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SILICON SHEET WITH MOLECULAR BEAM EPITAXY FOR HIGH EFFICIENCY SOLAR CELLS

First Annual Report for period 3/22/82 - 3/21/83

by

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Table of Contents

List of Figures

Silicon Sheet with Molecular Beam Epitaxy
for High Efficiency Solar Cells

1. Objectives of Program

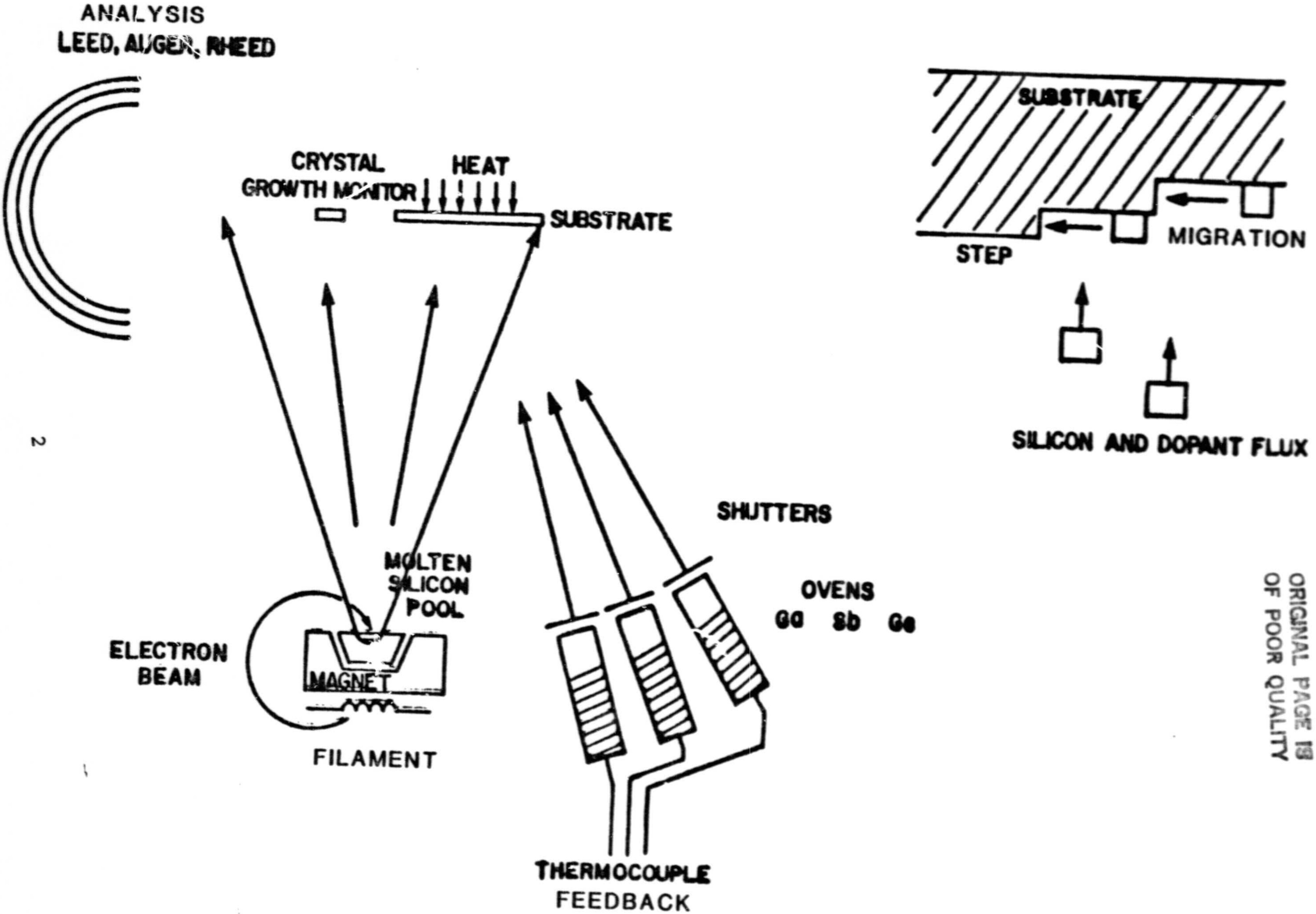
The goal of this program is to apply the capabilities of the new technique of Molecular Beam Epitaxy (MBE) to the growth of high efficiency silicon solar cells. Because MBE can provide well controlled doping profiles of any desired arbitrary design, including doping profiles of such complexity as built-in surface fields or tandem junction cells, it would appear to be the ideal method for development of high efficiency solar cells.

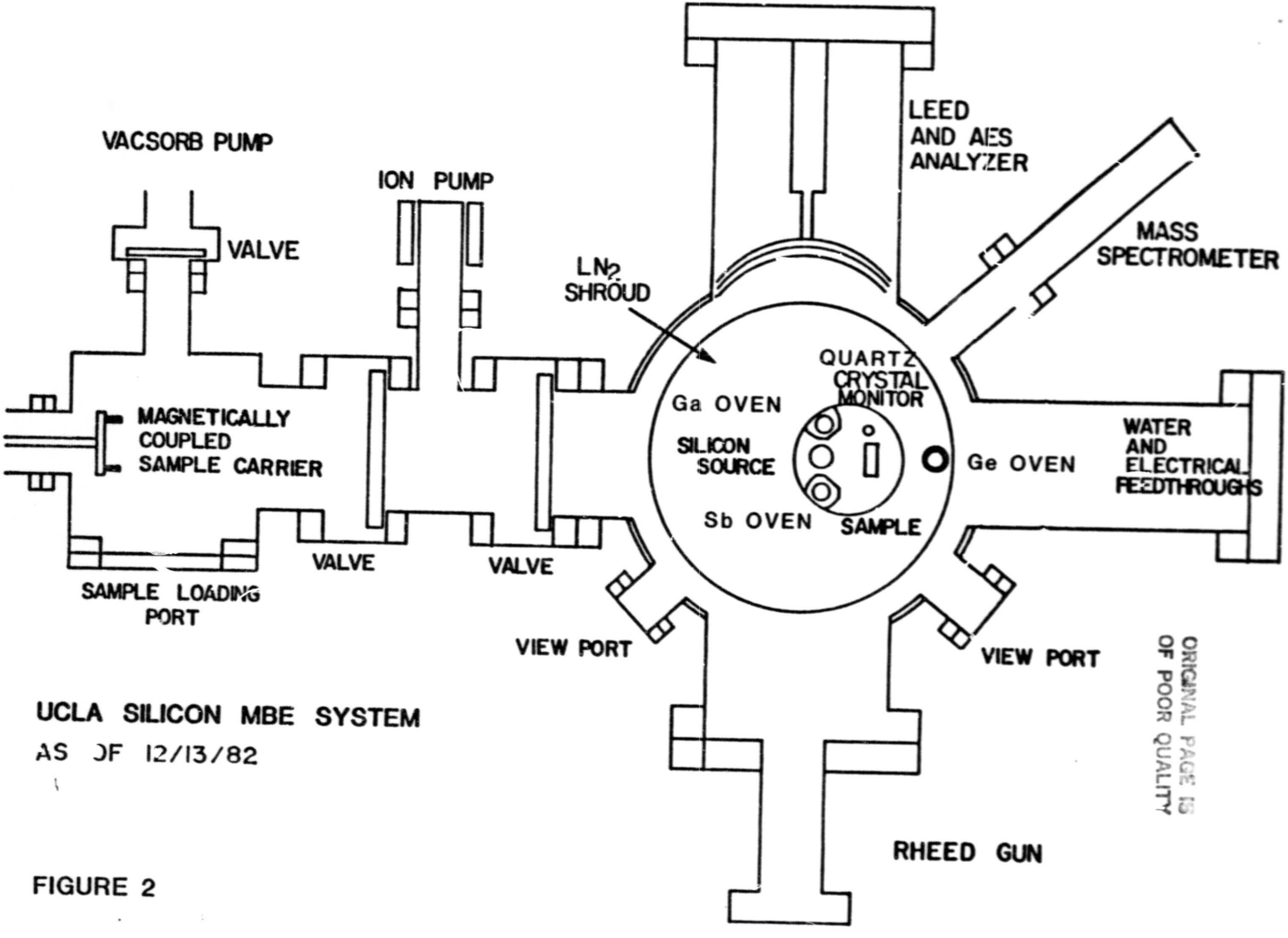
For the first year it was proposed that UCLA grow and characterize silicon films and p-n junctions by MBE to determine whether the high crystal quality needed for solar cells could be achieved. The results have been mixed as described below. One cannot yet predict the answer.

2. Technical Activity During the First Year

The UCLA MBE System (1,2) consists of a modified stainless steel Varian station with vac-ion pumps and titanium gettering and is capable of sustaining a base pressure of 5×10^{-11} Torr (see Figs. 1 & 2). Surface analysis includes low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and quadrupole mass spectroscopy used both for detection in desorption studies and for residual gas analysis. Silicon is evaporated from a molten pool of pure Si in a molybdenum crucible by means of a 6-KW electron bombardment gun. Ga and Sb beams are generated by resistively heated pyrolytic boron nitride effusion cells. The electron gun and effusion cells are housed in a liquid nitrogen shroud.

FIGURE 1 PROCESS SCHEMATIC OF SILICON MBE GROWTH





UCLA SILICON MBE SYSTEM

AS OF 12/13/82

FIGURE 2

Typical operating pressures during Si growth are 3 x 10^{-9} Torr.

Samples are inserted into the chamber via a load-lock with sample insertion time from atmospheric pressure to start of run on the order of one hour. The silicon substrate has been held between molybdenum clips and resistively heated (see Fig. 3). Atomically clean starting surfaces as determined by LEED patterns are typically produced by heating the Si substrate to 1200°C for one to two minutes. Auger analysis has disclosed no surface impurities other than some residual carbon, sometimes present at a small fraction of one monolayer.

A new radiatively heated sample holder to take 2" diameter wafers has been designed and is being put into use. This should completely eliminate mechanical stress as a source of dislocations during crystal growth. This is shown in Fig. 4.

Before the JPL grant was awarded, UCLA and JPL had already begun collaboration on this project. UCLA grew an MBE undoped layer about 0.6 microns deep on an n^+ (111) substrate supplied by JPL, (Sample S0102 MBE). JPL analyzed this by profilometer (5000 Å thick film), SEM and EBIC, using a Schottky diode contact. Lifetimes in both film and substrate were too short to detect any useful results.

A. <u>MBE Growth of Films - First Group</u>

On April 15, 1982, JPL provided UCLA with a group of high quality silicon samples as substrates for MBE growth. These were (100) samples, p-type, Boron doped at about 1-2 ohm - cm with good lifetimes and with diffusion lengths checked at JPL using the SPV technique to be of the order of 100 microns. Samples were cut to size at JPL: 1 cm x 3 cm x 0.04 cm.

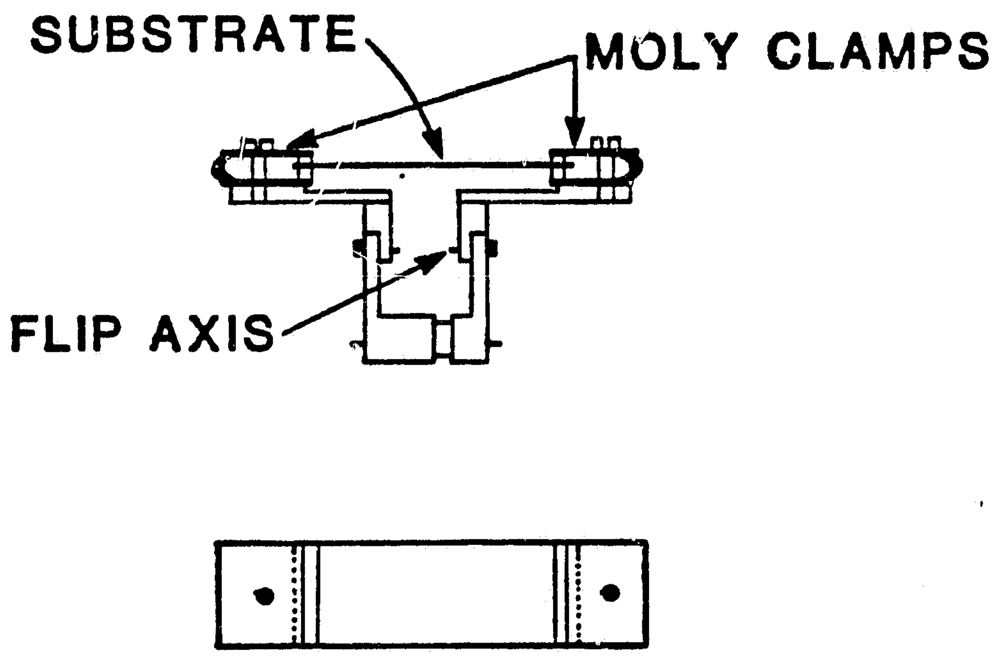


Figure 3   Resistively heated substrate holder

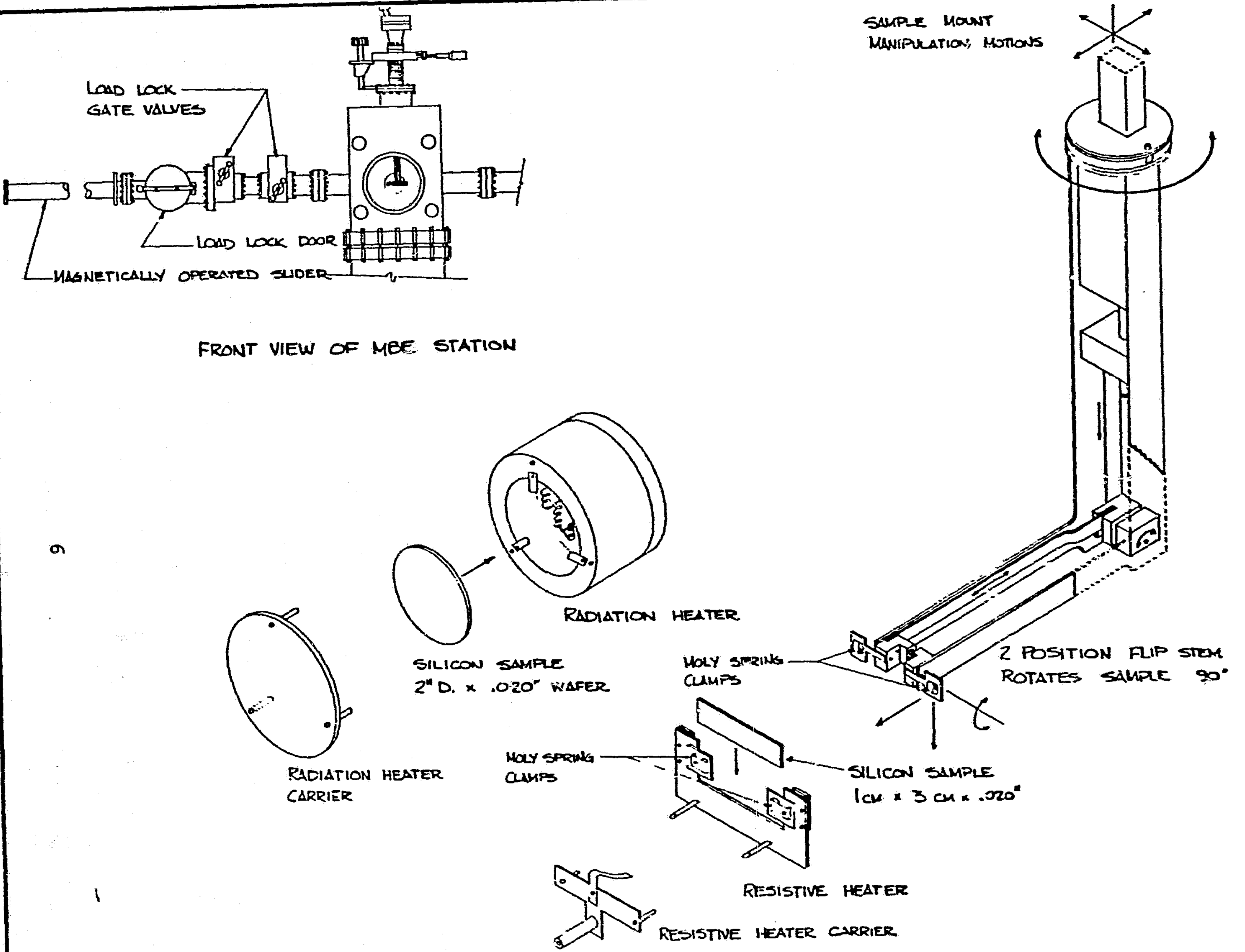


FIGURE 4 SAMPLE MOUNTING, HEATING, POSITIONING, AND CHANGING. UCLA SILICON MBE SYSTEM

UCLA cleaned the first of these, labeled MBE #7, by heating it for one minute at 1250°C in ultra-high vacuum, the standard UCLA cleaning before MBE growth begins.

UCLA cleaned sample MBE #8 this same way in high vacuum, then grew an MBE film about 1 micron thick doped with Sb, forming an n-p junction on the p substrate.

UCLA cleaned sample MBE #9 the same way as for MBE #8, then grew an Sb doped n-film producing an MBE grown n-p junction on the p-substrate.

B. Solar Cells Fabricated at JPL

JPL diffused n-layers about 0.35 microns thick into sample MBE #7 and into control samples MBE #1 and MBE #12 (both of which never went to UCLA) evaporated Ti-Pd-Ag contacts on all five samples (#1, #7, #8, #9, #12), and made solar cells from all of these five samples with no AR coating.

C. Results of the Fabricated Solar Cells

1. The diffusion lengths in two of the three substrates (MBE #7, #9) cleaned by UCLA at 1250°C remained high ($\sim$ 100 μ) as evidenced by the SPV measurement results.
2. The following table shows that the solar cell made from the UCLA MBE sample #9 with a grown n- on -p junction could be measured but had very poor performance compared to samples MBE #1 and MBE #12 made entirely at JPL. (Table 1)
   (MBE #8 developed a short during metallization and sintering of the back contact.)

Table 1

	UCLA MBE #9	JPL MBE #1 + #12
Jsc	27 ma	40 ma
Fill Factor	0.55	0.8
Voc	0.38 volts	0.56 volts
Efficiency	2.8%	6.7%

Samples MBE #1 and MBE #12 suffered a loss in diffusion length during processing at JPL; but even though they were not good cells they had much lower reverse leakage than the UCLA treated cells.

D. SIMS Analysis at JPL of MBE #8, #9

A secondary ion mass spectroscopy (SIMS) analysis carried out at JPL of portions of samples MBE #8 and MBE #9 revealed the following (see Figs. 5 and 6):

1. The Sb doping level in both MBE #8 and #9 rose gradually from the beginning of the MBE films and increased by a factor of ~ 6 during film growth in #8, less in #9. Neither sample had a good level plateau with abrupt onset as designed.
2. Carbon contamination appeared as a "spike" at the substrate-Epi interface for #8 and both carbon and oxygen were measurable throughout the two epi films and in the portions of the substrate sampled. The spike is significant in showing that part of one mono-layer of carbon was still present on the cleaned surface when growth began. (Later Auger studies have confirmed the presence of carbon at the interface and have shown that carbon can be removed by argon ion bombardment.)

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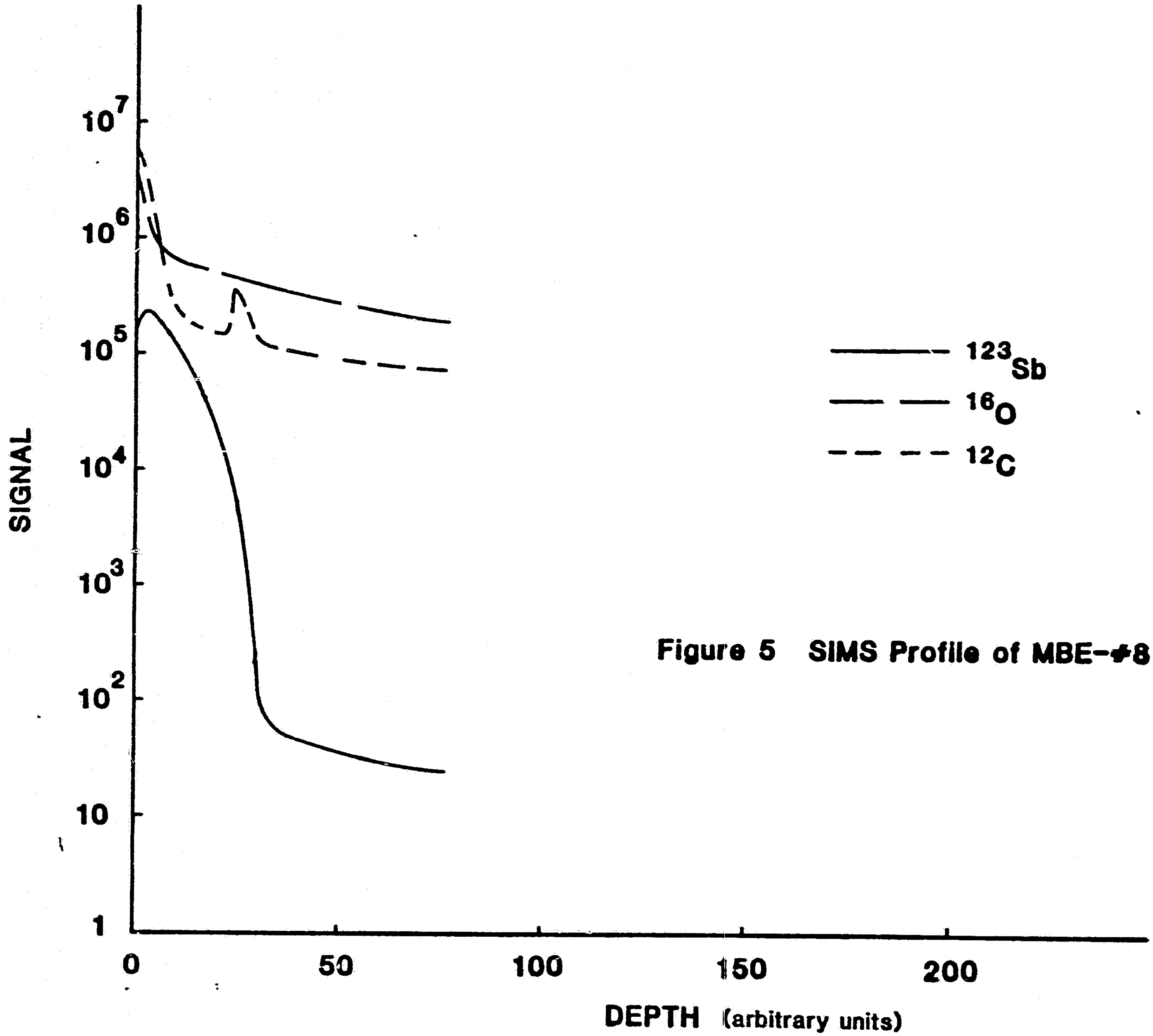


Figure 5 SIMS Profile of MBE-#8

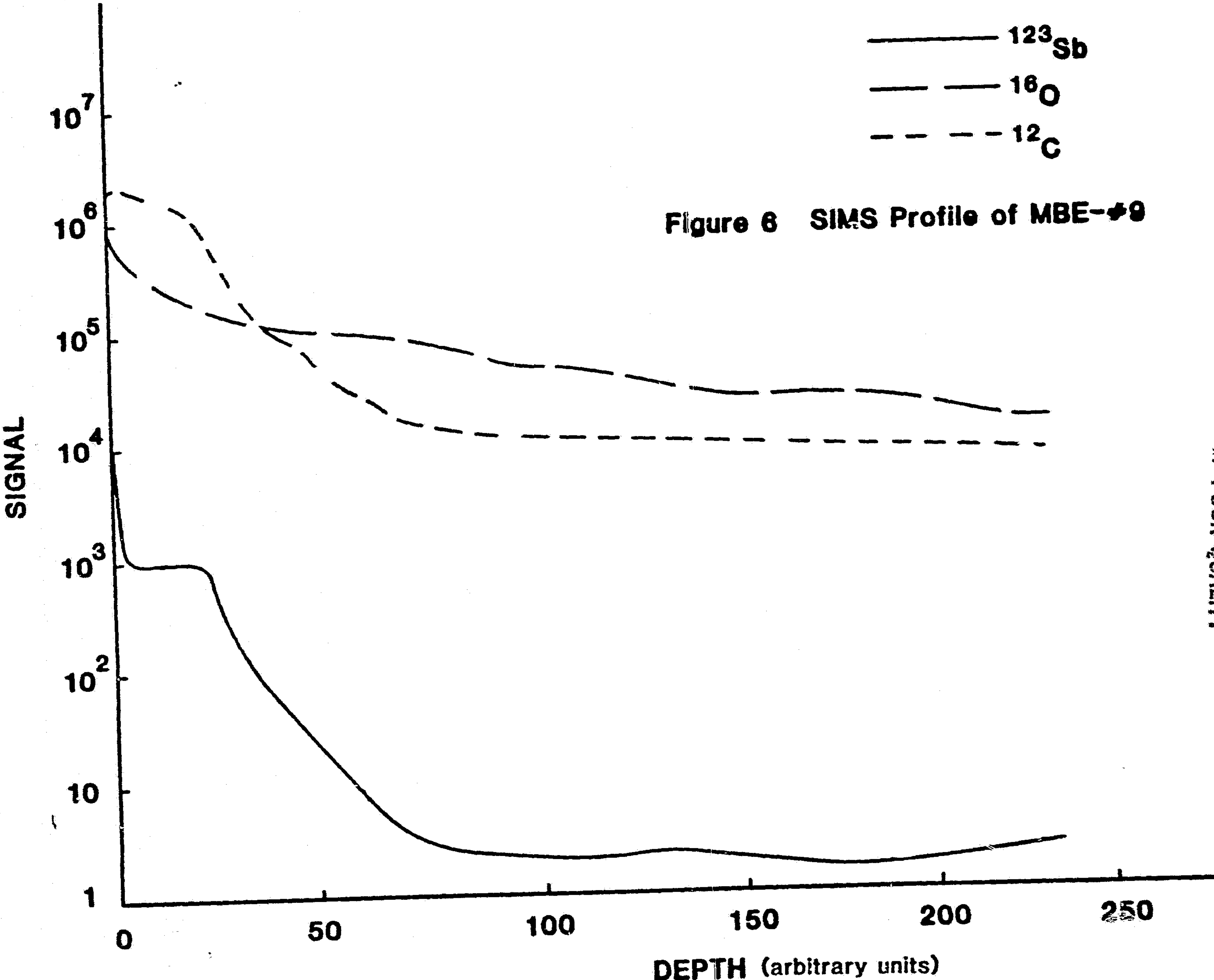


Figure 6 SIMS Profile of MBE-#9

E. JPL SIMS Analysis of UCLA Si-Ge Films

Subsequent SIMS analysis by JPL of several films grown by MBE at UCLA containing Ge as an alloy with Si or pure Ge on Si, have shown that a carbon spike at the interface occurred in all cases when Si MBE growth began, but was missing when pure Ge MBE growth began. This suggests that the e-gun filaments used to heat the silicon or the silicon crucible may be the source of carbon, since the Ge was evaporated with much lower power from a heated boron nitride effusion cell.

F. Silicon MBE Diodes - Reverse Characteristics

In a related program* carried out at UCLA during this same period (12/29/82) in which the goal was to make good Si mm wave diodes by MBE, Si MBE diodes were grown and a matrix of 10 mil mesa diodes that covered the entire sample surface was produced by etching. By analyzing the reverse leakage current and breakdown voltage over the matrix of diodes, it was found that the center portion of the sample had the predicted breakdown voltage (12 volts) and reasonably good reverse leakage currents, of $\sim 10^{-7}$ amps for a reverse current density of $\sim 10^{-3}$ amps/cm^2. Really good diodes, however should be at least 100 times less than this. Near the ends of the sample held by the molybdenum spring clamps, where local high temperatures and thermal mechanical stresses exist, the diodes were badly degraded, showing the action of dislocations in the substrate and/or MBE grown film.

It has now been recognized that the reverse leakage current in such mesa diodes is a very sensitive test of both crystal quality (dislocations) and lifetime killing impurities and generation centers near the interface. The best diodes grown by MBE at UCLA

*U. S. Air Force, WPAFB.

still had a reverse leakage current two to three orders of magnitude higher than expected for high lifetime material. Derived effective lifetimes near the junction for the MBE diodes were $\sim 10^{-9}$ secs, compared to 10^{-6} secs to 10^{-5} secs for good diodes.

Si-diodes are now being grown at frequent intervals during the MBE schedule and tested for reverse leakage current.

It is believed that the high reverse leakage is due either to excess dislocations, or to an unknown deep level impurity such as Cu, Ni or Fe that may be getting incorporated during growth.

The dislocations should be greatly improved by the new radiation heater described above and shown in Fig. 4.

We expect that SIMS analysis by JPL may disclose whether or not the above deep level impurities are present in the films. If so, we should be able to find their source in the vacuum system and eliminate them.

G. Dislocations as Revealed by SEM and Etch Pits

SEM and etch pit studies of MBE grown films have also been carried out at UCLA to look for dislocations. We have found high dislocation densities ($>10^{5}cm^{-2}$) near the spring clamp ends and where n^+ Sb films have been grown. We have not found significant densities elsewhere, ($<10^{3}cm^{-2}$).

H. High Purity Undoped Si MBE Films Grown

In a related program in which we are growing very pure high resistance films for Rockwell, Rockwell was unable to find any dislocations in the 0.6 micron MBE films UCLA supplied them, using an etch technique for thin films.

In terms of background doping levels, it is also encouraging that UCLA has grown undoped films for Rockwell with as low as 10^{13} cm^{-3} net donors or acceptors.

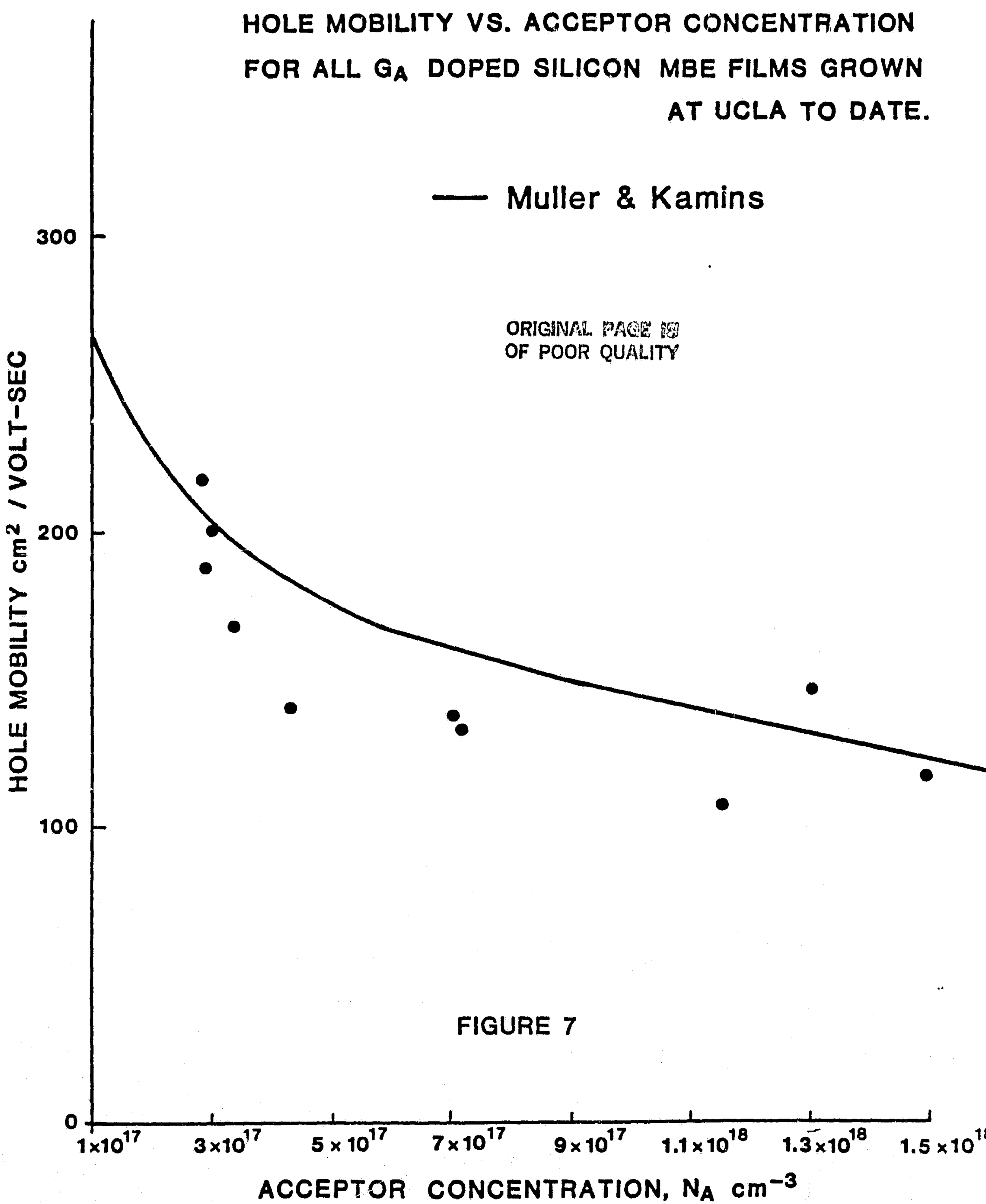
I. Mobility of UCLA MBE Si Films

During this year UCLA has acquired a Hall measurement system and has now measured the mobility of its MBE grown silicon films over a wide range of n-type (Sb) and p-type (Ga) doping. The results are shown in Figs. 7 and 8. Mobility in the MBE films is equal to good reported bulk values over the intermediate doping ranges for both n and p, but may fall below these bulk values at very low doping levels. Mobility definitely falls below the bulk levels at Sb levels above $2 \times 10^{18} cm^{-3}$. At this high Sb level values may be as little as 1/2 that of good bulk levels. We also have SEM evidence of poor crystalline quality at these high Sb levels. Fig. 9 illustrates two SEM views of MBE grown Si films doped at $7 \times 10^{17} cm^{-3}$ with dislocations.

The above values of mobility set some upper limits of dislocations in our intermediate range of doping: namely, we could not have over 10^3 to 10^4 dislocations cm^{-2} without degrading mobility(3).

J. Progress in Determining Sb Doping Kinetics

During this same year, R. Metzger at UCLA has finished a Ph.D. analysis of the kinetics of Sb behavior on silicon during MBE. As a result of his findings, we now know how to avoid the transient doping levels seen by SIMS in MBE #8 and #9. Metzger's findings(4), to be published, with those of S. Iyer(1) which determined the kinetics of Ga doping during Si MBE, give us the knowledge to produce good doping profiles without transients for either n- or p-type, at least up to the $10^{18} cm^{-3}$ level, while retaining good crystal quality.



HOLE MOBILITY VS. ACCEPTOR CONCENTRATION
FOR ALL G_A DOPED SILICON MBE FILMS GROWN
AT UCLA TO DATE.
Muller & Kamins
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HOLE MOBILITY cm² / VOLT-SEC
300
200
100
0
1×10^17
3×10^17
5×10^17
7×10^17
9×10^17
1.1×10^18
1.3×10^18
1.5×10^18
ACCEPTOR CONCENTRATION, N_A cm^{-3}

FIGURE 7

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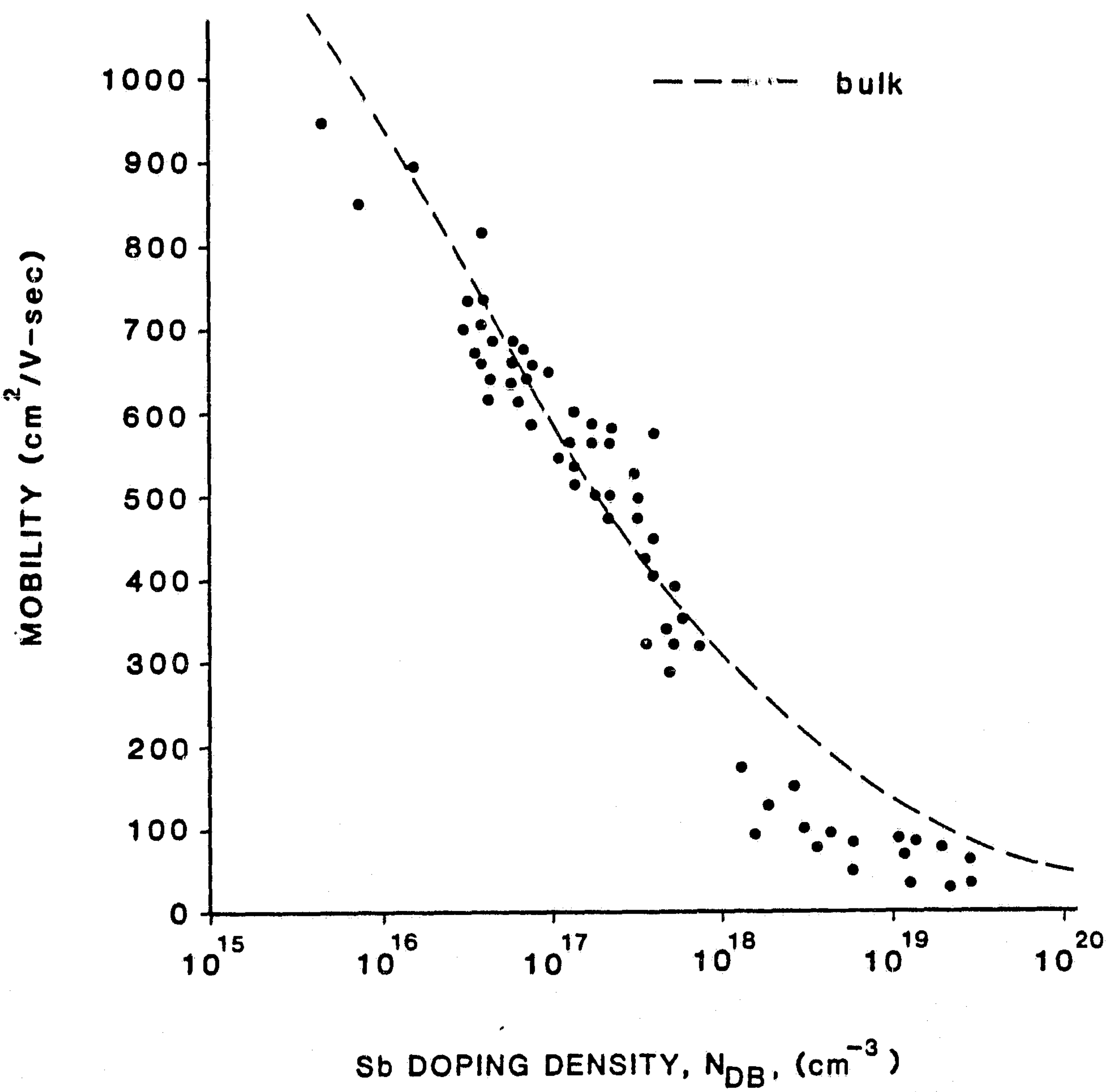
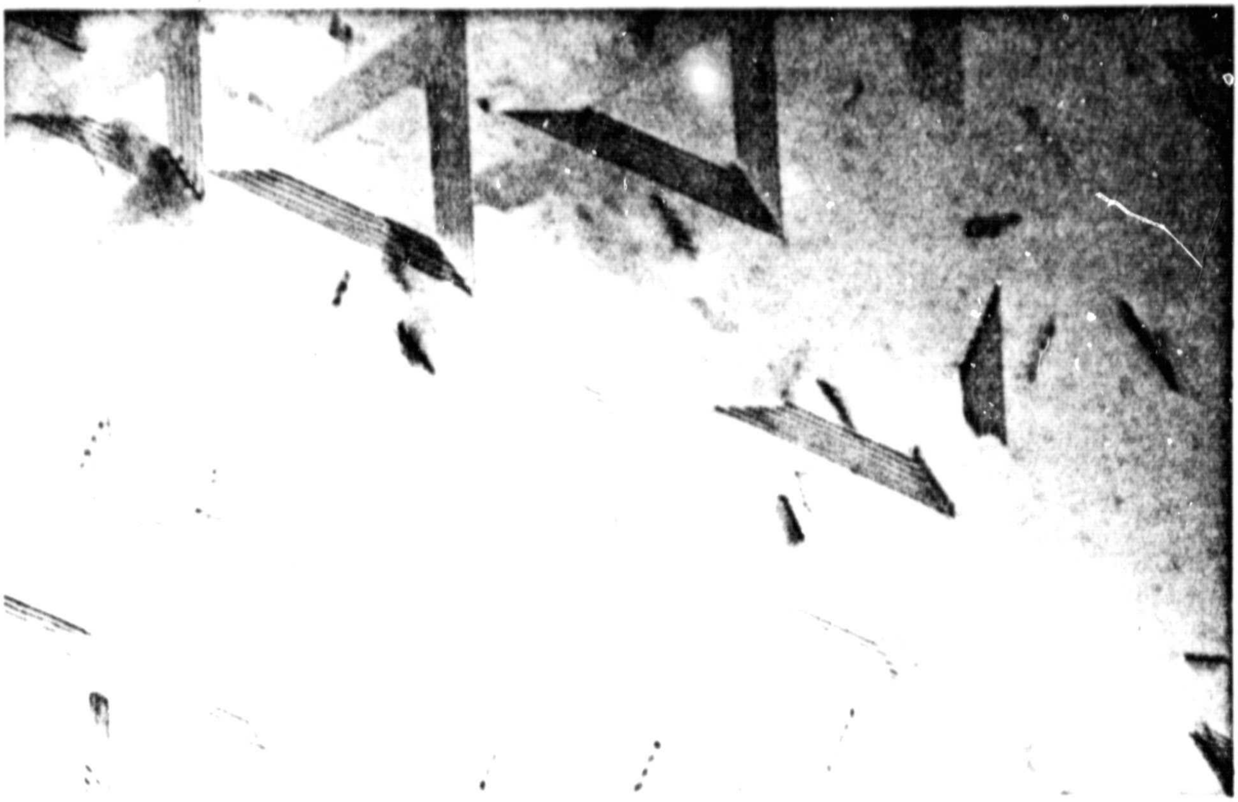


Mobility of all n-type (Sb doped) films grown at UCLA

Figure 8

Caption for Figure 9.

SEM views of MBE-grown Si films. a) classic stacking fault pattern with fault densities on order of $10^5 cm^{-2}$ in Ga doped to $8 \times 10^{17} cm^{-3}$ on (111) magnified 33,000 times; b) a line of dislocations in Sb doped to $7 \times 10^{17} cm^{-3}$ on (100) magnified 6,600 times.



a. Classic Stacking Fault Pattern

b. Line of Dislocations

Figure 9

In the case of MBE #8 and #9, Sb doping should have been carried out at substrate temperatures above 750°C to avoid slow transients. The 650°C temperature previously used is now known to have transient times as long as 2×10^4 seconds (2.15 microns at our growth rate), whereas at 750°C they are down to 8×10^2 seconds or 0.1 micron.

K. Tandem Cell Calculations

JPL carried out an initial study of the efficiency attainable using two silicon cells of different depths in tandem connected by a tunnel junction, using surface fields, so as to best utilize the short and long wavelength portion of the solar spectrum. The results are encouraging enough so that we plan to carry these calculations further, and to grow some test structures during the coming year by MBE to see if such a cell with its advantages can be realized.

3. Summary of First Year Effort

A. Major Accomplishments and Findings

i. The diffusion length of good quality substrates (100 to 200 microns) is not degraded by the high temperature cleaning used before MBE begins.

ii. One testable solar cell has been made by MBE growth of an n-on-p junction at UCLA and fabricated and tested at JPL. The cell had poor properties due to a poor quality p-n junction due either to dislocations or deep level impurities.

iii. It was demonstrated that the JPL SIMS analysis can give us profiles both of dopants and of troublesome impurities in MBE grown films.

iv. It was shown that UCLA can grow Si MBE films with good bulk mobility values for both n and p-type doping except at the extremely pure and extremely heavy doping limits, where MBE mobility falls below bulk values.

v. Doping with Sb is now understood so as to provide sharp n-type profiles without transient effects.

vi. UCLA has grown high purity MBE Si films with net doping density down to $10^{13}cm^{-3}$, with few or no dislocations detectable.

vii. Initial calculations indicate that a tandem Si cell should be tried; its profile is one that can be grown by MBE.

B. <u>Major Problem Areas</u>

i. UCLA has as yet been unable to grow p-n junctions by MBE in which the reverse leakage current is within two orders of magnitude of ideal, high lifetime material; furthermore, the full reason for this failure has not yet been determined. This will degrade solar cell performance until corrected.

ii. UCLA finds that crystal quality and mobility degrade badly for n^+ samples at Sb levels above $2 \times 10^{18}cm^{-3}$; it has also not been possible to produce p^+ doping with Ga above $2 \times 10^{18}cm^{-3}$.

C. <u>Minor Problem Areas</u>

i. It is found that there is often a measurable amount of carbon contaminant at the interface where growth begins. The carbon can be eliminated by argon ion bombardment. It is not known if the bombardment has any serious effect upon crystal or electrical quality, but it is unlikely to do so.

ii. The Sb doping level in the two junctions used for solar cells was not constant. The reasons for this are now understood and easily remedied by carrying out growth at a temperature above 750°C.

4. <u>Plans for Second Year Extension</u>

Application for an extension of this grant for a second year has been made and accepted.

A new full time member of the UCLA team has been hired on this project, Dr. P. Sparks, who just received her Ph.D. in Experimental Solid State Physics from Cornell University.

With the understanding of specific problems gained from the first year's effect and with the concerted efforts of Dr. Sparks working with Dr. Allen at UCLA, we expect to:

1. Demonstrate good quality p-n junctions;
2. Grow good solar cell structures that can be directly compared with JPL standard cells;
3. Grow cells with an extended back surface field;
4. Demonstrate tunnel junction action;
5. Grow and test a tandem solar cell.

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