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MASTER

TOPICAL POLYCRYSTALLINE SILICON SUBCONTRACTORS' REVIEW MEETING

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Four Seasons Motor Inn
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ORGANIZATION: SOLID STATE DIVISION, OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TN 37830

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TITLE: APPLICATIONS OF LASER ANNEALING AND LASER-INDUCED DIFFUSION TO PHOTOVOLTAIC CONVERSION*

ABSTRACT

Progress in the development of polycrystalline solar cells is hampered by the present poor state of knowledge about electronic and ionic processes at grain boundaries. A major difficulty in studying such processes is that conventional growth and thermal diffusion techniques used for doping semiconductors cause segregation of the dopant at grain boundaries and are unable to provide control of the fast diffusion which is known to occur along grain boundaries. In the first part of this presentation, we review the salient features of two new techniques for the study and control of grain boundary effects. Neutron transmutation doping is a method for circumventing segregation problems in bulk polycrystalline silicon. With such doping, long-range diffusion does not occur in the material and hence the dopants cannot migrate to grain boundaries. Laser annealing and laser-induced diffusion are two other newly developed techniques which we show

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here can be used to control grain boundary diffusion and segregation. With these techniques, the near-surface region of a sample actually melts but stays molten for such a short time (~ 10^{-7} sec) that significant dopant migration cannot occur. Furthermore, since the grain boundaries as such do not exist while the material is molten, rapid diffusion to them and along them does not occur. These new doping methods do not necessarily insure better efficiencies of cells made from polycrystalline materials, but they provide a degree of control of dopants that has not been available before and hence make possible more definitive studies of grain boundary effects. Laser techniques can also be used to promote growth, and evidence from EBIC and TEM indicates that pulsed-laser annealing changes the elementary structure of some types of grain boundaries.

In the second part of the presentation we will describe our efforts to understand the role of lithium in polycrystalline Si. It has been found that when Li is added to polycrystalline Si, it not only provides an excess free carrier for each ionized Li^+, but also dramatically improves the carrier mobilities. In polycrystalline Si, the electrical transport properties are believed to be governed by carrier trapping at grain boundaries. The traps, which would be neutral in undoped material, will be electrically charged after capture of free carriers in doped samples; potential barriers thus created impede the motion of majority carriers and promote minority carrier recombination. In n-type Si, many grain boundaries are thought to be negatively charged. Because Li is highly mobile in Si, Li^+ ions have a tendency to pair with the negatively charged trapping states at grain boundaries in the n-type material with the result that barrier heights are reduced and carrier mobilities increased. Using laser scanning techniques to study the influence of lithium on minority carrier recombination in selected areas of polycrystalline solar cells, it was found that recombination effects at some of the grain boundaries were diminished after the introduction of Li into the cell, while other grain boundaries are uneffected. The differences between grain boundaries which can and cannot be passivated by lithium diffusion are currently under investigation. Determination of barrier heights and densities of trapping states at the grain boundaries, which influence the electrical transport properties, by a surface potential probe method and by temperature dependent resistivity measurements will be reported. A comparison of experimental data with carrier trapping models and the mechanism of Li^+ interacting with grain boundaries will be discussed. The overall improvement of cell parameters by lithium diffusion is not significant in large grain polycrystalline solar cells (the efficiency increases by 0.5% on the average), however, Li provides an alternative passivation agent to atomic hydrogen for studying the physics and chemistry of different kinds of grain boundaries and should be valuable in the search for more effective methods to passivate small grain (~ 100 μm) polycrystalline Si.

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STUDIES OF GRAIN BOUNDARY EFFECTS AND PASSIVATION METHODS

RESEARCH OUTLINE

- INVESTIGATE NEW DOPING TECHNIQUES

  Bulk doping (< 10^{17} cm^{-3}): neutron transmutation doping (NTD)

  Emitter doping: laser-related doping techniques

- INVESTIGATE CONTROL OF GRAIN BOUNDARY DIFFUSION AND SEGREGATION BY LASER TECHNIQUES AND NTD

- CARRY OUT BASIC STUDIES OF GRAIN BOUNDARIES

  Microscopic structure - TEM

  Electrical transport properties - EBIC, SLS, etc.

- GRAIN BOUNDARY PASSIVATION

  Passivation by heavy doping in emitter region

  Passivation by H, Li, etc. diffusion

TYPES OF POLYSIL USED

DESCRIPTION	AVERAGE GRAIN SIZE
• MONSANTO SINGLE FZ PASS	MILLIMETER (COLUMNAR)
• TEXAS INSTRUMENT Cz CHARGE (CVD ON SINGLE CRYSTAL SEED)	~25 μm (COLUMNAR)
• CVD ON SiO_2 SUBSTRATE	~0.02 μm BEFORE LASER ~1.5 μm AFTER LASER

NEW DOPING TECHNIQUES

- **NEUTRON TRANSMUTATION DOPING OF SILICON**

  This is a method for preventing dopant segregation at grain boundaries in bulk samples

- **LASER RELATED DOPING TECHNIQUES - FOR EMITTER DOPING, BSF, AND OHMIC CONTACTS**

  a. Ion implantation, laser annealing

  b. Laser induced diffusion of dopant films

  c. Laser induced recrystallization of doped amorphous films

  d. Glow discharge implantation, laser annealing

  ADVANTAGES:

  Low processing temperature

  Prevent enhanced dopant diffusion along grain boundaries

LOW-COST ION IMPLANTATION TECHNIQUE

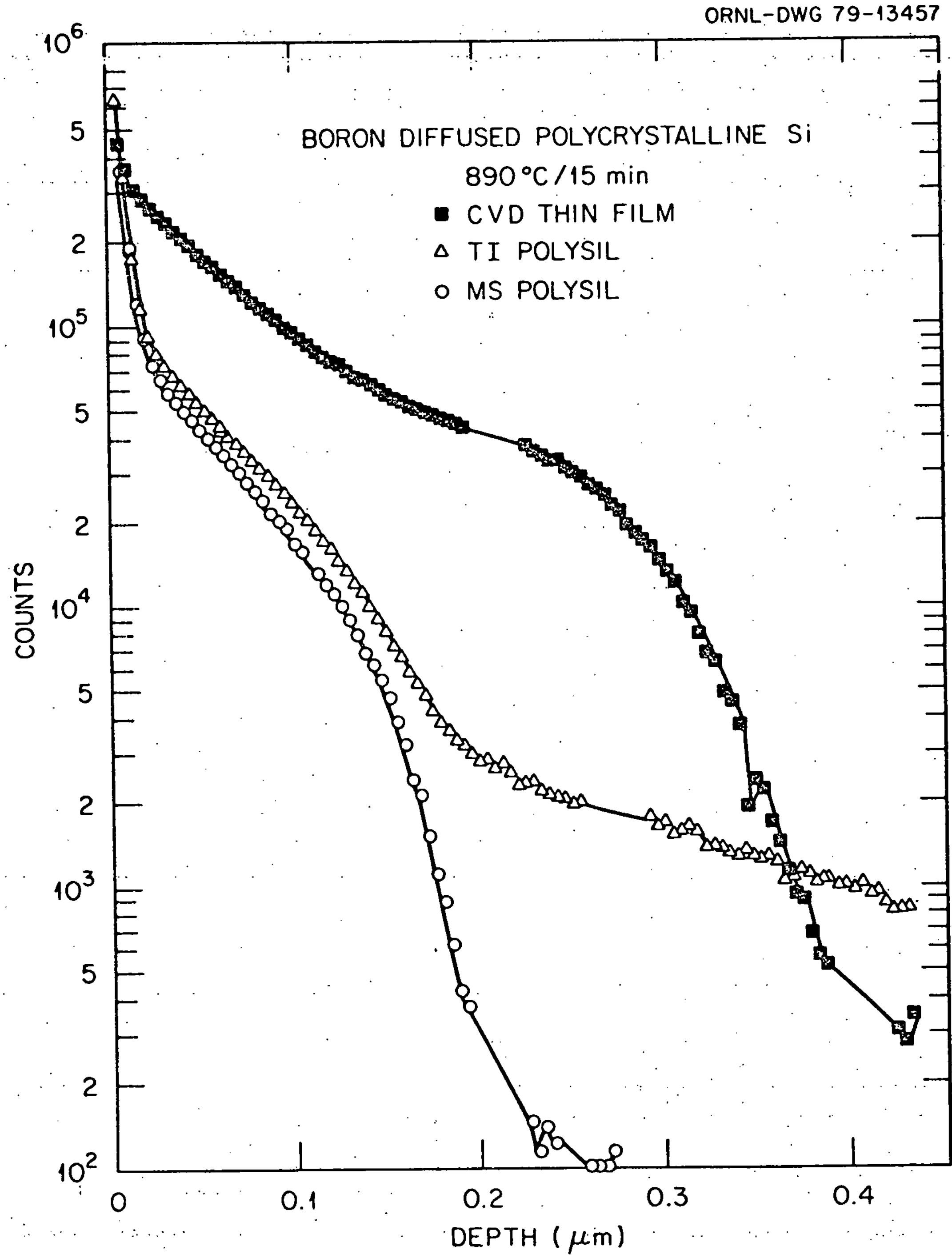
GLOW DISCHARGE PROCESS

TECHNIQUE:

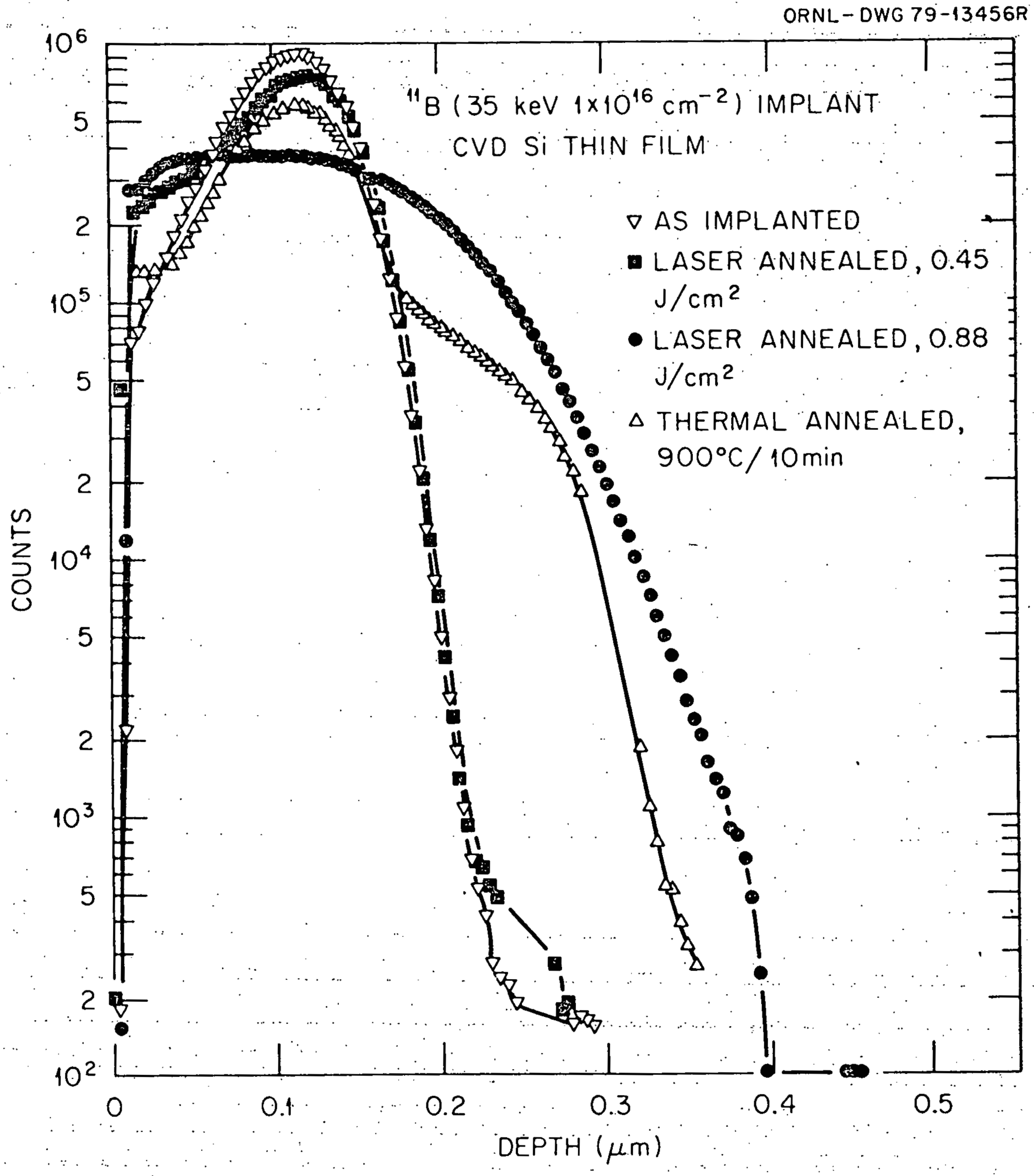
A GLOW DISCHARGE IN BF_3 (OR PF_5) PRODUCES BORON (OR PHOSPHORUS) IONS WHICH ARE IMPLANTED INTO THE Si CATHODE TO FORM A SHALLOW p^+ (OR n^+) EMITTER REGION.

ADVANTAGES:

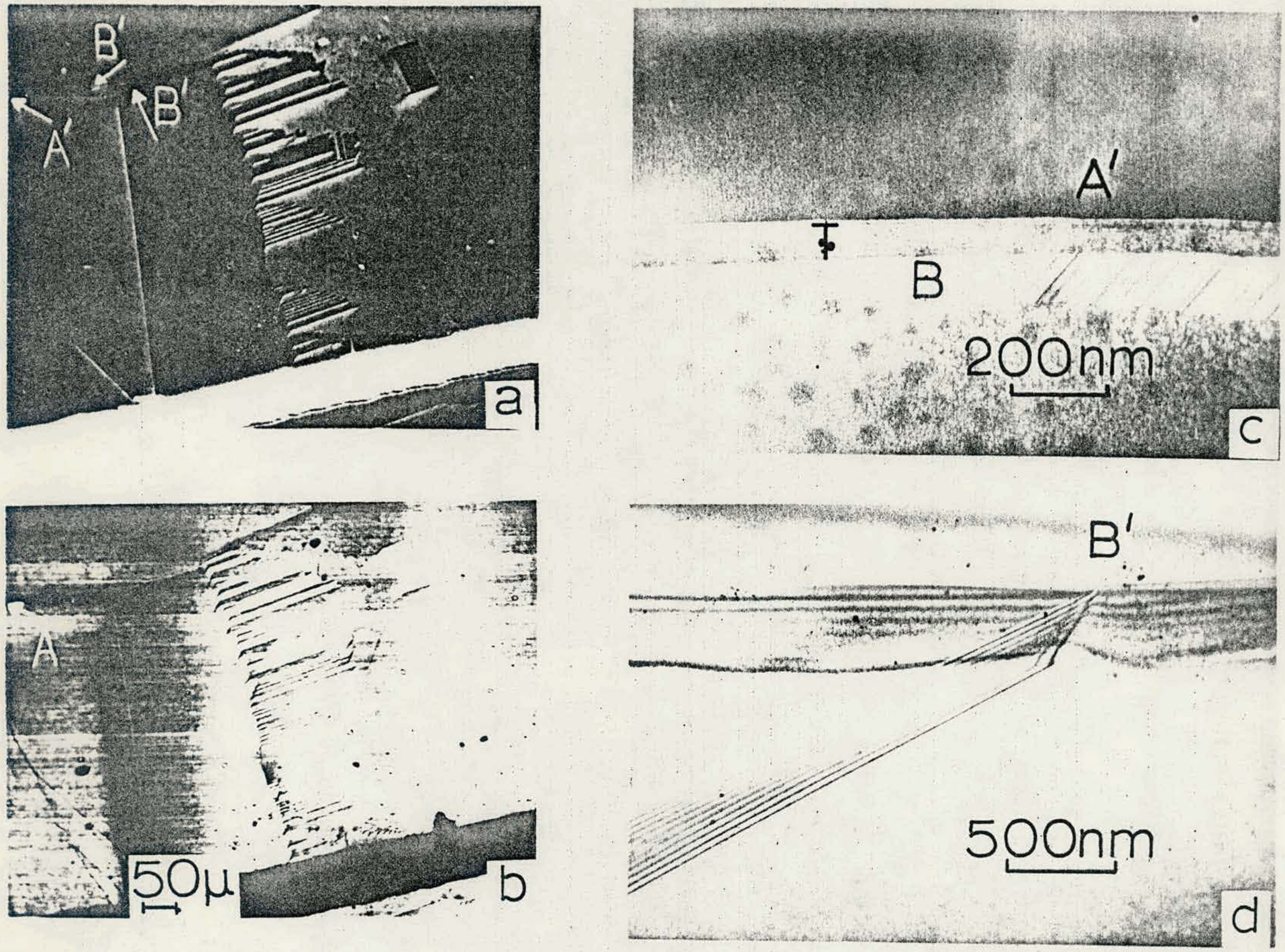
- LOW PROCESSING TEMPERATURES
- SIMPLE EQUIPMENT SET UP
- SURFACE CONCENTRATIONS CAN BE WELL CONTROLLED



SIMS results illustrating long range diffusion of B as grain size is decreased.



SIMS results indicating lack of grain boundary diffusion with laser annealing.

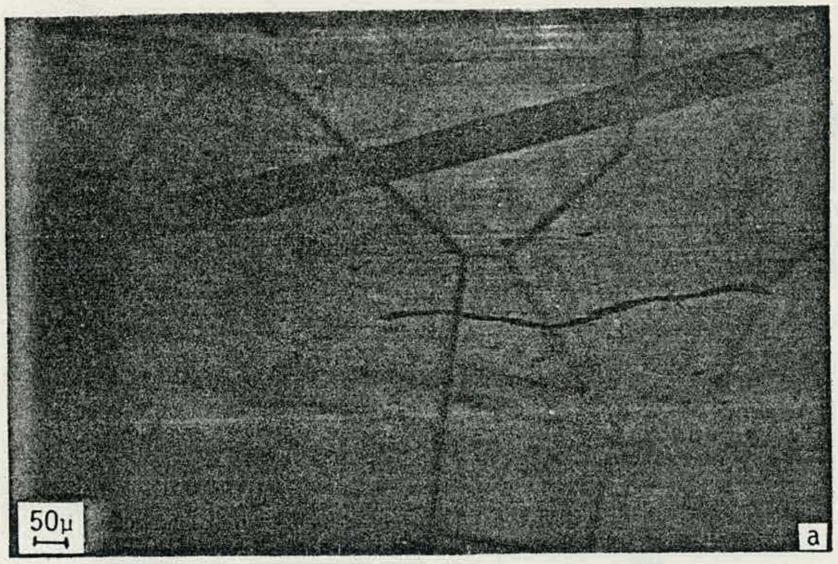


a. Image of a portion of a laser-annealed polycrystalline solar cell taken with an electron microscope operating in the standard (secondary electron emission) operating mode.

b. Image of the same area on the sample taken with the microscope operating in the EBIC mode showing A' (electrically active) and B' (electrically inactive) twin boundaries.

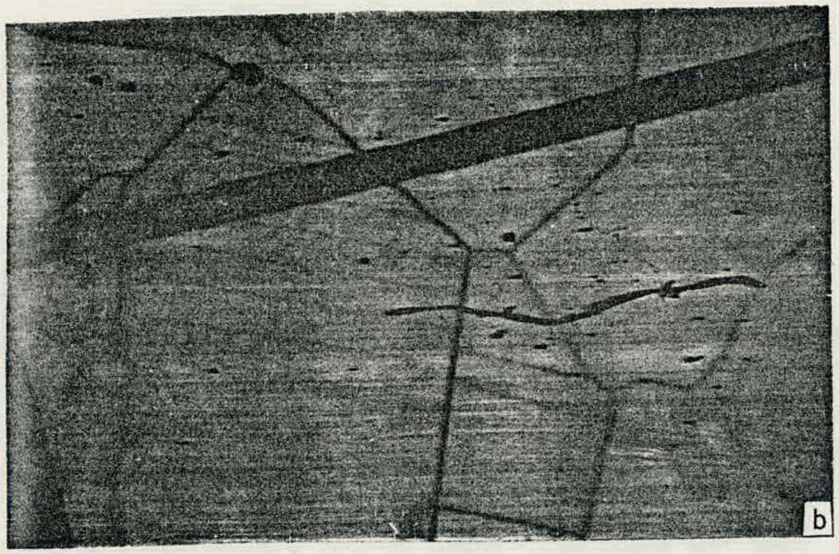
c. Area A', the electrically active, incoherent twin boundary has transformed into an inactive coherent twin boundary in the laser-melted region.

d. Area B', a typical electrically inactive, coherent twin boundary.

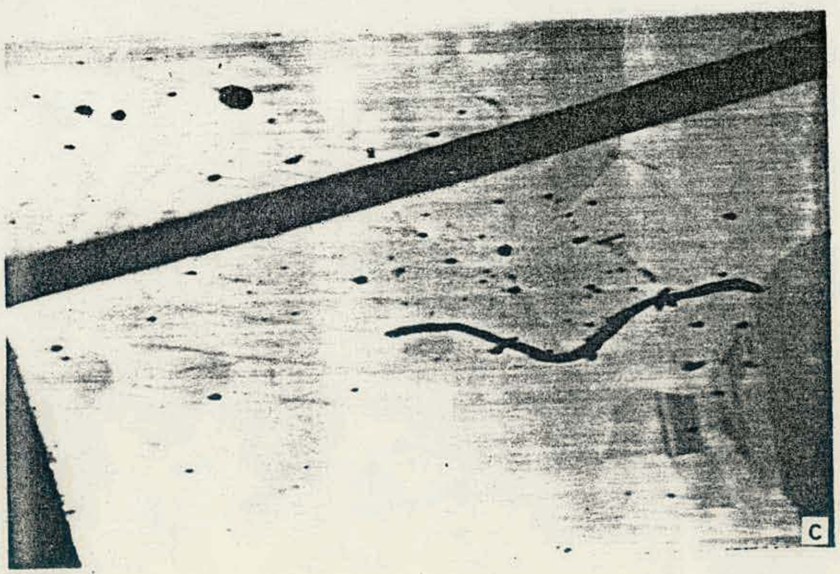


EBIC Images of Polycrystalline Si Solar Cells

a. Results when the e-beam has an energy of 30 KeV (max. penetration ≈ 6.5 μm). Grain boundaries are clearly visible.



b. Results with an e-beam energy of 15 KeV (max. penetration ≈ 2 μm). Grain boundaries are still visible.



c. Results with an e-beam energy of 10 KeV (max. penetration ≈ 1 μm). Grain boundaries have virtually disappeared. This is believed to be caused by grain boundary passivation in the heavily-doped emitter region.

Grain boundary passivation by heavy doping.

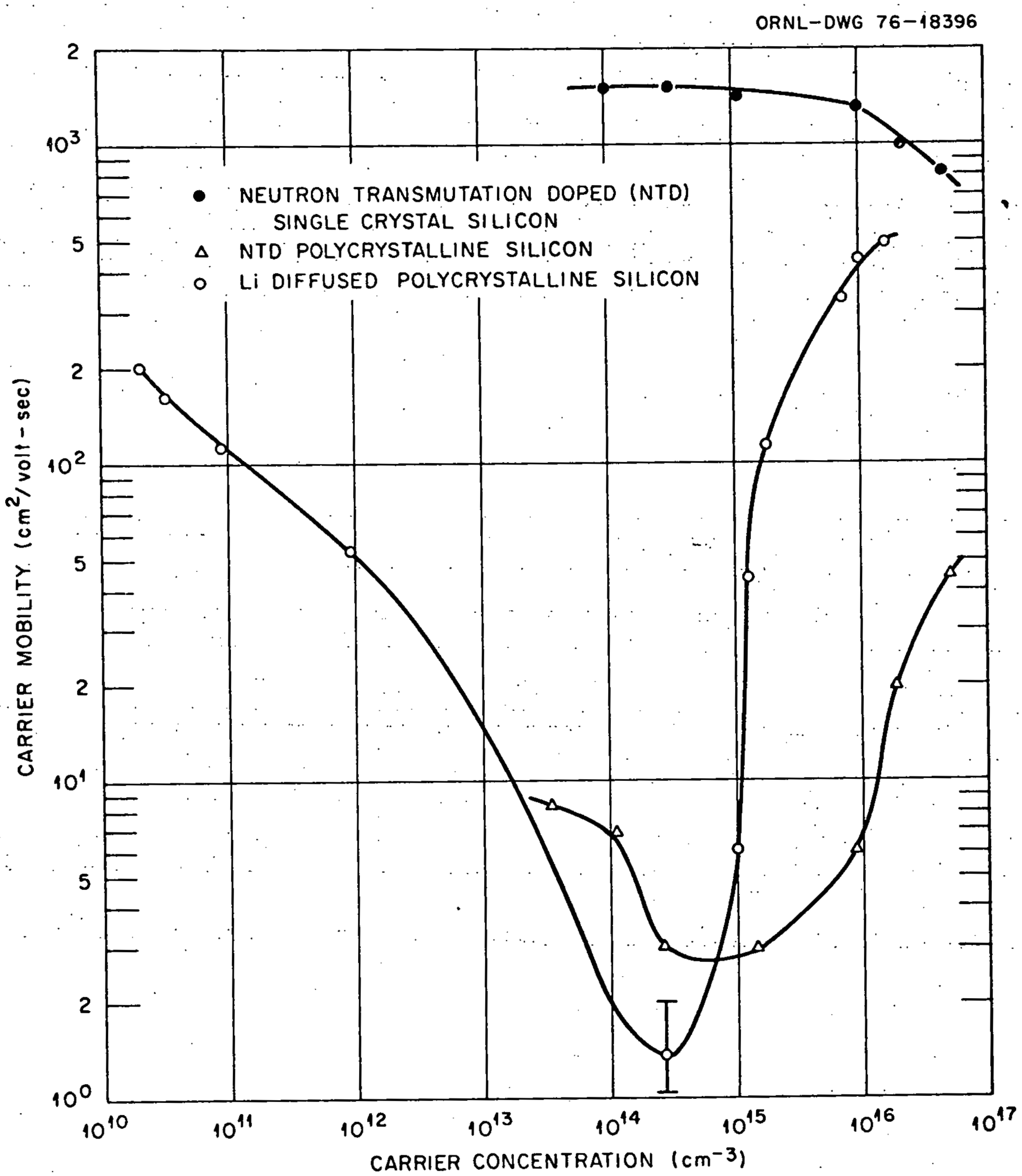


Illustration of high mobilities in Li-diffused small-grained (TI) polycrystalline Si.

Table 1. Electrical Parameters of Polycrystalline Si Before and After Lithium Diffusion (350°C)

Sample No.*	Diffusion Time (h)	Before n (cm^{-3})	Before μ (cm^2/V sec)	Before (Ω-cm)	After n (cm^{-3})	After μ (cm^2/V sec)	After (Ω-cm)
DC-1	2	4.8×10^{15}	17	75.3	3.2×10^{16}	296	0.67
MS-1	2	2.2×10^{15}	146	19.5	9.5×10^{16}	674	0.10
MS-2	4	2.3×10^{15}	349	7.6	8.9×10^{15}	768	0.91
MS-3	4	1.0×10^{16}	350	1.74	2.1×10^{16}	937	0.32

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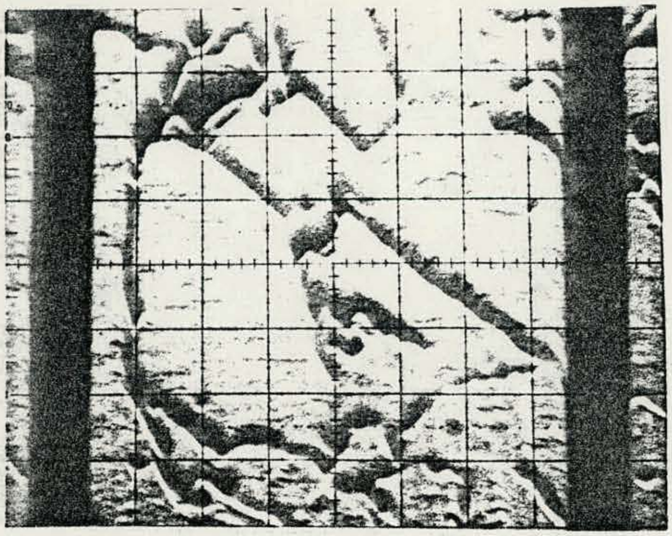
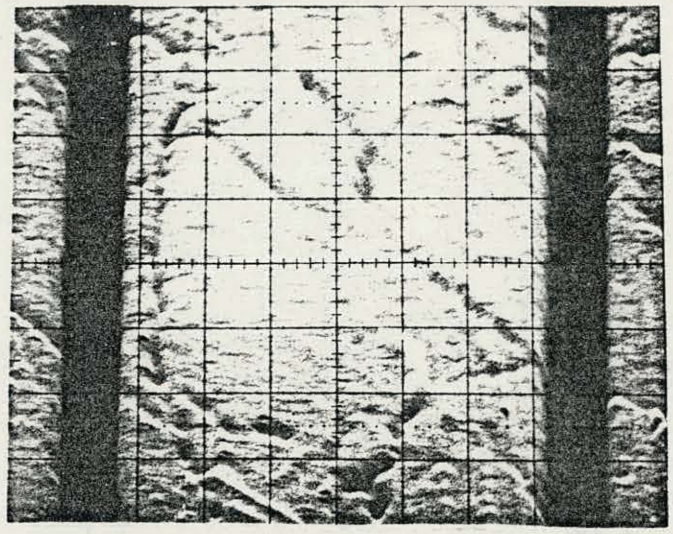


a



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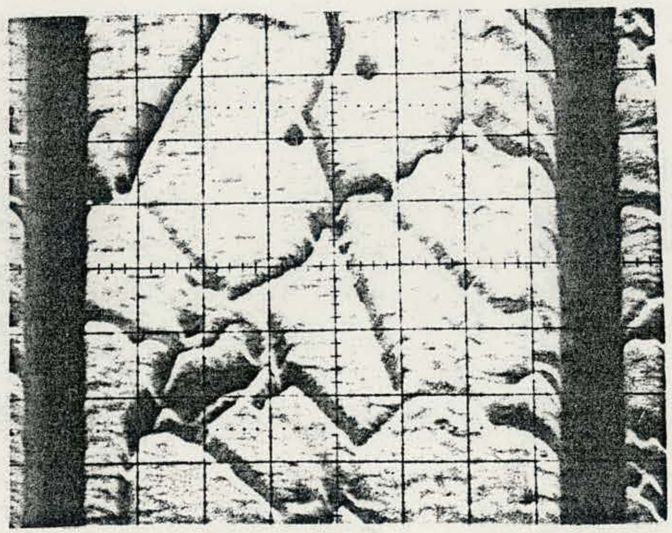

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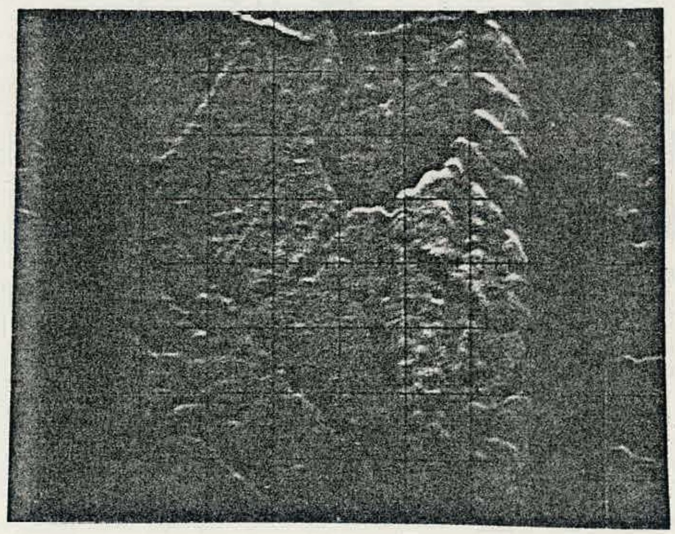

d

Scanning laser spot photographs showing effect of Li^+ passivation on grain boundaries.

(a,c) Electrically active grain boundaries before Li^+ passivation.

(b,d) Corresponding areas after Li^+ passivation.

Table 2. Stability of Electrical Parameters of Lithium Diffused Polycrystalline Si

Sample No.	Diffusion Time (h)	After Diffusion $\rho(\Omega\text{-cm})$	After Diffusion $\mu(cm^2/V.sec)$	After 60 days $\rho(\Omega\text{-cm})$	After 60 days $\mu(cm^2/V.sec)$
MS-35-3	3	2.5	1258	2.7	1277
MS-19-3	3	0.16	840	0.34	632
MS-20-6	3	0.67	879	0.71	957
MS-20-7	4	0.91	768	0.98	808

Table 3. A comparison of Cell Parameters before and After Lithium Diffusion (350°C/3h)

Sample	Before				After			
	V_{oc}	J_{sc}	FF	MCDL	V_{oc}	J_{sc}	FF	MCDL
MS-19-a	515	47.5	68.8	45	530	47.0	75.2	32
MS-19-c	522	48.5	74.1	32	543	47.9	75.8	20
MS-19-d	520	49.9	72.9	72	535	49.2	74.7	56
MS-19 (no Li)	530	48.4	67.5	54	528	48.6	68.2	61

CONCLUSIONS

- Transmutation doping and laser-related techniques provide control of grain boundary diffusion and segregation. They should be useful tools for studying polycrystalline Si.

- Two types of twin boundaries have been observed with TEM. Coherent twin boundaries, which are electrically inactive, were not altered by laser irradiation. Electrically active incoherent twin boundaries can be converted to coherent twin boundaries by laser irradiation.

- Lithium appears to be an effective agent for passivating grain boundaries in n-type silicon.

LIMITATIONS TO PROGRESS

- **LACK OF INFORMATION ABOUT THE MICROSTRUCTURE OF GRAIN BOUNDARIES**

  More TEM, SIMS, and Auger data will be accumulated.

- **INSUFFICIENT KNOWLEDGE OF ATOMIC BONDING PROPERTIES AT GB's**

  Quantum mechanical calculations are underway.

- **INADEQUATE RESOLUTION OF ANALYTICAL TOOLS**

  Upgrade SIMS equipment. Make EBIC and SLS measurements quantitative for more precise correlations with TEM results.

- **QUANTITATIVE INFORMATION ABOUT PASSIVATION**

  More quantitative informatin about the effects of various passivation techniques will be sought by SIMS, EBIC, SLS, and electrical properties measurements.

- **MONEY AND PERSON POWER EXPENDED ARE NOT GREAT ENOUGH**

PLANNED ACTIVITIES

- Study the structural differences of various types of electrically active grain boundaries, e.g., tilt, twist, and mixed boundaries.
- Study the electrical transport properties of different types of grain boundaries.
- Continue studies of the effects of laser radiation on the morphology of grain boundaries.
- Examine quantitatively the effectiveness of passivation by Li on different types of boundaries.
- Examine first qualitatively and then quantitatively the effectiveness of other passivation agents.