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**DEVELOPMENT OF SILICON RECRYSTALLIZATION AND
THIN-FILM SOLAR CELL PROCESSES**

Third Quarterly Technical Status Report for April 1—June 30, 1978

By
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November 1978

Work Performed Under Contract No. EG-77-C-01-4106

Spire Corporation
Bedford, Massachusetts

U.S. Department of Energy

Solar Energy

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DEVELOPMENT OF SILICON RECRYSTALLIZATION
AND THIN-FILM SOLAR CELL PROCESSES

Third Quarterly Technical Status Report
For the Period:
1 April to 30 June 1978

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Division of Solar Energy

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ABSTRACT

This third Quarterly Report for Contract EG-77-C-01-4106, "Development of Silicon Recrystallization and Thin-Film Solar Cell Processes", covers the period 1 April through 30 June 1978. It reviews the rationale for selection of the two-step recrystallization process that is being developed, presents the results of the latest first-step recrystallization experiments, and outlines the calculations appropriate to the design of second-step thermal process experiments. Results of a computer run for first-step recrystallization are also presented. The report concludes with an updating of the results obtained from the thermal and pulsed electron beam annealing of shallow implanted GaAs.

TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
1	INTRODUCTION.	1
2	SILICON RECRYSTALLIZATION PROGRAM.	3
	2.1 Recrystallization Reveiw	3
	2.2 Computer Modeling of First-Step Recrystallization	3
	2.3 Second-Step Heating Analysis	4
	2.4 First-Step Recrystallization Results	10
3	GaAs PROCESSING	44
	3.1 Program Objective	44
	3.2 GaAs Studies	44
4	FUTURE PLANS.	45
	4.1 Silicon Studies	45
	4.2 GaAs Studies	45
	REFERENCES.	46

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Polycrystalline Cell Fabrication Sequence	2
2	VXTEMP Calculation for the Time Dependence of Front-Surface Temperature	5
3	Temperature Profiles at Various Times for the Calculation in Figure 2	6
4	Untreated (F0) 0.46 μm (T4), Polysilicon Film	12
5	Treated (F2) 0.19 μm (T2), Polysilicon Film	12
6	Untreated (F0) 0.46 μm (T4), Polysilicon RHEED Pattern	15
7	Pulsed (F2) 0.46 μm (T4), Polysilicon RHEED Pattern	15
8	Untreated (F0) 0.9 μm (T2), Polysilicon RHEED Pattern.	16
9	Pulsed (F2) 0.19 μm (T2), Polysilicon RHEED Pattern	16
10	Surface Morphology Change of a 0.14 μm Film with Pulsed Beam Fluence	18
11	Surface Morphology Change of a 0.25 μm Film with Pulsed Beam Fluence	19
12	Surface Morphology Change of a 0.80 μm Film with Pulsed Beam Fluence	20
13	Detached T4F2 Film	22
14	RHEED Patterns for Untreated (T1F0) and Treated (T1F2), 0.14 μm Films	24
15	RHEED Patterns for Untreated (T2F0) and Treated (T2F0), 0.25 μm Films	25
16	RHEED Patterns for Untreated (T3F0) and Treated (T2F0), 0.40 μm Films	26
17	Untreated 0.1 μm Polysilicon Film on Silicon (S1T1F0)	29
18	Treated 0.1 μm Polysilicon Film on Silicon (S1T1F1)	30
19	Untreated 0.1 μm Polysilicon Film on Grown Oxide (S2T1F0)	31

LIST OF FIGURES (Concluded)

<u>Figure</u>		<u>Page</u>
20	Treated 0.1 μm Polysilicon Film on Grown Oxide (S1T1F1) . . .	32
21	Untreated 1.0 μm Polysilicon Film on Silicon (S1T2F0)	33
22	Treated 1.0 μm Polysilicon Film on Silicon (S1T2F1)	34
23	Untreated 1.0 μm Polysilicon Film on Grown Oxide (S2T2F0) . .	35
24	Treated 1.0 μm Polysilicon Film on Grown Oxide (S2T2F1)	36
25	1.0 μm Treated (F1) Film on Grown Oxide (S2) After Six Anodic Oxidation-Strip Cycles	38
26	RHEED Pattern for Treated 0.1 μm Film on Silicon	41
27	RHEED Pattern for Untreated (F0) and Treated (F1) 0.1 μm Film on Grown Oxide	42
28	RHEED Patterns for Anodic Oxidized and Stripped S1T2F1 and S2T2F1 Films	43

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	A-4 No. 3 Experiment	10
2	A-4 No. 3 RHEED Analysis	13
3	A-4 No. 4 Experiment	17
4	A-4 No. 4 RHEED Analysis	23
5	A-4 No. 5 Experiment	27
6	A-4 No. 5 RHEED Analysis	40

SECTION 1

INTRODUCTION

This is the third Quarterly Report for contract EG-77-C-01-4106, "Development of Silicon Recrystallization and Thin-Film Solar Cell Processes"; it covers the period 1 April through 30 June 1978. This program has two activity areas. The first involves recrystallizing of deposited silicon films for thin-film silicon solar cell use. The second, a smaller effort, concerns establishing the viability of directed energy processing of compound semiconductor materials for thin-film solar cell applications.

The objective of this work is illustrated in Figure 1. The major process steps, exclusive of film recrystallization itself, are:

1. Ion implantation for junction formation.
2. Pulsed electron beam annealing (PEBA) for activation of implanted dopants and restoration of lattice perfection.
3. Electrostatic bonding (ESB) of front-side-processed films to a supporting glass superstrate, combined with simultaneous film release from the deposition substrate.

Each of these procedures has, for silicon, previously been demonstrated as individual steps.⁽¹⁾ The process remaining to be demonstrated is the recrystallization of an as-deposited, small-grain film into crystallites of configuration and purity compatible with silicon solar cells having conversion efficiencies equal to or greater than 10 percent (AM1). Progress toward this goal is reported here.

The GaAs activities parallel the silicon effort, with respect to directed energy processing and electrostatic bonding, so as to provide a viable process technology for compound semiconductor films.

FIGURE 1. POLYCRYSTALLINE CELL FABRICATION SEQUENCE

SECTION 2

SILICON RECRYSTALLIZATION PROGRAM

This section concerns program elements that pertain to the recrystallization of deposited silicon films.

2.1 RECRYSTALLIZATION REVIEW

Recrystallization of as-deposited, small-grain silicon layers is the pacing process for realizing the cell fabrication sequence illustrated in Figure 1. Spire is attempting to accomplish this task by means of a two-step thermal treatment consisting of full-surface exposure to a pulsed electron beam, followed by scanned exposure to a focused electron beam. The objective of the first step is to convert the (as-deposited) stacked-grain film to a columnar grain film of small crystallite diameter. The objective of the second step is lateral expansion of the columnar grains to large ($50\mu\text{m}$) crystallites.

The cell performance analyses of Hovel⁽²⁾, and of Soclof and Iles⁽³⁾ indicate that $10\mu\text{m}$ thick columnar silicon films consisting of $50\mu\text{m}$ broad crystallites would allow the fabrication of 10 percent (AM1) n^+pp^+ BSF cells, if the recrystallization process itself did not seriously degrade minority carrier diffusion length and if grain boundary shorting effects could be minimized. The use of directed energy techniques for device fabrication minimizes cell processing grain boundary effects. Because directed-energy heating produces only localized effects, they can be expected to preserve carrier properties during recrystallization. Further, the controllable thermal gradients that can be obtained from directed energy heating can be expected to accomplish the recrystallization objective.

2.2 COMPUTER MODELING OF FIRST-STEP RECRYSTALLIZATION

An analytic model for pulsed electron beam heating, as applied to first-step recrystallization, was presented in Quarterly No. 1. This model was constrained to employ temperature-independent thermal properties for the material that is being heated because closed-form solutions could not be obtained for temperature-dependent thermal properties. Prior work at Spire, using a simple computer code for pulse heating, suggested that use of temperature-independent parameters could introduce a fluence error of up to a factor of two. As a consequence, a generalized computer code, VXTEMP, was developed for predicting pulsed heating effects.

Because early VXTEMP runs, done for other programs, gave fluence-to-melt values that compared favorably with the predictions of the analytic model, VXTEMP was run for an $0.3\text{ }\mu\text{m}$, polycrystalline silicon layer on a $250\text{ }\mu\text{m}$ molybdenum substrate. This structure, typical of what will be eventually required, cannot be easily treated by the analytic model. VXTEMP utilizes the finite element approach to solve the time-dependent diffusion equation. It has provisions for temperature-dependent thermal properties, multi-layer structures, and time-dependent energy deposition profiles.

The results of the VXTEMP run are shown in Figures 2 and 3. Figure 2 displays the time-dependence of the sample's front-surface temperature when exposed to a 0.26 cal/cm^2 Gaussian electron pulse centered at 50 nsec and having a FWHM of 21 nsec, a close approximation to the actual first-step pulse. In distinction to results obtained from VXTEMP for $0.3\text{ }\mu\text{m}$ of polysilicon on silicon, where this fluence causes front-layer melting, thermal relaxation through the high conductivity molybdenum substrate precludes the availability of heat of fusion at the surface. Figure 3 gives the temperature profiles of this sample at 50, 70, 100, 150, and 200 nsec. This figure shows the clamping of the surface at the melting point and an unusual interface phenomenon. For this pulse, the molybdenum at the interface rises above silicon's melting point, causing melting of a thin silicon layer at the interface. Since this beam is required for recrystallization of a $0.3\text{ }\mu\text{m}$ layer, the first-step treatment must not extend to the interface if the lifetime of the silicon layer is to be preserved.

2.3 SECOND-STEP HEATING ANALYSIS

Following conversion of the as-deposited, stacked-grain film into a columnar grain film by exposure to a full-area pulsed electron beam, programmed motion of a focused, DC-electron beam over the film surface is intended to induce lateral growth of the columnar grains into crystallites of a size compatible with solar cell performance requirements. The initial task in realizing this second-step heat treatment is determining the required electron beam parameters. The latter, at this time, must be tempered by the capabilities of available swept DC beams since developing equipment suitable to this task is not within the scope of this program.

FIGURE 2. VXTEMP CALCULATION FOR THE TIME DEPENDENCE OF FRONT-SURFACE TEMPERATURE

FIGURE 3. TEMPERATURE PROFILES AT VARIOUS TIMES FOR THE CALCULATION IN FIGURE 2

Heating in a swept DC electron beam can occur in two distinct modes. If the focused beam's sweep velocity is sufficiently large, the beam will move one diameter in a time that is short in comparison to the characteristic thermal diffusion time that is associated with both the material and the beam voltage. As a consequence, the instantaneous temperature profile at any newly heated point in the beam path will be determined only by the electron absorption profile, since forward diffusion of previously deposited thermal energy is precluded. This instantaneous temperature profile will, of course, decay along the thermal gradient once the beam has passed.

If the beam diameter is large in comparison to the film thickness, the thermal gradient (and temperature profile) will be unidirectional into the plane of the film, since loss of thermal energy through the edge of the heated area is small in comparison to loss in the normal direction. This configuration is analytically identical with the heat flow following pulsed-beam exposure; as such, the required beam parameters can be calculated from the analytic model presented in Quarterly Report No. 1.

At significantly lower sweep velocities, thermal diffusion does occur while the beam moves one diameter. As a consequence the instantaneous temperature profile at any newly heated point is determined by the superposition of both the instantaneous and previous heating effects. The latter are dominant, indicating that the instantaneous temperature profile is, within broad limits, independent of electron energy. Moreover, since thermal diffusion occurs within the time the beam moves one diameter, the resulting temperature profile is no longer unidirectional. As a consequence, the thermal gradient has significant components perpendicular to the scan axis. Analogous to growth from the melt, this heat flow configuration would give a curved liquid-solid interface, whereas the heat flow geometry of the fast scan heating mode would give a planar interface. The slow-scan heating mode can be analyzed within the framework of the laser heating analysis of Cline and Anthony⁽⁴⁾.

Initial work on the pulsed first step of the two-step recrystallization approach involved very thin ($<1\text{ }\mu\text{m}$) layers. A preliminary analysis using both the pulsed heating and the Cline and Anthony models indicates that DC electron beams suitable for second-step recrystallization of the fractional-micrometer-thick silicon films that can now be successfully processed through first-step recrystallization cannot be realized. Within the fast-scan heating mode, the electron guns are brightness limited at small beam diameters, while at large beam diameters they are perveance-limited.

Available beam currents are approximately two orders of magnitude lower than needed. The situation with respect to the slow-scan heating mode for fractional-micrometer films, while functionally no better, is at least not a physical limitation. The central problem here is that diode electron guns capable of operating at the required (low) current level are not available in swept-beam systems, while the triode guns that are found in swept-beam systems will not operate at these low power levels. While it is possible to build a diode-gun, swept-beam system suitable to this task, it is more logical to attempt to implement a recently constructed pulsed electron beam generator that would allow first-step treatment of significantly thicker films. This Spire funded system (MBS) should allow first-step heat treatment of silicon films up to $50\text{ }\mu\text{m}$ thick. Since practical thin-film silicon cells will have to be at least $10\text{ }\mu\text{m}$ thick, this latter course indeed appears to be reasonable.

There are two further considerations that influence the design of second-stage heating experiments. The first relates to the current density profile in available DC electron beam systems, while the second relates to uncertainties in current density requirements. These considerations affect the temperature gradient in the film and hence the mechanistic details of the recrystallization process itself.

Except for magnetically confined electron beams and beams propagated through a set of far-spaced apertures, the current density profile of a propagated electron beam is not constant. For typical triode-gun systems, the current density profile is Gaussian. Gaussian beams are characterized by their width at half-maximum intensity, FWHM. Relating FWHM beam diameter to an observed "spot size" on a film can only be done with great difficulty. As a consequence, it is experimentally convenient to establish a "spot size" beam diameter, then vary the beam current to produce the desired thermal effect. The result of this operating procedure is that the experiment is characterized by beam current rather than current density, and hence becomes apparatus-related rather than absolute.

The physical effect of a nonconstant beam profile is different for the two scan modes. In the slow-scan mode, the beam profile effect is compounded by lateral thermal diffusion, with the latter expected to be the more important. The result of the two effects is expected to be a slope-sided, heat-affected zone that is wider at the surface. This could lead to the growth of tilted columnar crystallites at the periphery of the pass region.

For the fast-scan mode, the physical effect of a nonconstant beam profile varies with the depth to be melted. For a configuration intended to melt the surface while only bringing the film-substrate interface to melt temperature, the beam's current density variation is expected only to produce a narrower heat-affected zone, assuming that solid-phase recrystallization is not important. For a configuration intended to produce liquid to a point at or near the film-substrate interface, the shape of the instantaneous liquid-solid interface is expected to be that of the beam profile. On cooling, this curved interface, and the greater heat loss from a depth within the film as compared to heat loss from the surface, is expected to lead to columnar crystallites of less than full film thickness at the perimeter of the sweep path. These parasitic crystallites would also be expected to be slightly tilted.

In the long run, the spacing between beam sweeps will have to be established experimentally. It is not possible at this time to estimate the influence of these parasitic edge-of-the-beam crystallites on the required path spacing or the recrystallization process. One can speculate, however, that at this level the effects of crystal growth morphology may become dominant.

The final consideration is that of the current density requirements. On assuming for the moment that the beam profile and beam diameter are known, the calculation of the thermal effects of both the fast- and slow-scanned, swept beams is dependent on the values taken for the film's thermal properties. The thermal properties are a function of temperature, and are not well known near silicon's melting point. The analytic model of pulse heating being used for the design of the second-stage fast-scan experiments cannot treat temperature-dependent thermal properties. While the VXTEMP code can take this into consideration, the lack of firm values appears to make this level of calculation unnecessary. The same considerations apply to slow-scan heating. As a consequence of this and other minor approximations, the predicted I-V relations for the required beam conditions may be in error by as much as a factor of two. The error, if it exists, is expected to give an underestimate of the required beam power.

Taking all these factors into consideration, it is apparent that the second-stage recrystallization experiment should be designed as a heuristic experiment. Beam voltage can be fixed. Visual "spot size" should be established and kept constant as a function of beam current. Sweep velocity should be established for each of the heating modes. The experiment should then be run as a function of beam current. The required upper beam

current limit is that which causes melting down to the film-substrate interface for each heating mode. The lower beam current limit, on assuming solid-phase recrystallization is not important, is that which produces no surface melting.

Initial contacts with respect to obtaining electron beam services indicates that the second-stage heating experiments can only be performed with difficulty. The fast scan heating mode, as might be expected, is most difficult. Large electron beam welding equipment is required for both the current levels and sweep control that are necessary. While the situation appears to be somewhat better for slow scan heating, the control of large machines while working at the low current levels required here poses some problems.

2.4 FIRST-STEP RECRYSTALLIZATION RESULTS

Three first-step silicon recrystallization experiments have been run since the two experiments reported in Quarterly No. 2. The data for the A-4 No. 3 experiment is listed in Table 1. The CVD polysilicon was deposited to the four thicknesses on each of two wafers. The wafers were then scribed in half, and one half was pulsed-beam processed in the standard PEBA configuration while the other half was retained as a control. The samples were analyzed by SEM and RHEED.

TABLE 1. A-4 NO. 3 EXPERIMENT

Substrate:	(100) silicon wafers, polished surface; 2" dia. x 0.015"; p-type		
CVD Polysilicon:	SiH ₄ in H ₂ at 790°C		
Film Thickness:	T1	0.09	μm
	T2	0.19	
	T4	0.46	
	T5	1.5	
Pulsed Beam Fluence:	F0	0.0	cal/cm ²
	F1	0.15	
	F2	0.26	

Figure 4 is a 3,000X SEM view of the surface and fractured edge of the T4F0 sample ($0.46\text{ }\mu\text{m}$, no pulsed-beam exposure). The features seen on the sample surface (light pebble-grain region) are triangular dendrites that arise from the CVD operation. They do not appear to have any significance for this work. The striations on the fractured edge of the film are interpreted as conchoidal fracture lines, as might be expected from a randomly oriented, small-grain film. As-deposited F0 films of the other thicknesses were qualitatively similar to Figure 4.

Figure 5 is a 3,000X SEM view of a T2F2 ($0.19\text{ }\mu\text{m}$, 0.26 cal/cm^2) film. The lower density of surface dendrites, as compared to Figure 4, is not germane to this work. While the features visible on the fractured edge appear to be different from those seen on untreated films, no more than this observation can be claimed at this time.

All samples were then subjected to RHEED analysis at a testing laboratory, whose report is presented in Table 2. Before discussing these results, it is useful both to restate the experimental objective and establish the conclusions drawn from this experiment. Concerning the conclusions, the results of this experiment appear to indicate that full-surface exposure of a polysilicon film that has been deposited directly on a monocrystalline silicon substrate is capable of producing epitaxial regrowth of columnar crystallites. This is a necessary condition to the success of the proposed approach. If the pulsed electron beam exposure were not capable of producing columnar crystallites in a situation where epitaxial crystallization is possible, it would be improbable that this treatment would yield columnar crystallites in a situation where recrystallization proceeded from an unorganized, foreign surface. To restate the experimental objective, the primary purpose of this experiment was to establish that the necessary condition could be met.

The data presented in Table 2 provides a variety of other information. On examining the F0 data as a function of film thickness, it appears (1) that CVD of polysilicon from SiH_4 in H_2 at 790°C produces close to epitaxial deposits near the interface, and (2) that this organization first decreases and then increases with increasing film thickness. As a consequence, the T1 and T5 films are not particularly useful for this experiment. This change in crystal morphology with thickness is consistent with most observations. For present purposes, it is unfortunate that the CVD films were so highly organized. Further CVD films from SiH_4 should be done in N_2 rather than H_2 .

FIGURE 4. UNTREATED (F0) 0.46 μm (T4),
POLYSILICON FILM

FIGURE 5. TREATED (F2) 0.19 μm (T2),
POLYSILICON FILM

TABLE 2. A-4 NO. 3 RHEED ANALYSIS

Sample	Analysis Report
T1F0	Minor random poly-Si; possible (400) single crystal; twins
T1F1	Crystals in epitaxy; possible (400) single crystal; twins
T1F2	Crystals in epitaxy; possible single crystal
T2F0	Strong random poly-Si; crystals in (400) epitaxy; twins
T2F1	Similar to T2F0
T2F2	Very weak random poly-Si; many crystals in (400) epitaxy; twins
T4F0	Mostly random poly-Si
T4F1	Mostly random poly-Si; many crystals in (400) epitaxy parallel to surface; twins
T4F2	Epitaxy with (400) parallel to surface; twins; unidentified polycrystalline phase
T5F0	Many random poly-Si crystals in (400) epitaxy; twins
T5F1	Similar to T5F0
T5F2	Similar to T5F0

Examining the T2 and, particularly, the T4 films as a function of treatment fluence, the improvement in film organization with increasing fluence is quite evident. This change is illustrated by the comparison between Figures 6 and 7 and Figures 8 and 9. Figure 6 is the T4F0 film. The multiplicity of spots and the residual (random) ring pattern are to be compared to the much simpler spot pattern of the T4F2 sample shown in Figure 7. (Note in Figure 7 that the weak spots occurring at one-third the lattice spacing are due to twins and that the faint ring structure is an unidentified second phase that is not pure silicon.)

Figure 8, the T2F0 sample, is qualitatively similar to the T4F0 (Figure 6) sample in that it displays a complicated spot pattern and a random ring pattern. The T2F2 sample shown in Figure 9 has a simple spot pattern and only very faint ring patterns. No further inferences were drawn from this experiment.

The fourth recrystallization experiment was, in essence, a repeat of the third experiment, except that the CVD films were deposited from SiH_4 in N_2 at 900°C in an effort to obtain a less organized starting film. The pertinent data for this experiment is listed in Table 3. The samples were again analyzed by SEM and RHEED. The SEM work was done in general, at higher magnification in an attempt to bring out the structural details of the fractured film edge.

Figure 10 shows the T1F0, T1F1, and T1F2 films at 50,000X. A distinct change in surface morphology is evident on the T1F2 sample. Figure 11 displays the same phenomena, at 20,000X for the T2 samples. Similar changes were observed in the T3 samples. By contract, the T4 samples, shown in Figure 12 at 20,000X did not exhibit this change in surface morphology.

Using the analytic model of pulsed-beam heating presented in Quarterly No. 1 and the parameters of the beam used for this experiment, it is expected that the F2 fluence would produce actual melting to a depth of approximately $0.35\text{ }\mu\text{m}$. Considering the accuracy of the model and the parameters, it can be supposed that the three thinner films, 0.14 , 0.25 and $0.40\text{ }\mu\text{m}$, would be melted down to, and for the thinnest films, into the substrate while the $0.80\text{ }\mu\text{m}$ (T4) film would only be melted to approximately half its thickness. On cooling, the T1-T3 films would regrow from a monocrystalline substrate, while the T4 film would regrow from a small-grain, polycrystalline base. The change in surface morphology observed for the three thinner samples can then be correlated with epitaxial regrowth.

**FIGURE 6. UNTREATED (F0) 0.46 μm (T4),
POLYSILICON RHEED PATTERN**

**FIGURE 7. PULSED (F2) 0.46 μm (T4),
POLYSILICON RHEED PATTERN**

FIGURE 8. UNTREATED (F0) 0.19 μm (T2),
POLYSILICON RHEED PATTERN

FIGURE 9. PULSED (F2) 0.19 μm (T2),
POLYSILICON RHEED PATTERN

TABLE 3. A-4 NO. 4 EXPERIMENT

Substrate:	(100) silicon wafers, polished surface; 2" dia. x 0.015"; p-type	
CVD Polysilicon:	SiH ₄ in N ₂ at 900°C	
Film Thickness:	T1	0.14 μ m
	T2	0.25
	T3	0.40
	T4	0.80
Pulsed Beam Fluence:	F0	0.0 cal/cm ²
	F1	0.15
	F2	0.25

FIGURE 10. SURFACE MORPHOLOGY CHANGE OF A $0.14\ \mu\text{m}$ FILM WITH PULSED BEAM FLUENCE

FIGURE 11. SURFACE MORPHOLOGY CHANGE OF A $0.25\ \mu\text{m}$ FILM WITH PULSED BEAM FLUENCE

FIGURE 12. SURFACE MORPHOLOGY CHANGE OF A $0.80\ \mu\text{m}$ FILM WITH PULSED BEAM FLUENCE

An anomaly was observed in small areas of the T4F2 sample. This effect is shown in Figure 13. The upper picture is a 500X view of an area where the CVD film became detached from the substrate as a result of the F2 treatment. This phenomenon occurred in small, roughly circular areas thought to correspond to localized "threads" in the pulsed beam. These "threads", due to anode contamination, are regions of very high fluence. Film detachment in these areas is probably due to bending moments generated by thermal expansion. The lower photograph in Figure 13 is a 20,000X view of the edge and surface of a piece of film from one of these areas. The surface morphology of this sample is more characteristic of those samples that melted to the interface (Figure 10, T1F2, and Figure 11, T1F2) than of the normal regions of the T4F2 (Figure 12) film. While the edge morphology of this sample is suggestive of the edge morphology of the monocrystalline substrate, there is no evidence that the observed flakes are monocrystalline.

The RHEED analysis is listed in Table 4. As was observed in the A-4 No. 3 experiment (Table 2), the F1 (0.15 cal/cm^2) treatment, as expected, was insufficient to produce full recrystallization while the F2 (0.25 cal/cm^2) treatment, again as expected, was sufficient. Also, as was observed in the A-4 No. 3 experiment, the effectiveness of the F2 treatment decreased with increasing film thickness. The one abnormality in Table 4 is the lack of improved crystal organization in going from T4F1 to T4F2. This can be explained on the following basis. Since the total energy of the pulsed beam is fixed, high energy "threads" imply lower energy density in the other parts of the beam. Since the film detachment shown in Figure 13 is thought to be due to threads, it is not unreasonable to propose that the fluence in the "normal" regions of the beam used for the T4F2 sample was actually less than F1.

Figure 14 shows the RHEED patterns for the T1F0 and T1F2 samples. The presence of Kikuchi lines and the complete absence of ring patterns in the T1F2 sample is particular noteworthy. Figure 15 shows the RHEED data for the T2F0 and T2F2 samples. The reduced perfection of the T2F2 sample, as compared to the T1F2 sample, is evident in the ring structure and the absence of Kikuchi lines on the T2F2 plate. This progression is completed with Figure 16, the RHEED plates for the T3F0 and T3F1 samples.

FIGURE 13. DETACHED T4F2 FILM

TABLE 4. A-4 NO. 4 RHEED ANALYSIS

Sample	Analysis Report
T1F0	Random poly-Si with slightly preferred orientation, (100) perpendicular to surface, i.e., (100) texture
T1F1	Random poly-Si and crystals in epitaxy
T1F2	Complete epitaxy (100); Kikuchi lines visible
T2F0	Poly-Si with mixed (100) and (111) texture
T2F1	Mostly random poly-Si with some preferred orientation; mixed (100) and (111) texture
T2F2	Random poly-Si plus (100) epitaxy
T3F0	Poly-Si with mixed (100) and (111) texture; very faint (100) epitaxy
T3F1	Poly-Si with mixed (100) and (111) texture
T3F2	Random poly-Si plus (100) epitaxy
T4F0	Poly-Si with mixed (100) and (111) texture
T4F1	Poly-Si with mixed (100) and (111) texture; very faint (111) epitaxy
T4F2	Poly-Si with mixed (100) and (111) texture

**FIGURE 14. RHEED PATTERNS FOR UNTREATED (T1F0)
AND TREATED (T1F2), 0.14 μm FILMS**

FIGURE 15. RHEED PATTERNS FOR UNTREATED (T2F0) AND TREATED (T2F0), 0.25 μm FILMS

FIGURE 16. RHEED PATTERNS FOR UNTREATED (T3F0)
AND TREATED (T2F0), 0.40 μm FILMS

Experiments A-4 No. 3 and A-4 No. 4 conclusively demonstrated that a "proper" electron beam pulse will produce, at a minimum, columnar recrystallization of CVD polysilicon deposited on a monocrystalline silicon substrate. Moreover, the film thickness that can be treated is within 20 percent of that predicted by the analytic model. These results make it reasonable to proceed with an examination of the first-step recrystallization process for CVD polysilicon deposited on a foreign substrate.

The fifth A-4 type experiment was the first that examined the recrystallization of the CVD film from a foreign substrate. This was accomplished by growing a 850°C steam oxide (approximately 500A) on half the substrates and then depositing polysilicon, from SiH₄ in N₂ at 800°C, on both bare and oxide-covered substrates. The pertinent data for this experiment is listed in Table 5. Only two film thicknesses, 0.1 μm (T1) and 1.0 μm (T2), were used in this work, since previous studies showed that these values bracketed the range of interest. Further, the previously used lower fluence, 0.15 cal/cm², was eliminated, since it had not proved to be effective.

TABLE 5. A-4 NO. 5 EXPERIMENT

Basic Substrate:	(100) silicon wafers, polished surface; 2" dia. x 0.015", p-type		
Deposition Substrate:	S1, as-received wafers S2, nominally 500A, steam oxide (850°C)		
CVD Polysilicon:	SiH ₄ in N ₂ at 800°C		
Film Thickness:	T1	0.1 μm	
	T2	1.0 μm	
Pulsed Beam Fluence:	F0	0.0	cal/cm ²
	F1	0.25	

As was the case for previous experiments, analysis was by SEM and RHEED. Additionally, pieces of both the S1T1F1 and S2T2F1 samples were processed through successive anodic oxidation-chemical stripping cycles in an attempt to obtain a surface morphology profile of the films.

Figures 17 through 24 are SEM photographs of the various films. Figure 17 shows the S1T1F0 film at 2,000 and 20,000X. These films do not appear to be different from previous thin polysilicon layers. Figure 18 shows this film after pulsing (F1; 0.25 cal/cm^2). The change in surface morphology is evident and, in accord with previous experiments, indicates film melting. Figures 19 and 20 are SEM photographs of the S2T1 samples prior to (S2T1F0) and following (S2T1F1) pulsed-beam treatment. The slight film cracking seen in Figure 19 is probably due to densification of the 850°C steam oxide. (A $1,000^\circ\text{C}$ oxide would be more appropriate). The cracking seen in the pulse-processed sample, Figure 20, is at least partially due to the relatively low temperature oxide but is also apparently due to a higher-than-expected, pulsed-beam fluence (see below). Areas within a cracked region, however, both before and after pulsed-beam treatment, are comparable to the corresponding films that were deposited directly on silicon (S1) substrates.

Figures 21 and 22 are the SEM views of the $1 \mu\text{m}$ (T2) films on silicon (S1) before (F0) and after (F1) pulsing, respectively. Figure 21 is characteristic of the previous films in this thickness range. The severe cracking of the film shown in Figure 22, along with the change in surface morphology, suggests that the pulsed-beam fluence, for unknown reasons, was significantly higher than 0.25 cal/cm^2 , since this fluence had not previously caused cracking in films of this thickness range. (The actual pulsed-beam fluence can only be determined by its effect on a target. Shot abnormalities can cause the "setup" fluence to be significantly higher or lower. While the reason for an abnormal shot can almost always be determined after its effect has been observed, such shots are sufficiently infrequent that it is not practical to attempt to preclude their occurrence by disassembly of the plasma diode for inspection prior to each shot.)

Figures 23 and 24 show the $1.0 \mu\text{m}$ (T2) film deposited on the grown oxide (S2) before and after pulsing, respectively. Their similarity to Figures 21 and 22, respectively, is so great that no further discussion of the latter figures is necessary.

FIGURE 17. UNTREATED 0.1 μm POLYSILICON FILM ON SILICON (S1T1F0)

FIGURE 18. TREATED 0.1 μm POLYSILICON FILM ON SILICON (S1T1F1)

FIGURE 19. UNTREATED 0.1 μm POLYSILICON FILM ON GROWN OXIDE (S2T1F0)

FIGURE 20. TREATED 0.1 μm POLYSILICON FILM ON GROWN OXIDE (S2T1F1)

FIGURE 21. UNTREATED 1.0 μm POLYSILICON FILM ON SILICON (S1T2F0)

FIGURE 22. TREATED 1.0 μm POLYSILICON FILM ON SILICON (S1T2F1)

FIGURE 23. UNTREATED 1.0 μm POLYSILICON FILM ON GROWN OXIDE (S2T2F0)

FIGURE 24. TREATED 1.0 μm POLYSILICON FILM ON GROWN OXIDE (S2T2F1)

Recalling that the growth of large silicon crystals on a foreign substrate is thought to require both a pulsed and a swept electron-beam treatment, and remembering that the objective of the pulsed-beam treatment is only to produce full-film-thickness, columnar crystallites, it is readily seen that verification of the columnar nature of a very small crystallite film is an exceedingly difficult technical task; that is, pulsed-beam, recrystallized films on silicon can grow epitaxially from the substrate to give macroscopic columnar crystals. By contrast, pulsed-beam, recrystallized films deposited on grown oxide, an amorphous layer from which epitaxial regrowth is not possible, can, at best, be expected to have small-cross-section, columnar crystallites. The problem is to confirm that treated films of this type are indeed comprised of columnar structures. The simplest of the proposed approaches is to follow the surface morphology of a film in an SEM as the film thickness is reduced. The easiest way to remove the film's surface controllably is anodic oxidation and stripping. This procedure was tried on some T2F2 films from this experiment. Because all samples were badly cracked after puling, this effort was largely unsuccessful. Figure 25 is a 2,000X SEM view of an S2T2F1 film after six oxidize-and-strip-cycles. The heavy substrate attack at film cracks is evident. While film cracks were the principal problem in this test, using repeated anodize-strip cycles for layer removal does, in general, appear to be feasible.

The RHEED analysis for this experiment is summarized in Table 6. While the results, at first glance, appear to be negative, this is not the case. Based on the known characteristics of the pulsed electron beam used in this experiment, full-depth recrystallization can only be expected for the $0.1\text{ }\mu\text{m}$ (T1) samples. In the case of the polysilicon deposited directly on monocrystalline silicon (S1), a situation in which epitaxy is possible, epitaxial regrowth via directional freezing in the field of the unidirectional thermal gradient is possible. The RHEED analysis for film S1T1F1 (and corresponding films in earlier experiments) confirms this expectation. For the case of polysilicon deposited on a foreign surface, directional freezing under the unidirectional thermal gradient can, at best, be expected to produce full-film-thickness, columnar crystallites unless the density and orientation of the nucleation sites at the original liquid-solid interface is controlled. Because there is no known way to accomplish this control, the cross section of the columnar crystallites and their rotational organization would be expected to be similar to those of the starting CVD film. As a consequence, RHEED

FIGURE 25. 1.0 μm TREATED (F1) FILM ON GROWN OXIDE (S2)
AFTER SIX ANODIC OXIDATION-STRIP CYCLES

analysis of a recrystallized film would be expected to show a pattern like that of the starting film. This is what was observed for the S2T1F1 sample. The point of the attempt to thin the recrystallized film successively through repeated anodic oxidation-stripping cycles was, by SEM observation of surface morphology, to confirm that full-film-thickness, columnar crystallites had indeed been formed. The second-step, electron-beam sweep is needed to convert the small columnar crystallites to large columnar crystallites that will at least be coherent over the area examined by the RHEED probe beam.

Figure 26 is the after-pulsing RHEED plate from the 0.1 μm film deposited on silicon (S1T1F1). Except for the twinning, which may be due to residual nitride at the CVD interface, this pattern is as clean as the one shown in Figure 14, indicating the pulsed beam was behaving as expected. Figure 27 shows the RHEED patterns for untreated (F0) and treated (F1) 0.1 μm films on grown oxide. That these two patterns are essentially identical is, as was explained above, what would be expected. It should be noted that the ring pattern shown by S2T1F1 indicates that the interfacial oxide is still present; if it had been consumed during the pulsed-beam processing, a pattern like that shown in Figure 26 would have been observed.

The RHEED patterns for the S1T2F0, S1T2F1, S2T2F0, and S2T2F1 films, as expected, are quite similar to the random polysilicon patterns observed on other thick films. Figure 28 shows the RHEED pattern for a sample of the S1T2F1 film processed through three anodic oxidation/strip cycles and a sample of the S2T2F1 film processed through six thinning cycles. The spot and Kikuchi line structure seen on the S2T2F1 sample is due to the substrate; the ring pattern is due to the film.

This last experiment completes the development work on the first step of the two-step recrystallization process.

TABLE 6. A-4 NO. 5 RHEED ANALYSIS

Sample	Analysis Report
S1T1F0 S1T1F1	Not analyzed Complete epitaxy (100); twins
S2T1F0 S2T1F1	Random poly-Si Random poly-Si
S1T2F0 S1T2F1	Random poly-Si with preferred orientation As S1T2F0
S2T2F0 S2T2F1*	Random poly-Si Random poly-Si and crystals in epitaxy

*After six anodize-strip cycles. (The unetched sample was lost in preparation.)

FIGURE 26. RHEED PATTERN FOR TREATED $0.1\ \mu\text{m}$
FILM ON SILICON

FIGURE 27. RHEED PATTERN FOR UNTREATED (F0) AND TREATED (F1)
0.1 μm FILM ON GROWN OXIDE

FIGURE 28. RHEED PATTERNS FOR ANODIC OXIDED AND STRIPPED S1T2F1 AND S2T2F1 FILMS

SECTION 3

GaAs PROCESSING

This section deals with aspects of the program pertaining to GaAs and similar compounds.

3.1 PROGRAM OBJECTIVE

The program objective is to implement the energy beam processing technology that has been developed for silicon films to the preparation of films of III-V materials. Because of its availability, GaAs has been chosen in this exploratory work as representative of the III-V compounds. Low-grade single-crystal GaAs has been used for most of this work, to avoid processing technology complications.

3.2 GaAs STUDIES

Work has continued on implantation of Mg, Be, Zn, Si, Te, and Se. Implant voltages were selected to give shallow 500Å deep junctions to all species. The n-type dopants gave about an order of magnitude lower sheet resistance than the p-dopants, presumably due to higher electron mobility. While all the dopants tried produce usable p-n junctions, diffusing species, such as Zn, prevent shallow junction formation.

PEBA annealing of implanted junctions has, to date, produced low-resistivity layers, but poor cells. In general, V_{oc} values comparable to those obtained from thermal annealing have not been obtained. While most of this work has been done with implanted Zn, a species that may be difficult to activate because of its rapid diffusion in GaAs, the results do suggest less than complete activation.

An attempt was made to construct a 2x2 cm GaAs cell by Zn implantation and thermal annealing, and to compare its performance with the state-of-the-art. While V_{oc} 's were competitive, I_{sc} was lower than the state-of-the-art by a factor of two. This is attributed to either the poor mobility of the starting material or incomplete activation of the implanted species.

SECTION 4

FUTURE PLANS

4.1 SILICON STUDIES

The immediate plan for the silicon effort is to establish contact with organizations capable of providing the types of swept DC electron beams that will be required for the second recrystallization step, and to implement the second-step experiments.

4.2 GaAs STUDIES

The GaAs studies are to be continued in the present mode, with greater emphasis on pulsed annealing and reduced emphasis on thermal annealing. Ion beam epitaxy work will be started.

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