N76 12504

ENHANCED CRYSTALLINITY OF LOW TEMPERATURE DEPOSITED SILICON FILMS ON GRAPHITE SUBSTRATES

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ABSTRACT

The previously developed technique for silicon crystallinity enhancement in silicon films deposited at low temperature is applied to graphite substrates. The measured increase in silicon crystallinity is comparable to that observed earlier using a quartz substrate. The distribution of aluminum in the silicon films is determined using Auger spectroscopic depth profiling. Carbon diffusion from the substrate into the silicon film is shown to be negligible at a substrate temperature of 600°C.

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In a previous paper we have shown a technique to enhance silicon crystallinity at low substrate temperatures for vacuum deposited silicon thin films.[1] An ultrathin Si-Al-Si (100Å-500Å-100Å) sandwich coating was used prior to silicon deposition. The silicon films thus deposited show a lower limit of 5μ for the silicon grain size. Optical microscopic measurement of the etched films further show that silicon grains as large as 200μ are produced.[2]

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In this work the same technique is applied to graphite substrates. Graphite is chosen because of its desirable properties as a substrate material for silicon thin film solar cells. Earlier work in which silicon films were deposited on graphite at high temperature showed significant diffusion of silicon and carbon into each other and the formation of silicon carbide.[3] Later work showed that, at a substrate temperature below 800°C, much less diffusion was observed.[2] Therefore, the Si-Al-Si sandwich coating technique should be applicable to the graphite substrate at 600°C to enhance silicon crystallinity without significant SiC formation. In addition, the difficulty encountered in our earlier study in determining the aluminum distribution is solved in the present work with a extra silicon coating as described later.

Silicon and aluminum were vacuum deposited onto graphite and quartz using conventional electron beam heating. The deposition rate was ca 40Å/min for both Si and Al. Other experimental parameters and Auger depth profiling measurement have been described elsewhere.[1,3] Commercial extruded graphite and fused quartz were used. Graphite substrates cut from a rod were used in both the unpolished and polished form. The latter was polished on Grit 320 SiC paper. Both graphite and quartz substrates were used in each deposition, the latter being used as a reference to be compared with the earlier work.[1] Substrates were outgassed at 800-900°C before deposition in a vacuum of 1×10^{-6} Torr.

An ultrathin Si-Al-Si (100Å-500Å-100Å) sandwich layer was first deposited onto the substrates which were held at room temperature. The substrates were then heated to 600°C and a thick silicon film of ca 2000-3000Å was deposited. Without further annealing the substrates were cooled down to room temperature and another layer of silicon (ca 300Å) was deposited. This last silicon coating is shown to be necessary to prevent the oxidation of aluminum, most of which stays near the surface of the film.[1] It also eliminates the presence of SiO_2 in the aluminum-rich region after exposing the film to air, since SiO_2 formation is restricted to a few monolayers. This technique allows reliable Auger determination of the aluminum distribution in the silicon film.

In this work we present the X-ray diffraction patterns of the silicon films deposited on graphite and quartz. In our earlier work[1] silicon films deposited on quartz showed a highly preferred (111) orientation with the 220/111 peak intensity ratio of ca 10-20%. Transmission electron micrograph of the same films showed spot diffraction pattern which implied a lower limit of 5μ for the silicon grain sizes. Since the same deposition technique is used in both studies,[4] the degree of silicon preferred orientation from the 220/111 intensity ratio is taken as a measure of the crystallinity enhancement over the pure silicon films deposited on quartz at 600°C. The latter showed both a powder-like X-ray diffraction pattern, with 220/111 being ca. 60%, and diffused electron diffraction rings.[1]

Figure 1 shows the X-ray diffraction pattern for the silicon films deposited on graphite. Also shown is the X-ray diffraction of a Si film deposited on quartz which is obtained from the same experiment and is used as a reference. The 220/111 intensity ratio is ca 25% and 16% for the silicon films on graphite and quartz, respectively. Unpolished graphite was used in this case. Similar results were obtained using polished graphite substrates. These compare very well with the earlier work. Also seen in Fig. 1 is the (111) peak of aluminum which was not observed in our earlier work. This indicates the necessity of the described final silicon coating for the observation of aluminum. Auger depth profiles for the same films are shown in Fig. 2. Silicon film deposited on quartz shows a higher concentration of aluminum near the surface than in the bulk film. This confirms our earlier observation.[1] For the silicon film on graphite, the aluminum concentration stays nearly the same and is lower than on quartz. Also observed is the diffusion of both aluminum and silicon into the graphite substrate. Quantitative determination of the aluminum distribution in graphite is difficult due to the scattering of data and an uncertainty in the sputtering rate of graphite.

The aluminum distributions described above are consistent with the observation that the aluminum (111) peak is more clearly seen in the silicon film on quartz than in the silicon film on graphite. Carbon diffusion from the graphite substrate into the silicon film is also shown to be negligible from Auger profiling, in agreement with earlier work.[2] In several cases silicon

C.8

deposition was made with a different Si-Al-Si sandwich coating. Using a Si-Al-Si (100Å-500Å-100Å) sandwich coating, the silicon 220/111 intensity ratio was found to be similar to that using the Si-Al-Si (100Å-500Å-100Å) coating.

In summary, our results indicate that, using graphite substrates, an enhancement in silicon crystallinity can be obtained which ic omparable to that using quartz substrates. Carbon diffusion into the silicon film is shown to be negligible at a substrate temperature of 600°C. Silicon diffusion into the graphite substrate is also low compared with that at 1200°C substrate temperature.[3] Furthermore, graphite in the unpolished form gives enhancement in silicon crystallinity similar to that on polished graphite. This may prove to be a further favorable economic factor in using graphite as a substrate material for silicon thin film solar cells.

This work was supported by the U. S. Energy Research and Development Administration.

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1. C.-A. Chang, W. J. Siekhaus, T. Kaminska and D. T. Huo, Appl. Phys. Lett. 26, 178 (1975).
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4. This implies that the same mechanism of silicon crystallization from the Si-Al eutectic melt should be involved in both studies.

FIGURE CAPTIONS

Fig. 1. X-ray diffraction patterns for the silicon films deposited on (a) graphite, and (b) quartz, using the Si-Al-Si sandwich coating technique.

Fig. 2. Auger depth profiles for the silicon films deposited on (a) graphite (a) graphite, and (b) quartz, using the Si-Al-Si sandwich coating technique. Sputtering rate of the silicon films is ca 50Å/min for (a) and ca 30Å/min for (b).

Electron Energy Loss Spectroscopy of the Silicon (111) Surface

The motivation behind this study is mainly two-fold:

(1) In dealing with the usual bulk properties of solids, one always assumes having a crystal with translation symmetry so that one never has to worry about surface effects. However, when we study a specimen using a probe which is sensitive to a few atomic layers, or when we have a specimen which has a large surface-to-volume ratio such as a thin film or micro-particle, surface effects become important. It is therefore interesting to see what the effects are and how they differ from those of the bulk.

(2) In order for silicon solar cells to be economically competitive with conventional energy sources, we are forced to consider using thin silicon films because of high material cost. In using thin films, we are faced with several problems which lower the efficiency considerably, viz. (a) film-substrate diffusion, in which the substrate material can diffuse into the film and hence increases the resistive losses, (b) imperfections and grain boundary scattering and trapping and (c) dominant surface effects because of large surface-to-volume ratio. It turns out that the existence of the surface introduces surface states which can act as electron traps, thereby decreasing the conversion efficiency. Therefore, our aim is to remove all such surface traps. However, we cannot do this without a detailed knowledge of what these surface states are and where they are located in the band structure, because the effectiveness of a surface state as an electron trap depends critically on its location in the band structure. (In fact, the closer the state is to the mid-gap region, the more effective it is as a trap.) Once the location is known, we can then proceed on to introduce some impurities on the surface and study the effects of such impurities on the surface and study the effects of such impurities on the surface states. One such impurity we have studied is oxygen.

Experimental Procedures

The experiment was performed in an ion-pumped stainless steel ultra-high vacuum system, capable of reaching pressures of 2×10^{-9} torr or below. The specimen was a 2500 ohm-cm p-type silicon crystal oriented along the (111) direction, which was polished and degreased prior to introduction into the chamber. The loss spectroscopy was performed by PHI 15-25G Auger electronics at a primary energy of 100 eV with a resolution of approximately 1 eV. At a higher primary energy, we have a fairly good understanding of the energy loss process, but with a poorer resolution. The reverse is true for low primary energies. The present choice is considered to be optimum as far as the loss process, resolution, relative contributions from the bulk and the surface are concerned.

Two surface structures have been studies, viz. the disordered surface and the (2x1) surface. The former was obtained by argon ion bombardment whereas the latter was obtained by cleavage at room temperature. The loss spectra were observed as a function of exposure to oxygen, which was introduced to the system by means of a leak valve.

Results & Discussion

The results we obtained bear close resemblance to those of Rowe and Ibach on the silicon (111) — 7x7 surface. In Fig. 1, we show the loss spectra of the silicon (111) — 2x1 surface as a function of oxygen exposure. On the clean surface, bulk and surface plasmons were observed at loss energies of 16.5 eV and 10.6 eV respectively. The 5 eV transition is possibly a bulk transition. Three surface state transitions were observed, viz. S_1 at 2.5 eV, S_2 at 7.4 eV and S_3 at 14.5 eV, which were also found on the Si(111) — 7 x 7 surface, at slightly different energies. The S_o transition at ~0.6 eV as seen in high resolution energy[2] loss spectroscopy is lost in the elastic background; however, according to a recent theoretical calculation on the 2 x 1 surface the S_o and S_1 transitions have similar initial states and are therefore directly correlated. By exposing the surface to oxygen, the S_1 and S_3 transitions practically disappear

at a coverage of 0.1 monolayer, while S_2 increases. Combination with UPS data shows that this is probably due to an oxygen transition. At a coverage of 0.5 monolayer, the plasmon peak splits and this is clearly observable at $\theta = 0.65$. The effect was explained by Rowe and Ibach[3] as due to an oxygen transition close to the surface plasmon peak. One also notices a continuous shift of the bulk plasmon peek towards higher energies at increasing oxygen coverage. At the same time, a loss peak at 3.3 eV appears and becomes well established at monolayer coverage. This can also be attributed to an oxygen transition.

The loss spectrum obtained on the clean disordered silicon (111) surface is identical to that obtained by Rowe and Ibach.[3] The variation of the spectrum as a function of oxygen exposure is similar to that on the (2x1) and (7x7) surfaces, except for one important difference, viz. the plasmon splitting is observable at a much lower coverage of ~0.1-0.2 monolayer. According to the dielectric theory, this is probably due to the larger energy for the oxygen transition (11.5 eV instead of 11 eV on the 7x7 surface). This is physically reasonable because both on the (7x7) and (2x1) surfaces, the structures are relaxed to have stronger back-bonds, leaving a positive weaker potential (due to the silicon ion) on the vacuum side of the interface. Therefore, ELS gives us further information on the relative potential strengths under different surface conditons.

Future Studies

From these studies, one observes that on the disordered and the (2x1) surfaces one monolayer of oxygen is very effective in removing surface states and the states it introduces are deep in the valence band. The only drawback is that the Si-O system is not very stable. Stabilization by further oxidation is possible, but will pose difficulties in making electrical contacts to the surface, which are necessary in solar cell fabrications. So, we are now diverting our attention toward the Si-Al system. Aluminum, besides being a conductor and a dopant, has been used successfully to enhance crystal growth of silicon films at 600° C,[4] and is therefore an interesting material to pursue.

At the same time, we are looking into the possibility of using LEED rotation diagrams as a means of locating surface states, both occupied and empty in the band structure, by using a recent theory on the effects of surface states on LEED measurements.[5] This, together with the results from ultraviolet photoemission studies will give us a complete picture of the surface states in silicon, of different surface structures and with different adsorbates.

References

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Phosphorus Segregation in Single Crystal Silicon

A 1 in. diameter, p-type, 2.5K Ω-cm silicon single crystal wafer was diffused at 1000° C with phosphorus for 14 hrs. The source was an Emulsitone spin-on solution providing a surface concentration of about 10^{20} p/cm^3. After diffusion the wafer was cooled in air, then etched in phosphor-silica etch (1:1:30, HF:HNO_3:H_2O).

The sample was thereafter placed into an ultra-high vacuum system and outgassed by heating to 800° C for 1 hr. After heating, the surface was sputter etched at room temperature until the auger spectrum no longer changed with time (Fig. A). This spectrum shows the presence of SiO_2, Si, C, and O.

The sample temperature was raised to 800° C in less than one minute and held at this temperature for 4 min. Auger scans for phosphorus were taken at intervals during the temperature treatment (Fig. B). The sample was cooled and a final auger trace made (Fig. C).

Figure B shows the phosphorus signal as a function of time and temperature. It indicates 1) that phosphorus segregates to the surface and 2) that the equilibrium concentration of phosphorus on the surface is a function of sample temperature. Figure C shows the increased phosphorus signal but no other changes.

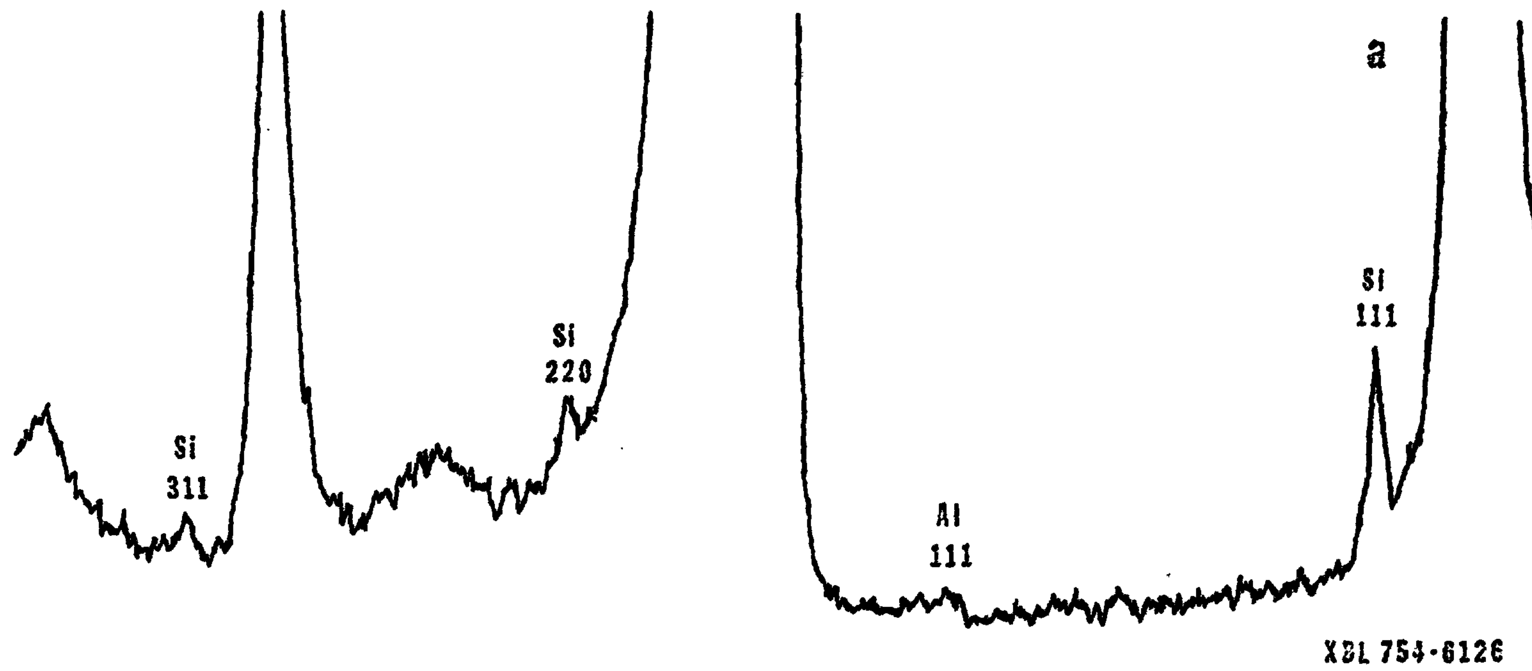


Fig. 1

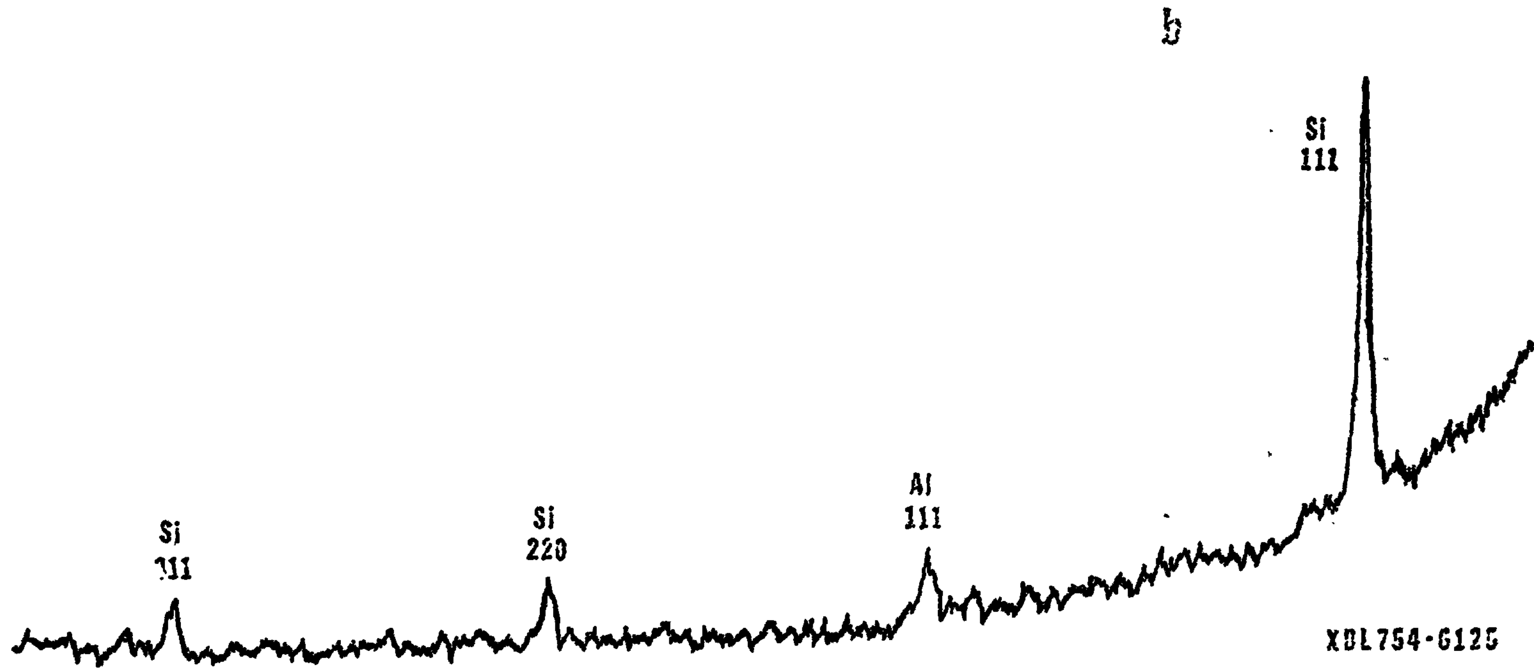


Fig. 1 cont.

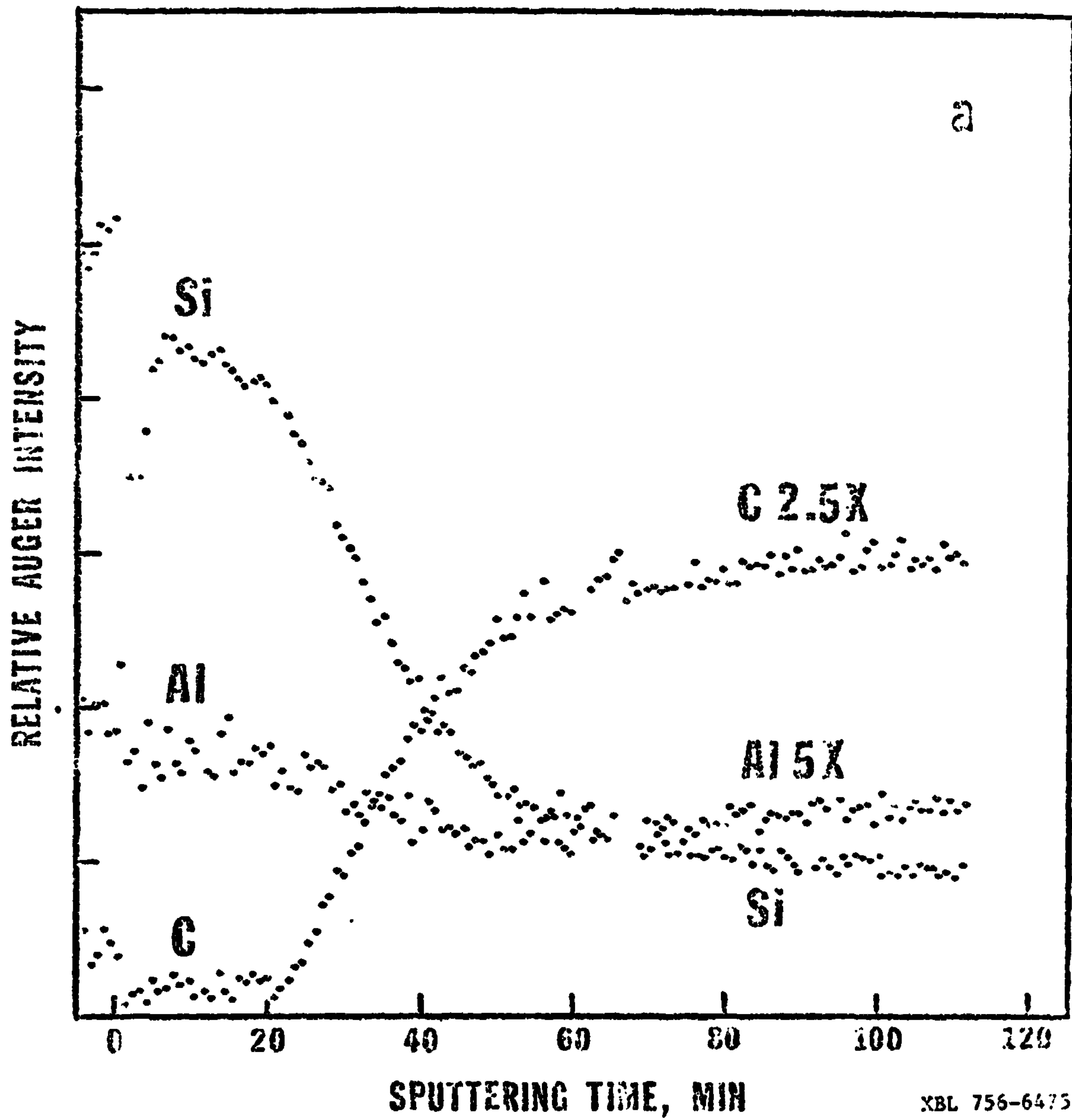


Fig. 2

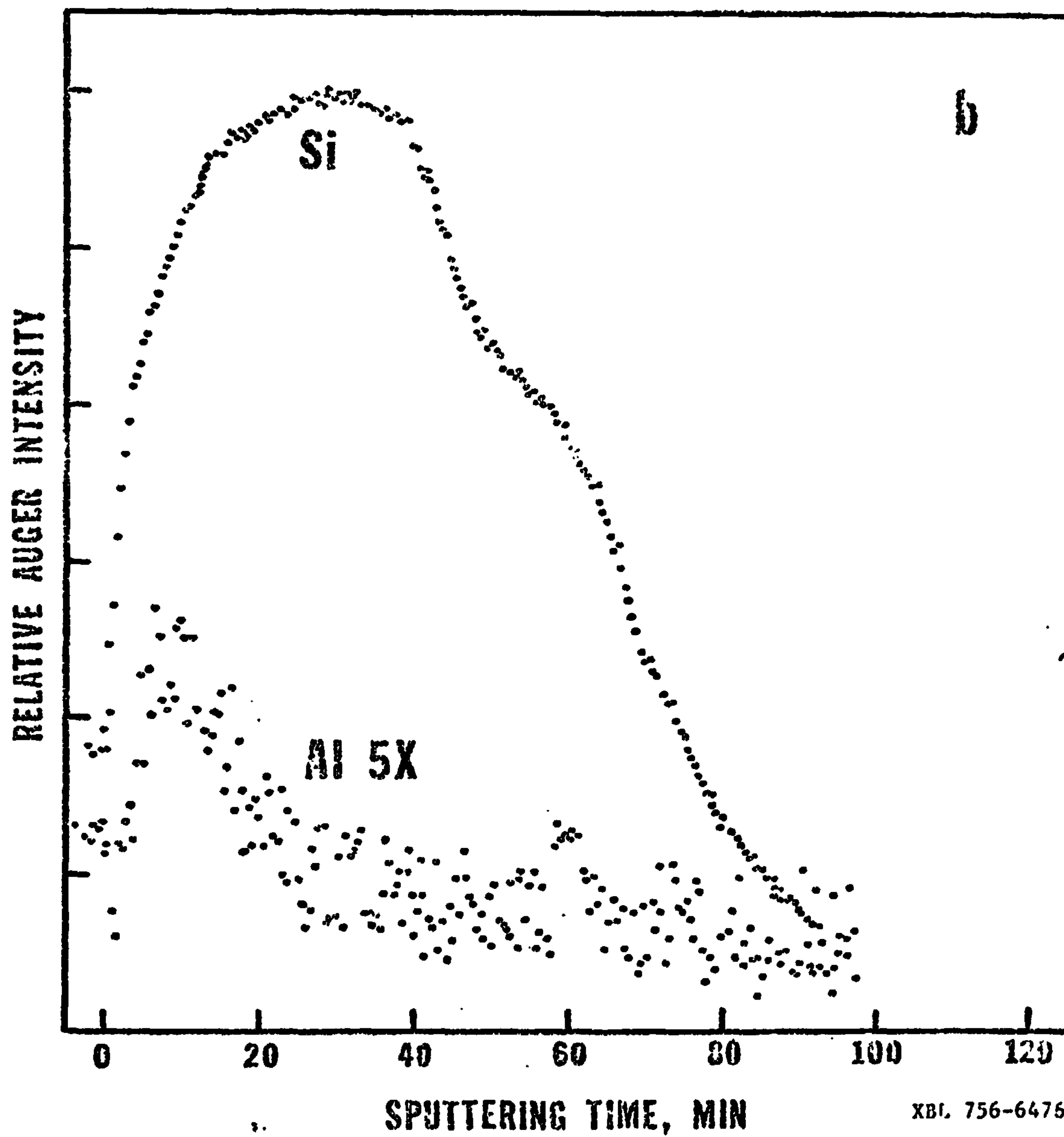


Fig. 2 cont.

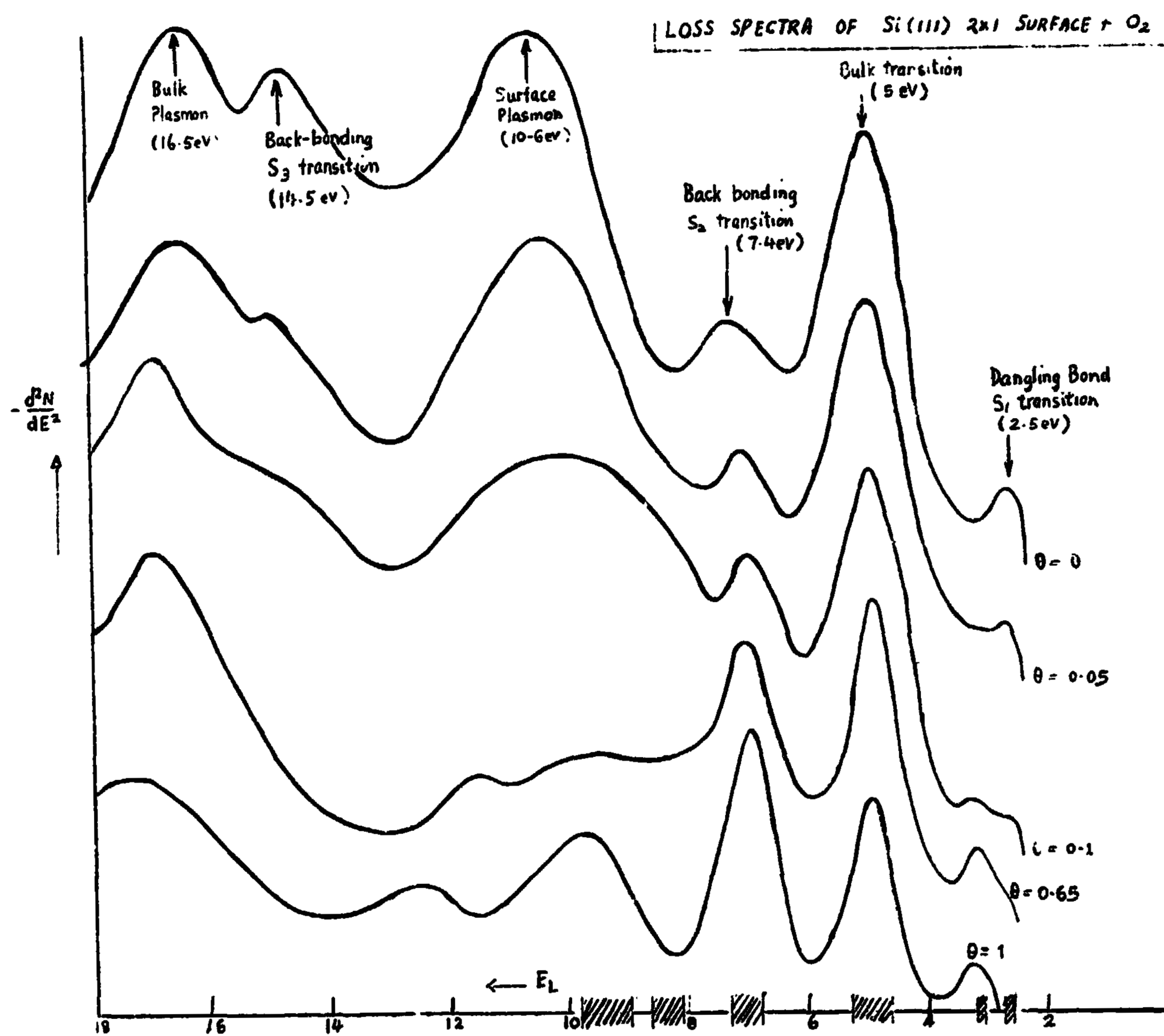
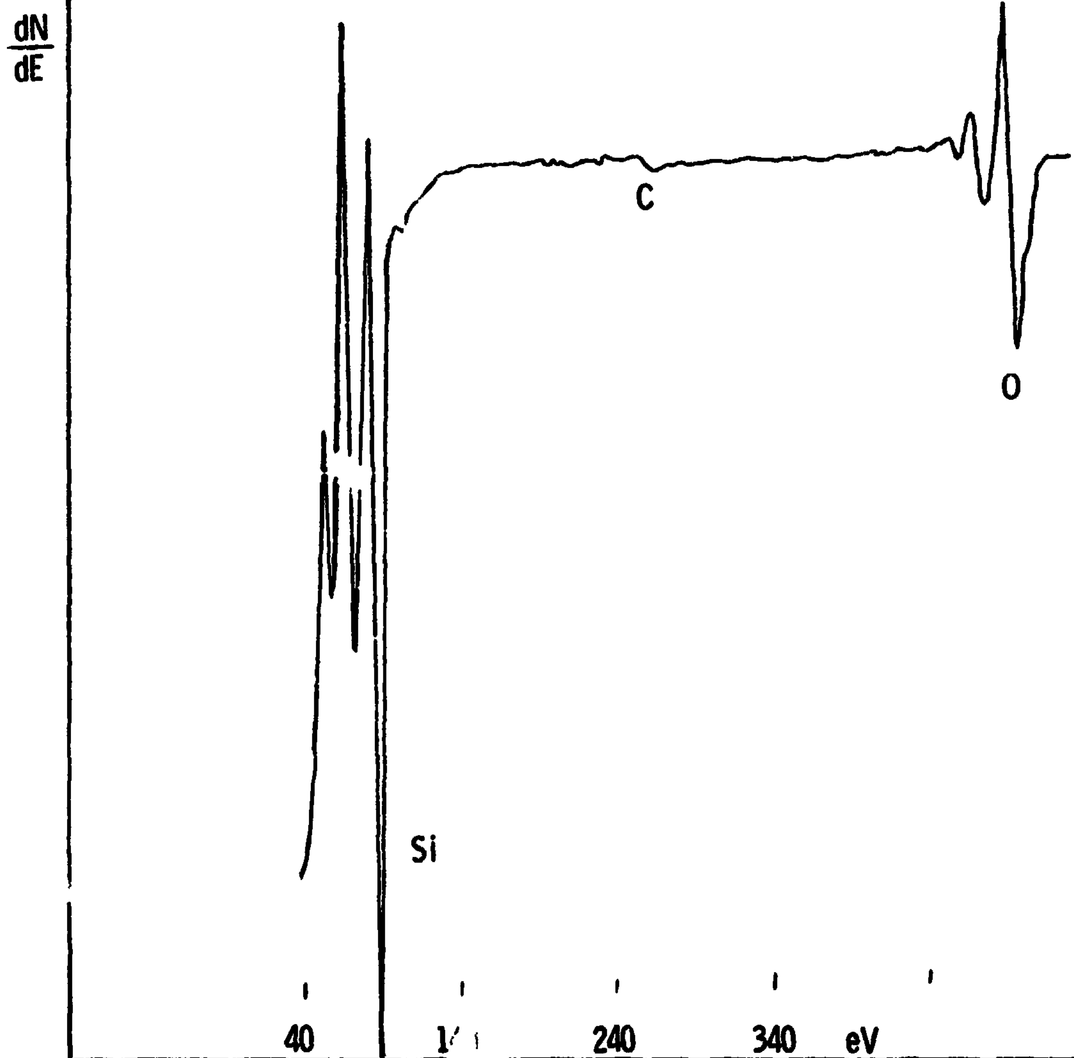

LOSS SPECTRA OF Si(111) 2x1 SURFACE + O2
Bulk Plasmon (16.5ev)
Back-bonding S3 transition (14.5 ev)
Surface Plasmon (10.6ev)
Bulk transition (5 eV)
Back bonding S2 transition (7.4ev)
Dangling Bond S1 transition (2.5eV)
θ = 0
θ = 0.05
θ = 0.1
θ = 0.65
θ = 1
E_L
18
16
14
12
10
8
6
4
2

FIG A.

AUGER SPECTRUM OF SPUTTERED SURFACE



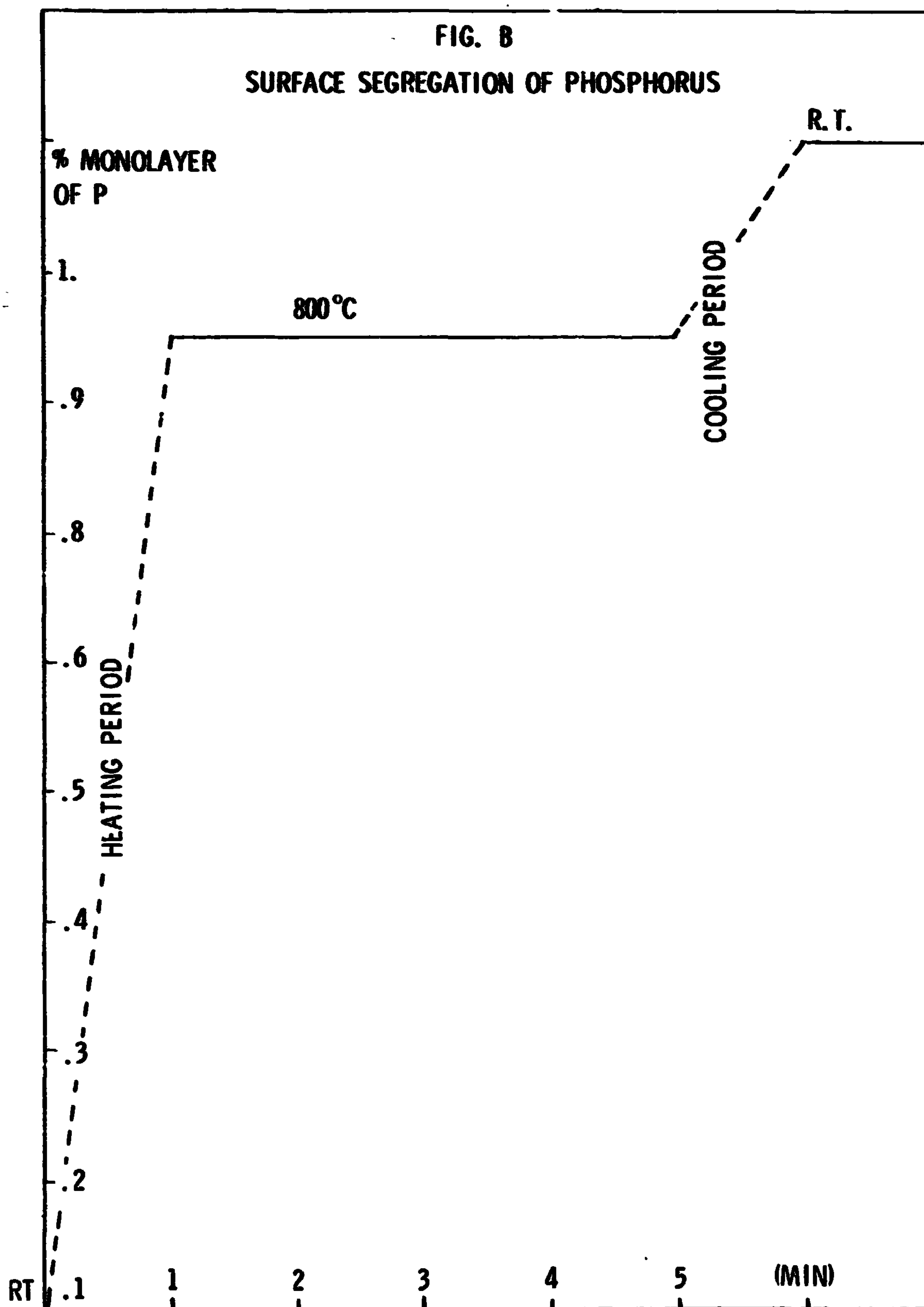


FIG. B
SURFACE SEGREGATION OF PHOSPHORUS
% MONOLAYER
OF P
R.T.
800°C
COOLING PERIOD
HEATING PERIOD
1.
.9
.8
.6
.5
.4
.3
.2
RT
.1
1
2
3
4
5
(MIN)

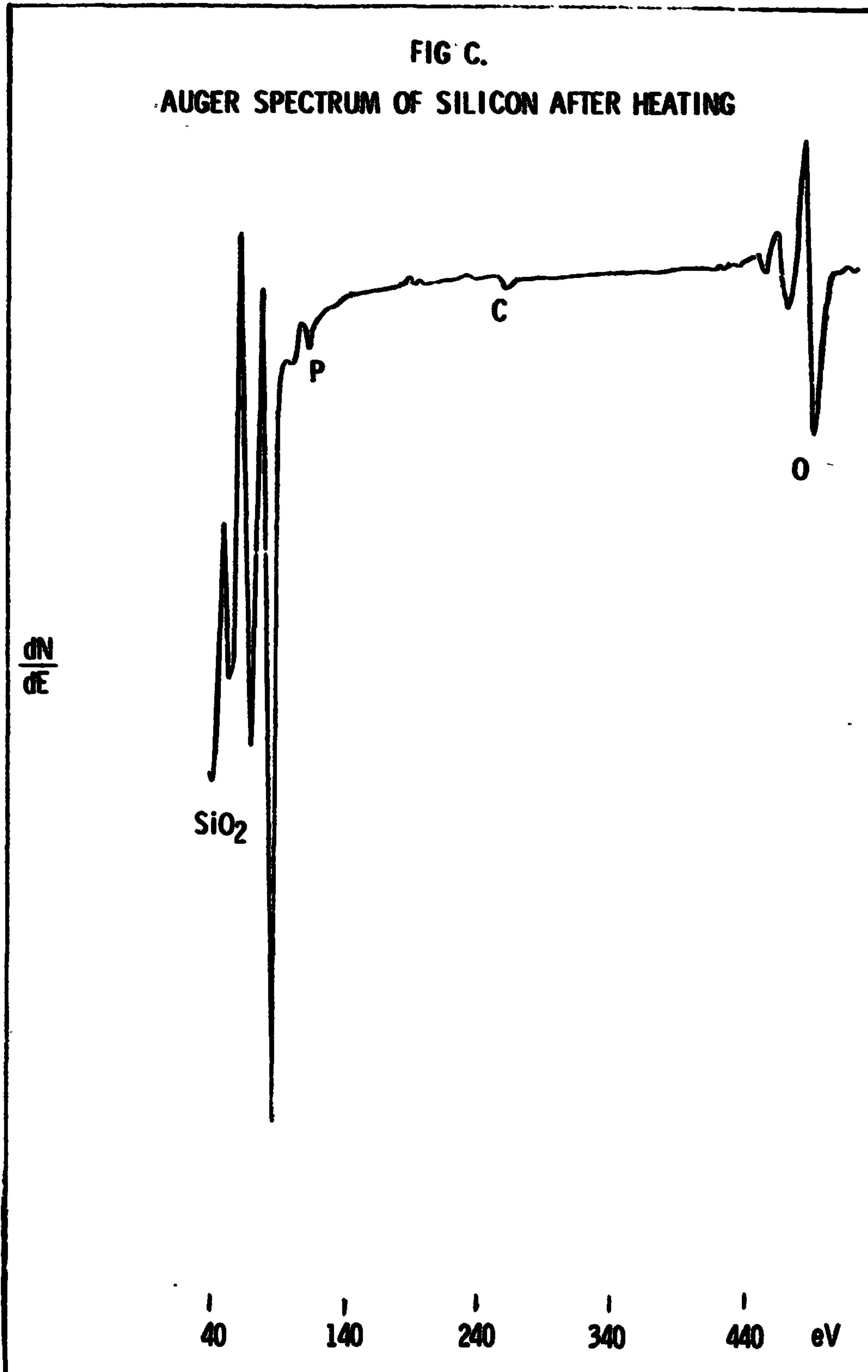


FIG C.
AUGER SPECTRUM OF SILICON AFTER HEATING
P
C
O
dN/dE
SiO2
40
140
240
340
440
eV

WORK PLAN

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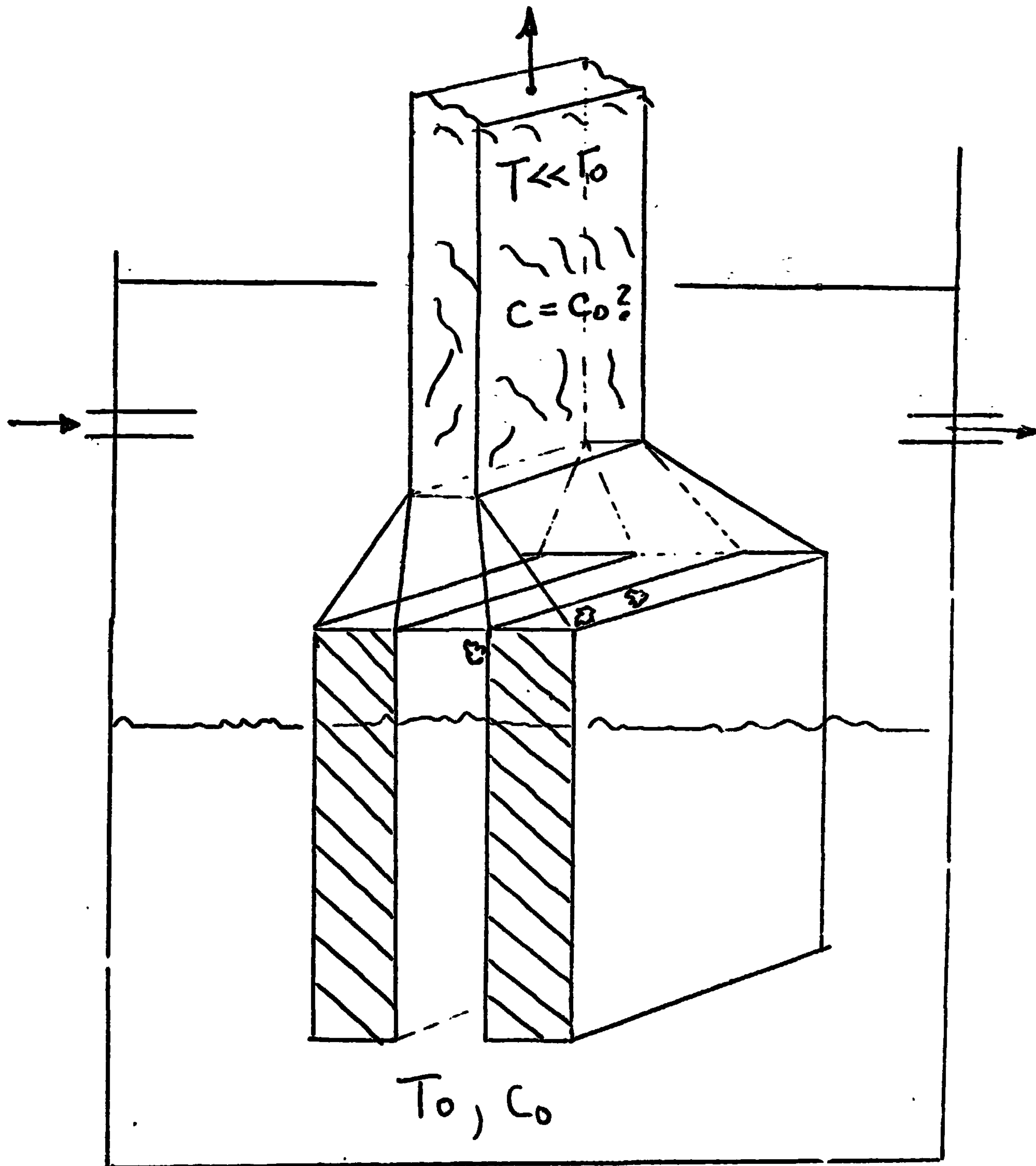
WORK AREA	ACTIVITY	GOAL
CATALYSIS OF CRYSTALLIZATION	LEED intensity /vs time at given temperature as f(surface impurity)	Determine activation energy for recrystallization as f(impurity)
	Modify evaporation equipment to allow clean deposition.	
Catalysis of CVD	Deposition rate as f(surface charge)	Low Temperatrue CVD
	Reaction kinetics by modulated molecular beam analysis	Identify critical steps in deposition reaction
	Dopant impurity concentration and distribution at the surface during deposition	Surface charge??
Grain Boundary	Fracture?	What is at grain boundaries?
	Free surface impurity segregation	
Surface States	Install UV system	Surface states as a function of dopant in the energy gap. Absolute energy location.
	Install monoenergetic e- source	
	Analyze single crystal surface plus dopant.	

NLAFSKY'S MA[illegible]E



I would like to make a comment on an item listed under prog objectives: the influence of surfaces on sheet formation.

EFG - like processes clearly place a very strong emphasis onto an unstable and little understood region: the meniscus, and consequently a majority of present ERDA deadlines teeter and wobble with the rise and fall of the meniscus from the High Meniscus Mode (HMM) to the Low Meniscus Mode (LMM).

The form and the stability of the meniscus depend critically on surface tension, a phenomenon delicately depending on surface composition and chemistry. Surface composition at this point will be fluctuating and unpredictable, since all the impurities dissolved in the melt want to segregate out at this point, where there are but two places to go to the surface and to the interfaces (twinning) which the ribbon probably creates for itself to store away the excess impurities which it cannot segregate onto the surface, and which it cannot reject into the remaining liquid through the bottleneck of the capillary.

If my surface science perspective is correct, then

1) the sheet surface is high in impurities (SiC crystals are growing there)

2) the twinning surfaces are high in impurities (Dr. Mlávsky's SEM data indicate this)

3) significant progress will come in size stability and sheet crystallinity if the EFG process is run in an atmosphere capable of removing at the meniscus surface any impurities that might be segregating there. Under these clean surface conditions a stable surface tension would be established. It should be easier to produce a thin (100 μ) film than a thick one, because the very property of the surface, to segregate impurities, has been turned to a constructive advantage.

I certainly would not treat lightly the question raised by Joe Morabito, whether not any starting material of higher impurity might wreck the EFG process entirely, unless one takes the position that things cannot possibly get worse than they are.

I make this point: processes and products of high surface to volume ratio are controlled by surface effects.

RIBBON STARTS

impurities segregate, but return to melt is blocked

in contrast to Czochralsky, ribbon impurity concentration=melt conc.

IMPURITIES SEGREGATE ONTO MENISCUS SURFACE

Surface tension changes, Meniscus changes shape. Surfaces saturates

Bulk saturates, reliefs by creating large number of grain and twin

boundaries onto which impurities can be deposited. And SiC grains .

Repeat.

periodic fluctuations in shape, crystal perfection and impur

(Kressel et al.) Boundaries loaded with impurities (Mlafsky's [illegible])

C U R E

Zone refining process with impurity removal from surface.

Choose large surface to volume ratio (100) and [illegible], and purge

with corrosive gas.

Do not try dirty silicon.

Meniscus stable

Purity stable

ERDA stable.

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OF POOR QUALITY

WORK PLAN

WORK AREA	ACTIVITY	GOAL
SURFACE TENSION	Measure surface tension as f(surface concentration of impurities)	Know thy meniscus
SURFACE SEGREGATION	Measure surface impurity concentration as f(bulk concentration) and f(temperature)	Keep the meniscus clean and produce good ribbons. Investigate EFG - Surface segregation purification process. (EFG _SSPP)
Surface Chemistry	Measure surface concentration at molten Si surface as f(background gas)	