalline Si deposited by CVD onto Si<sub>3</sub>N<sub>4</sub> at and above 900°C exhibit dendrites protruding above the Si surface to heights of 2 μm. The CVD Si layers examined in the latter two studies, however, differed from those used in this work either in thickness, substrate, or preparation. It may well be that grain size and structure in this temperature range can greatly depend on such parameters.

Silicon layers can crystallize in the solid phase when in contact with Al and annealed at a temperature above 400°C. All three types of deposited Si appeared to crystallize faster at higher temperatures. This observation is not surprising because many crystallization processes are thermally activated. It was initially hoped that grain size distributions could be used to establish crystallization rates quantitatively. However, this proved impossible because Al dissolution seemingly removed

Si crystallites which adhered poorly to the substrate or were contained wholly in the Al. Furthermore, qualitative comparison of crystallization rates is valid only for the time scale specifically investigated, i.e., the early phases of crystal growth.

Nakamura *et al.*<sup>13</sup> studied the interaction of 640° CVD Si with Al layers. Their interpretation of Al as a solvent and transport medium agrees with our findings. Electron diffraction and electron channeling results confirm their assumption that the precipitates are crystalline. Coalescence of crystallites is probably an intermediate state in the formation of large single-crystal islands. Nakamura *et al.*<sup>25</sup> show a sample initially composed of 1.2  $\mu\text{m}$  of Al on 0.5  $\mu\text{m}$  of 640° CVD Si, annealed for 55 h at 535°C. This sample contains large faceted islands very similar in appearance to the single-crystal island obtained using 900° CVD Si shown in Fig. 6(a). It thus seems possible to drive both types of Si to the same state by an appropriate choice of annealing temperature and time. Further study is needed to test this hypothesis.

Evaporated Si and 640° CVD Si demonstrate the same general annealing behavior. This observation lends credence to the notion that deposited Si layers with similar grain sizes should exhibit similar crystallization characteristics. Indeed, 900° CVD Si having a much different grain structure interacts quite differently. Grain size, however, may not be the only contributing factor. Interfacial contamination, residual stress, or impurities may play a significant role and could account in part for the observed differences.

Previous studies have indicated that Al layers as thin as 30 Å can enhance the crystallization of amorphous Si layers.<sup>26-28</sup> The work of Nakamura *et al.*<sup>13</sup> showed that the morphology of 640° CVD Si after annealing depends on the thickness of the Al layer. When a thin Al layer is used (i.e., 360 or 500 Å) on 900° CVD Si, crystallization still occurs but at a rate much slower than in the case of a thick Al layer ( $\sim 1 \mu\text{m}$ ). This retardation in rate could be the result of a reduction in the amount of available transport medium. Crystallization rate does not appear to depend strongly on Al-layer thickness in the range 8000 Å to 1.1  $\mu\text{m}$ , however.

The details of Si crystallization depend on many parameters; nevertheless, the general trend is that deposited Si layers go from a state of finer grains to one of coarser grains. This observation is consistent with the idea that the driving force for the crystallization process is a lowering of the free energy of the Si layer by the growth of larger crystals.<sup>13</sup> The 900° CVD Si (due to its larger initial grain size) would start at a lower energy state than 640° CVD Si and evaporated Si and therefore would have a smaller driving force resulting in a slower crystallization rate, as observed. The Al provides a medium through which Si atoms can migrate in the solid phase at relatively low temperatures. However, thermodynamic arguments do not account for the kinetics of Si transport and grain growth which, in all probability, strongly influence the crystallization process.

Finally, two points are noteworthy in a practical sense. First, extensive reactions between Al and Si, as observed in this work, are usually considered undesirable in terms of device fabrication and aging. We have noted, however, that in cases where the native oxide layer was not removed from the deposited Si prior to Al evaporation little or no reaction was observed. Thus an oxide layer might be considered to reduce or eliminate reactions of this type. Unfortunately, such a solution is unattractive because the oxide would disturb the intimate electrical contact needed between the layers. Nakamura *et al.*<sup>29</sup> have described a solution which does not suffer from this limitation. Second, the implications of the growth of single-crystal Si on an amorphous substrate ( $\text{SiO}_2$ , in this case) warrants further consideration. The largest single-crystal islands observed here are near the dimensions of active semiconductor devices.<sup>30</sup> By controlling the size and location of such crystals, one could achieve device isolation *ab initio*. It is furthermore conceivable that such structures could be useful in the low-cost production of photothermal or perhaps even photovoltaic arrays.

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<sup>1</sup>*Crystal Growth: An Introduction*, edited by P. Hartman (North-Holland, New York, 1973).

<sup>2</sup>C. D. Ouwens and H. Heijligers, *Appl. Phys. Lett.* **26**, 569 (1975).

<sup>3</sup>C. H. Fa and T. T. Jew, *IEEE Trans. Electron. Devices* **ED-13**, 290 (1966).

<sup>4</sup>S. P. Bellier and L. B. Ehlert, *Semiconductor Silicon* 1973, edited by H. R. Huff and R. R. Burgess (Electrochemical Society, Princeton, N. J., 1973), p. 304.

<sup>5</sup>C. G. Currin, K. S. Ling, E. L. Ralph, W. A. Smith, and R. J. Stirn, *Conference Record of the 9th Photovoltaic Specialists Conference* (IEEE, New York, 1972).

<sup>6</sup>A. L. Hammond, *Science* **184**, 1359 (1974).

<sup>7</sup>D. E. Carlson and C. R. Wrauski, *Appl. Phys. Lett.* **23**, 671 (1976).

<sup>8</sup>R. Grigorovich, *Mater. Res. Bull.* **3**, 13 (1968).

<sup>9</sup>S. R. Herd, P. Chaudhari, and M. H. Brodsky, *J. Non-Cryst. Solids* **7**, 309-327 (1972).

<sup>10</sup>M. H. Brodsky, R. S. Title, K. Weiser, and G. D. Petit, *Phys. Rev. B* **1**, 2632 (1970).

<sup>11</sup>N. A. Blum and C. Feldman, *J. Non-Cryst. Solids* **11**, 242-246 (1972).

<sup>12</sup>L. C. Csepregi, J. W. Mayer, and T. W. Sigmon, *Phys. Lett. A* **54**, 157 (1976).

<sup>13</sup>K. Nakamura, M. A. Nicolet, J. W. Mayer, R. J. Blattner, and C. A. Evans, Jr., *J. Appl. Phys.* **46**, 4678 (1975).



- <sup>14</sup>R. P. Elliott, *Constitution of Binary Alloys First Supplement* (McGraw-Hill, New York, 1965).
- <sup>15</sup>W. K. Chu, J. W. Mayer, M. A. Nicolet, T. M. Buck, G. Amsel, and F. Eisen, *Thin Solid Films* **17**, 1 (1973).
- <sup>16</sup>P. B. Hirsh, *Electron Microscopy of Thin Crystals* (Butterworth, London, 1965).
- <sup>17</sup>R. H. Geiss, *Proceedings of the 1976 Scanning Electron Microscopy Conference*, Toronto (Part II) (IIT Research Institute, Chicago, 1976), p. 337.
- <sup>18</sup>D. L. Davidson, *Res. Dev.* **25**, 34 (1974).
- <sup>19</sup>R. Woldseth, *X-Ray Energy Spectrometry* (Kevex Corp., Burlingame, Calif., 1973).
- <sup>20</sup>F. J. Biondi, *Transistor Technology* (Van Nostrand, New York, 1968), Vol. 3, p. 116.
- <sup>21</sup>R. M. Anderson, *J. Electrochem. Soc.* **120**, 1540 (1973).
- <sup>22</sup>A. Emmanuel and H. M. Pollock, *J. Electrochem. Soc.* **120**, 1586 (1973).
- <sup>23</sup>N. Nagasima and N. Kubota, 23rd National Symposium of the American Vacuum Society, Chicago, 1976 (unpublished).
- <sup>24</sup>P. Rai-Choudhury and P. L. Hower, *J. Electrochem. Soc.* **120**, 1761 (1973).
- <sup>25</sup>K. Nakamura, J. O. Olowolafe, S. S. Lau, M. A. Nicolet, J. W. Mayer, and R. Shima, *J. Appl. Phys.* **47**, 1278 (1970).
- <sup>26</sup>J. E. Green and L. Mei, *Thin Solid Films* **34**, 27 (1976).
- <sup>27</sup>C. A. Chang and W. J. Siekhaus, *Appl. Phys. Lett.* **29**, 208 (1976).
- <sup>28</sup>J. E. Green and L. Mei, *Thin Solid Films* **37**, 429 (1976).
- <sup>29</sup>K. Nakamura, S. S. Lau, M. A. Nicolet, and J. W. Mayer, *Appl. Phys. Lett.* **24**, 277 (1976).
- <sup>30</sup>B. Hoeneigen and C. A. Mead, *Solid-State Electron.* **15**, 819 (1972); **15**, 891 (1972).