CONF-810349--1

APPLICATIONS OF LASER ANNEALING AND LASER-INDUCED DIFFUSION TO PHOTOVOLTAIC CONVERSION

MASTER

CONTRACTOR: SOLID STATE DIVISION

OAK RIDGE NATIONAL LABORATORY*

OAK RIDGE, TN 37830

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III-V COMPOUND CONTRACTORS IN-DEPTH REVIEW MEETING

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RALEIGH, N. CAROLINA

ABSTRACT

Over the past several years it has been demonstrated that a variety of techniques involving pulsed laser irradiation of both single crystal and polycrystalline silicon by pulsed lasers can result in the reproducible achievement of high efficiency silicon solar cells. Pulsed laser annealing (PLA) after an ion implantation (II) step results in melting (for a time of order 100 nsec) and essentially defect-free liquid phase epitaxial regrowth within $\sim 0.5\mu m$ of the surface. Complete electrical activation of a number of dopant ions, at concentrations exceeding ordinary solubility limits, has been demonstrated and crystalline (polycrystalline) silicon solar cell efficiencies of 16.6% (12.5%) have been obtained. Other p-n junction and solar cell fabrication techniques that have been demonstrated include laser induced diffusion of thin dopant films deposited on samples (resulting in 14% efficient c-Si solar cells), and laser induced epitaxial recrystallization of doped amorphous silicon films deposited on single crystal substrates. Pulsed laser processing has also been demonstrated to have several other unique and beneficial advantages in polycrystalline silicon substrates. For example, grain boundaries do not exist during laser melting, while dopant

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DISCLAIMER

diffusion is taking place; the short melt durations involved further limit dopant diffusion; precipitates present after conventional high temperature dopant diffusion can be removed; and, certain types of electrically active grain boundaries can be made inactive by pulsed laser irradiation. Finally, grain growth in fine-grained polycrystalline silicon films, via pulsed laser melting and recrystallization, has been demonstrated.

Because little is known about the application of similar pulsed laser processing techniques to compound semiconductors, particularly in connection with the formation of shallow p-n junctions, a part of our program during the past year has been devoted to studies of pulsed laser processing of GaAs, and to seeking compound semiconductor solar cell fabrication techniques that are compatible with the use of pulsed lasers. Specific areas of activity and accomplishments include the following:

(1) We have identified the parameters needed to optimize pulsed ruby laser annealing of ion implanted GaAs, at room temperature and without encapsulation. Pulsed ruby laser annealing of high dose Mg and Zn implants in GaAs has been shown to yield the highest electrical activation ($\sim 80\%$) achieved by any annealing technique to date. It has been established that the pulsed ruby laser energy density "window" for this annealing extends from 0.4 to 0.8 J/cm^2. A laser beam spatial homogeneity $\sim 0.1\ J/cm^2$ is required to obtain uniform p-n junction depth; such homogeneity can be obtained using a diffusing light pipe.

(2) Formation of large area, homogeneous ohmic contacts, suitable for the back surface of a solar cell, has been demonstrated via laser induced diffusion of Sn (in n-type GaAs) or Mg (in p-type GaAs). This method of contact formation allows one to avoid a thermal processing step, which may be a significant advantage in processing polycrystalline GaAs solar cells.

(3) Initial studies of pulsed laser recrystallization and grain growth, in polycrystalline CVD GaAs films deposited on foreign substrates, have been carried out with samples held at room temperature and at 500°C during laser irradiation. SEM pictures show that laser irradiation produced considerable flattening and coalescence of the topographical variations that are characteristic of initial GaAs CVD on foreign substrates. Thus, in situ pulsed laser recrystallization may have applications in improving initial film morphology prior to later stages of GaAs CVD growth.

(4) Significant concentrations of defects are induced in the near-surface region of GaAs by pulsed laser irradiation at room temperature and with no encapsulation. The principal defect is believed to be associated with As loss in the near-surface region; the problem is thus unique to compound semiconductors. (No comparable problem has been observed in PLA of silicon.) This defect is believed to be responsible for the unsatisfactory performance to date of the $\sim 0.5\ cm^2$ II/PLA GaAs solar cells that we have fabricated. Substrate heating and/or encapsulation during laser irradiation are currently being investigated as possible means of minimizing or solving this problem.

(5) Studies of the interdiffusion of deposited GaAs films and germanium substrates, resulting from pulsed laser irradiation, were also initiated during the first year of this contract.

DOPING AND P-N JUNCTION FORMATION IN SILICON USING PULSED LASERS (@ ORNL)

LASER-INDUCED DIFFUSION (LID)

- ELEMENTAL FILM (E.G., AN N-TYPE DOPANT, ~100 Å THICK) EVAPORATED ONTO P-TYPE SILICON SUBSTRATE
- DRIVE INTO SUBSTRATE (WITH MELTING & RECRYSTALLIZATION) WITH A SINGLE LASER PULSE (~1-2 J/CM^2, $\tau \sim 15$ NS)
- RESULTS:

  HIGHLY DOPED NEAR-SURFACE REGION; SUBSTITUTIONAL DOPING; CRYSTALLINE STRUCTURE; P-N JUNCTION FORMATION
- ~14% EFFICIENCY C-SI SOLAR CELLS

LASER-INDUCED RECRYSTALLIZATION (LIR)

- DOPED (E.G., N-TYPE) SILICON FILM (AMORPHOUS OR FINE-GRAINED POLY, ~ 1,000 Å THICK) EVAPORATED ONTO POLY- OR SINGLE-CRYSTAL SILICON SUBSTRATE (E.G., P-TYPE)
- EPITAXIALLY REGROW FROM SUBSTRATE WITH SINGLE LASER PULSE
- RESULTS: EPITAXIAL RECRYSTALLIZATION
P-N JUNCTION FORMATION

ION IMPLANTATION/PULSED LASER ANNEALING (II/PLA)

- USE ION BEAM TO IMPLANT DOPANT IONS TO DEPTH ~1,000 Å
- REPAIR (ANNEAL) LATTICE DAMAGE AND ACTIVATE IMPLANTED CARRIERS WITH A SINGLE LASER PULSE
- RESULTS:

  HIGHLY DOPED NEAR-SURFACE REGION
  DOPANTS IN SUBSTITUTIONAL SITES
  EPITAXIAL RECRYSTALLIZATION
  P-N JUNCTION FORMATION
- ~ 16.6% EFFICIENCY C-SI SOLAR CELLS
~ 12.5% EFFICIENCY POLY-SI (WACKER) SOLAR CELLS

PULSED LASER PROCESSING OF GaAs*

Planned Activities	Accomplishments
● Identify Parameters Needed to Optimize Pulsed Ruby Laser Annealing (PRLA) of Ion Implanted (II) c-GaAs: Energy Density Window for High Activation Laser Spatial Homogeneity Requirements Selection of Implanted Ions/Dose	Completed
● Initiate Studies of Grain Growth/Recrystallization in Thin Poly-GaAs Films on Low Cost Substrates, Using Films from Other SERI Contractors.	Done: CVD GaAs Mo & Graphite Substrates 20°C & 500°C Irradiations
● Seek Fabrication Techniques Compatible with the Application of Laser Processing to Polycrystalline and Thin Film GaAs Solar Cells: Laser Induced Diffusion (LID) of Dopant Films (p-n Junctions; Ohmic Contacts; BSF) II/PRLA (p-n Junctions)	(1) Ohmic Contacts without Thermal Processing (LID) (2) p-n Junction Formation (LID and II/PRLA)
● Initiate Studies of Diffusion from Low Cost Substrates During Pulsed Laser Irradiation of Deposited GaAs Films.	Done: Ion Beam Coated GaAs Films/Ge Substrates

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* "The proposed program will be carried out at ORNL over a two or more year period. An effort will be made to begin all subtasks during calendar year 1980." (From: Program Plan & Task Schedule).

PULSED LASER PROCESSING OF GaAs (CONTINUED)

PLANNED ACTIVITIES	ACCOMPLISHMENTS
• FABRICATE AND TEST SHALLOW HOMOJUNCTION SOLAR CELLS MADE BY ION IMPLANTATION/PULSED LASER ANNEALING.	INITIAL FABRICATIONS CARRIED OUT: p^{+}-N (II/PLA), 0.5 CM^2 PERFORMANCE UNSATISFACTORY TO DATE
NEW ACTIVITIES	
• STUDY DEFECTS INDUCED IN GaAs BY PULSED LASER/PULSED ENERGY BEAM IRRADIATION.	IN PROGRESS (TEM, SEM, ELECTRICAL PROPERTIES, DLTS)
• PULSED LASER ANNEALING OF ION IMPLANTED c-GaAs WITH: SUBSTRATE HEATING, ENCAPSULATION	IN PROGRESS

PROBLEMS ENCOUNTERED IN MEETING PAST PROGRAM GOALS

- LOW FUNDING LEVEL (~ 1 PY)

BOTTLENECK {
- LASER INDUCED DEFECT STUDIES
- CONTINUED PV CELL FABRICATION

PULSED RUBY LASER ANNEALING (PLA) OF ION IMPLANTED (II) GaAs

PREVIOUS INVESTIGATIONS (ELECTRON & LASER BEAMS)

- SEMI-INSULATING (CR-DOPED) GaAs
- FORMATION OF CONDUCTING REGIONS
- OHMIC CONTACTS

THIS WORK

- SEMICONDUCTING (p- AND n-TYPE) GaAs
- EVALUATE AND OPTIMIZE II/PLA TECHNIQUES FOR PRODUCING SHALLOW p^+-n & n^+-p JUNCTIONS

OPTIMIZATION OF II/PLA PARAMETERS

- DETERMINATION OF PULSED LASER ENERGY DENSITY (E_ℓ) "WINDOW" FOR HIGH ACTIVATION OF IMPLANTED IONS, WITHOUT SURFACE DAMAGE (VAPORIZATION)
- DETERMINATION OF SPATIAL HOMOGENEITY REQUIREMENTS ON THE PULSED LASER BEAM (UNIFORM ANNEALING & JUNCTION DEPTH; LOCAL DAMAGE)
- SELECTION OF IMPLANTED IONS FOR HIGH ELECTRICAL ACTIVATION, CARRIER MOBILITY

EXPERIMENTAL CONDITIONS

ION IMPLANTATION

- ZN AND MG (p^+) IN n-GAAS
  SI AND SE (n^+) IN p-GAAS
  (SUBSTRATE CARRIER CONCENTRATIONS $\lesssim 1 \times 10^{17}/\text{cm}^3$)
- DOSES: 1 & 5×10^{15} IONS/cm^2
  1×10^{14} IONS/cm^2 (SI ONLY)
- PROJECTED RANGES (IMPLANT ENERGY):
  ~ 600 Å & 350 Å

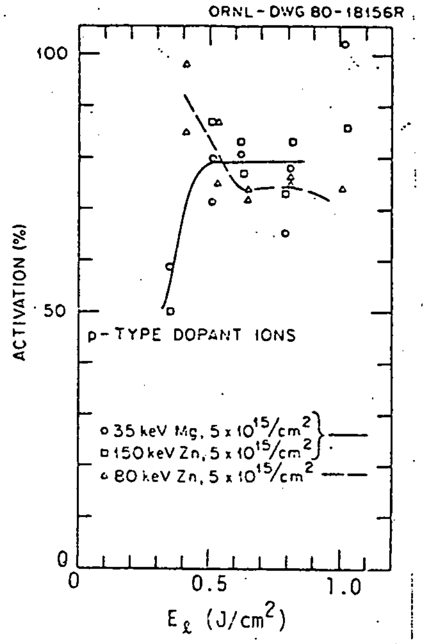
PULSED RUBY LASER ANNEALING

- $0.3 \leq E_\ell \leq 1.0$ J/cm^2 (ROOM TEMP.)
  $0.1 \leq E_\ell \leq 0.5$ J/cm^2 (500°C SUBSTRATE HEATING)
  τ_{FWHM} = 20-25 NSEC
- BENT, DIFFUSING LIGHT PIPE FOR LASER BEAM SPATIAL HOMOGENIZATION
- IN AIR @ ROOM TEMP. } NO ENCAPSULATION
  IN N_2 @ 500°C } NO ENCAPSULATION

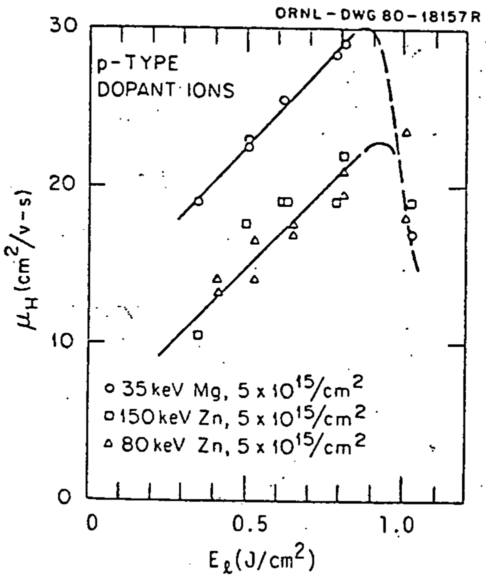
ANALYTIC TECHNIQUES

- ELECTRICAL PROPERTIES OF II/PLA LAYERS
  (HALL EFFECT & SHEET RESISTIVITY; VAN DER PAUW TECHNIQUE)
- CARRIER PROFILES (ANODIC STRIPPING)
- DOPANT REDISTRIBUTION PROFILES (SIMS)
- RECRYSTALLIZATION THRESHOLD (TEM)
- COMPARISONS WITH RESULTS OF THEORETICAL MODEL CALCULATIONS

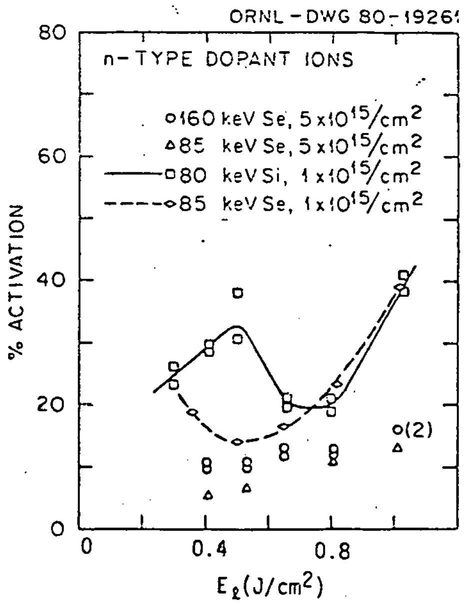
PULSED LASER ANNEALING { ROOM TEMP. IN AIR NO ENCAPSULATION



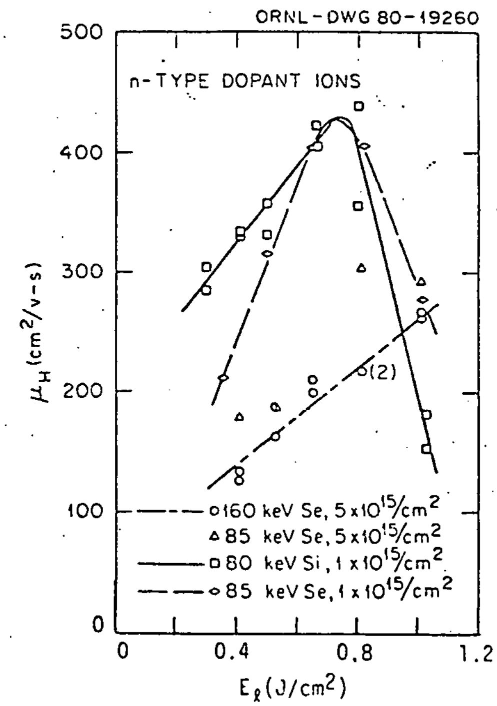
Percent electrical activation vs E_ℓ for p-type implants.



Hall Mobility vs E_ℓ for p-type implants.

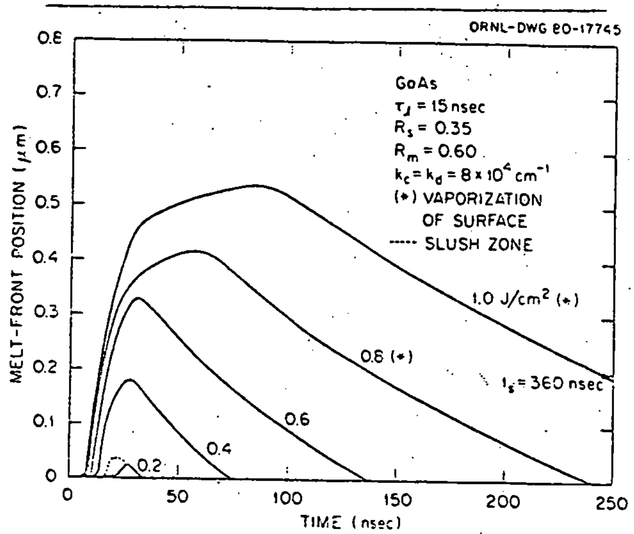


Percent electrical activation vs E_ℓ for n-type implants.

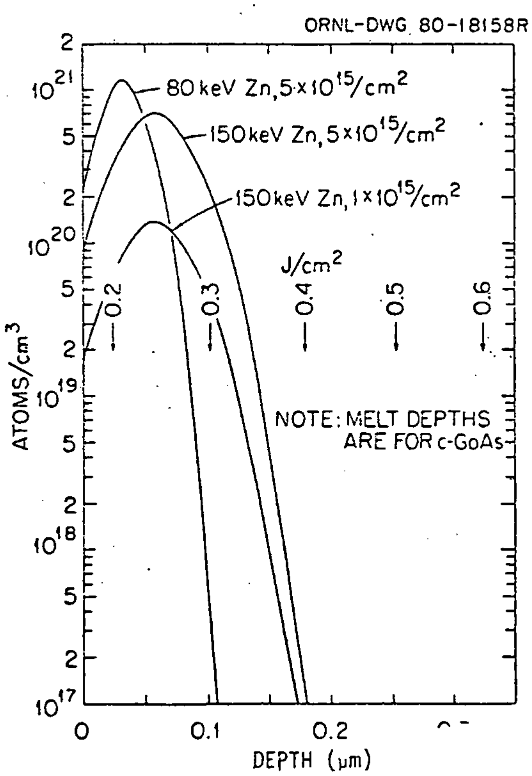


Hall mobility vs E_ℓ for n-type implants.

COMPARISON WITH THEORETICAL MODEL CALCULATIONS



Calculated melt-front profiles for GaAs. τ_ℓ is the pulse duration time (FWHM near-gaussian shape) and t_s is the time for the surface to resolidify for 1.0 J/cm^2.



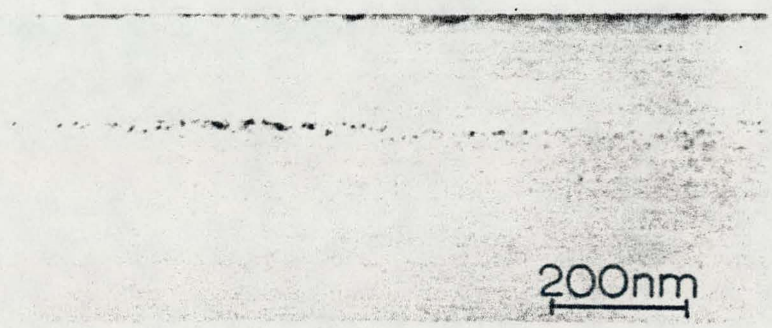
LSS ion implantation profiles typifying the implantation conditions in this work. The arrows indicate the maximum depth of melt front penetration, as a function of E_ℓ, as calculated for crystalline GaAs

ION IMPLANTED, PULSED RUBY LASER ANNEALED c-GaAs

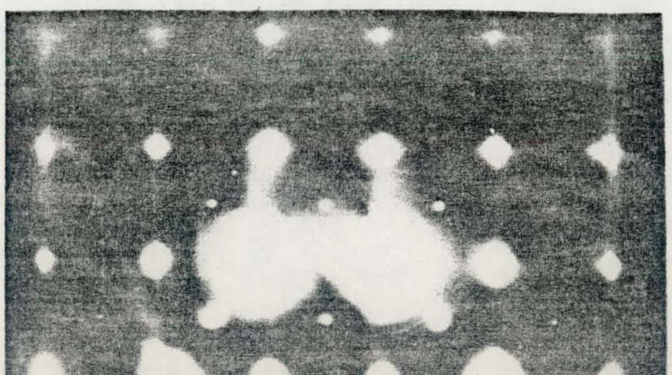
ZN & SE IMPLANTS (RP ~600 Å)

TEM CROSS-SECTIONS

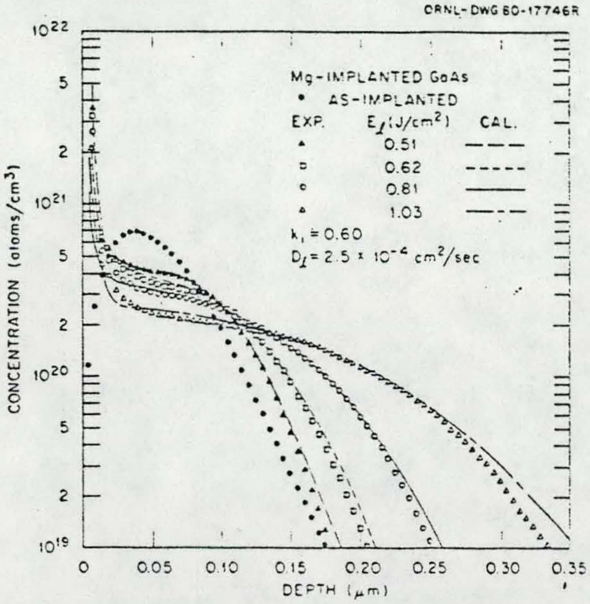
$E_{\ell} = 0$ $E_{\ell} = 0.25\ \mathrm{J/cm^2}$



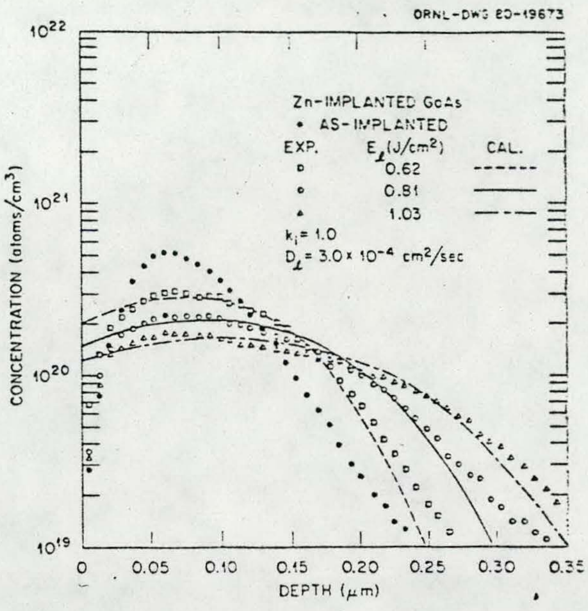
$E_{\ell} = 0.36\ \mathrm{J/cm^2}$



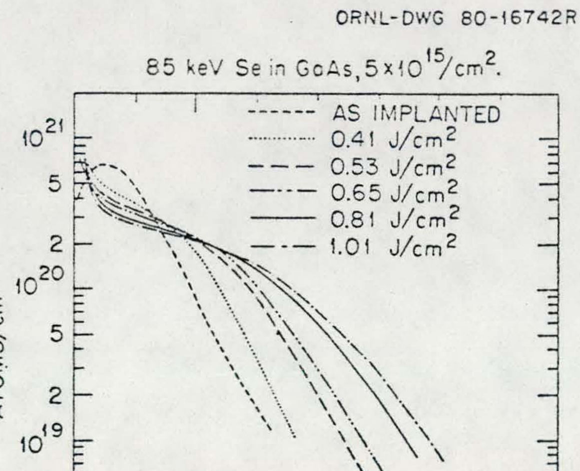
DOPANT ION REDISTRIBUTION (SIMS)



Experimental and calculated profiles of Mg in GaAs.



Experimental and calculated profiles of Zn in GaAs.



Dopant redistribution resulting from pulsed ruby laser annealing of Se ion implants.

OHMIC CONTACTS ON LOW CARRIER DENSITY GaAs VIA DIFFUSION OF DOPANT FILMS

PROBLEM: WANT TO AVOID

- ION IMPLANTATION
- THERMAL PROCESSING STEP (FLEXIBILITY; POLY-GaAs)
- 3-LAYER METALLIZATIONS
- SPATIAL VARIATIONS IN SPECIFIC CONTACT RESISTANCE

GOAL: SIMPLE, LOW COST; LARGE AREA; HIGHLY HOMOGENEOUS } CONTACTING METHOD (E.G., FOR THE BACK SURFACE OF GaAs SOLAR CELLS)

APPROACH: FORMATION OF A HIGHLY DOPED N^+ OR P^+ NEAR-SURFACE REGION, BY LASER INDUCED DIFFUSION OF A THIN (~150A) EVAPORATED METALLIC N^- OR P^-TYPE DOPANT FILM. (CAN BE FOLLOWED, IF DESIRED, BY REMOVAL OF EXCESS SN (OR MG) AND APPLICATION OF SIMPLE METALLIZATION DIRECTLY TO N^+ OR P^+ REGION.)

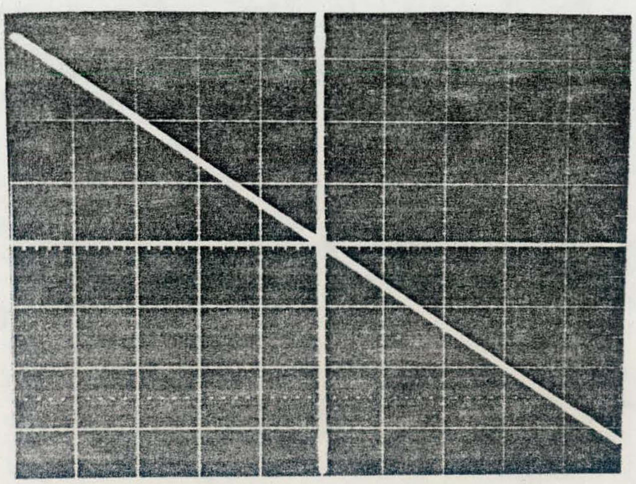
RESULTS:

TIN(N^+)

- FILM THICKNESS ~150-450 Å
- $E_\ell \sim 0.50\ J/cm^2$ (PULSED RUBY LASER, FWHM = 20 NS)
- ($\gtrsim 0.3\ J/cm^2$ FOR 150 Å)

MAGNESIUM(P^+)

- FILM THICKNESS $\gtrsim$ 200 Å
- $E_\ell \sim 0.40\ J/cm^2$ (PULSED RUBY LASER, FWHM = 20 NS)



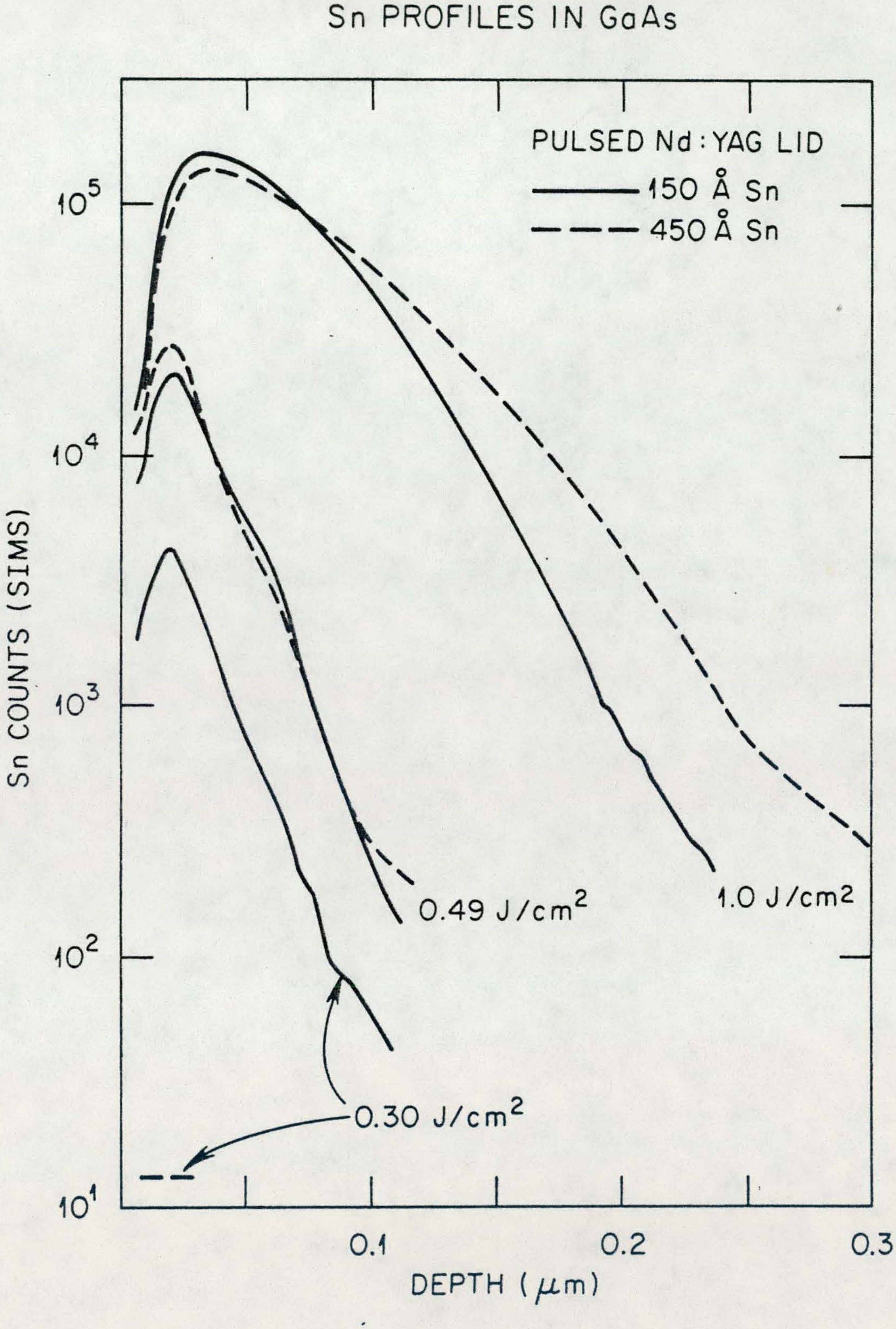
SPECIFIC CONTACT RESISTANCE $1 \times 10^{-4}\ \Omega\text{-}cm^2$, OVER ~$CM^2$ AREAS (AFTER CORRECTION FOR PROBE RESISTANCE AND SPREADING RESISTANCE)

SCALE:

50 mV/DIV.

50 mA/DIV.

ORNL-DWG 81-7387



SOLAR CELL FABRICATION USING II/PLA GaAs

1. Energy density window for high activation of implanted ions:

   $0.4 \le E_\ell \le 0.8\ J/cm^2$ (ruby laser, $\tau_{FWHM} \sim 20$ ns.)

2. High ($\gtrsim 80\%$) activation for high dose p-type implants

   Lower ($\lesssim 40\%$) activation for n-type implants.

3. P-N junction depth: 2,500-4,000 Å

   (varying with E_ℓ and implanted ion type)

4. E_ℓ inhomogeneity is not a limiting factor in forming planar junctions at well-defined depths. From SIMS:

   E_ℓ inhomogeneity $\sim 0.1\ J/cm^2$ (diffusing light pipe) results in depth variation < 300 Å (< 25% of depletion region width @ base region carrier density $\sim 10^{17}/cm^3$).

5. Easy ohmic contact formation without thermal processing:

   Front Surface: High Doping Levels ($\sim 10^{20}/cm^3$)

   (Evaporation, electroplating,....)

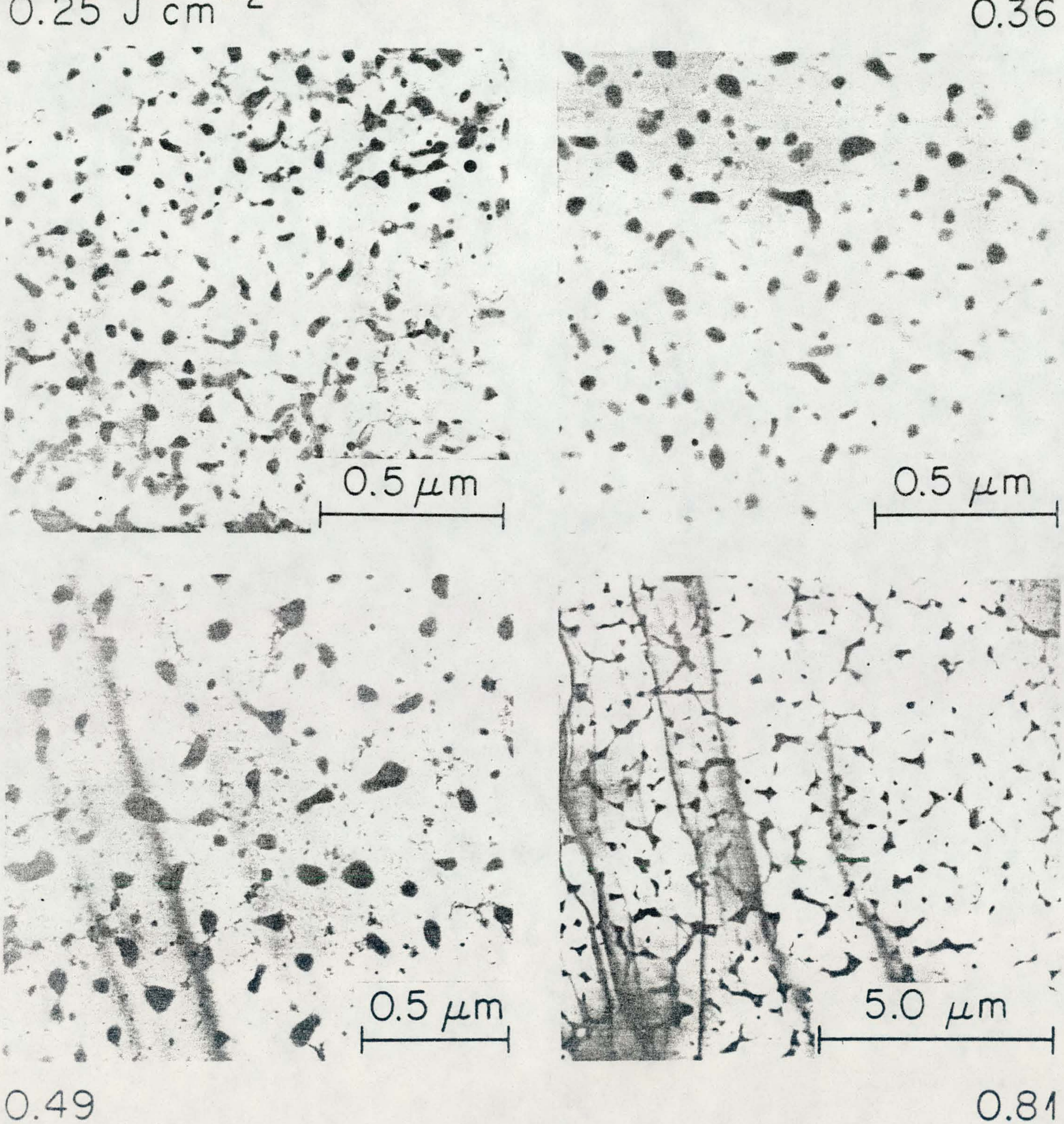
   Back Surface: Laser Induced Diffusion of Dopant Films

6. High optical absorption $\alpha^{-1} \sim 2,000$ Å
   High surface recombination velocity
   II/PLA junction depth $\sim 2,500$-$4,000$ Å
   } Combined

   Some thinning (anodic oxidation) of II/PLA region is needed, to bring p-n junction within $\lesssim 1,000$ Å of surface, for a high efficiency homojunction solar cell.

7. Limiting factor at present time:

   Laser Induced Defects


0.25 J cm^{-2}
0.36
0.5 μm
0.5 μm
0.5 μm
5.0 μm
0.49
0.81

PULSED LASER RECRYSTALLIZATION/GRAIN GROWTH OF POLY-GaAs FILMS ON LOW COST SUBSTRATES

PURPOSE

1. GRAIN GROWTH (THEORETICAL MODELING: MAXIMUM MELT DEPTH $\lesssim 1$ μM.)

2. REMOVAL OF PINHOLES AND SURFACE TOPOGRAPHY VARIATIONS AT AN EARLY STAGE OF CVD FILM DEPOSITION ($T \leq 1$ μM), USING IN-SITU IRRADIATION

SAMPLES

GaAs/MOLYBDENUM (PROF. S. K. GHANDHI)

$\lesssim 1$ μM GRAIN SIZE

GaAs/GRAPHITE (PROF. SHIRLEY CHU)

~ 5 μM GRAIN SIZE

INITIAL APPROACH

SEM/TEM/SIMS CHARACTERIZATION OF PULSED LASER IRRADIATED FILMS

CONCLUSIONS

PINHOLE REMOVAL AND FLATTENING OF INITIALLY NONUNIFORM FILMS IS POSSIBLE PRIOR TO FURTHER CVD GROWTH, VIA PULSED LASER IRRADIATION

POSSIBLE PROBLEM: GA-RICH RESIDUE MAY INTERFERE WITH LATER CVD GROWTH

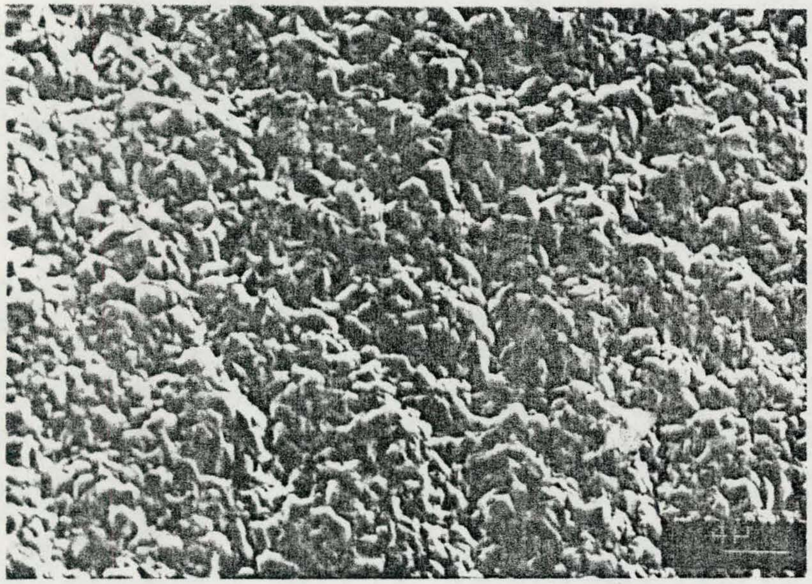
IN-SITU CVD GROWTH EXPERIMENTS NOW NEEDED

PULSED LASER RECRYSTALLIZATION OF CVD POLY-GaAs

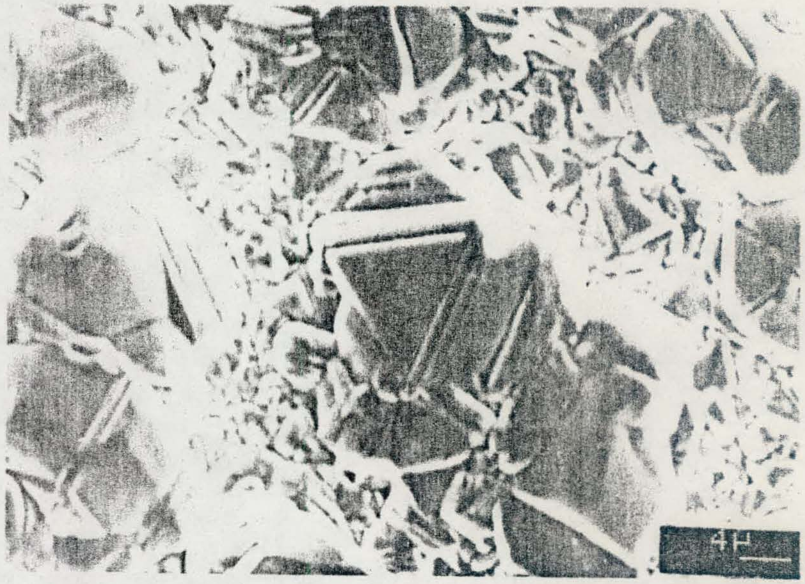
$T_{SUB} \sim 20°C$

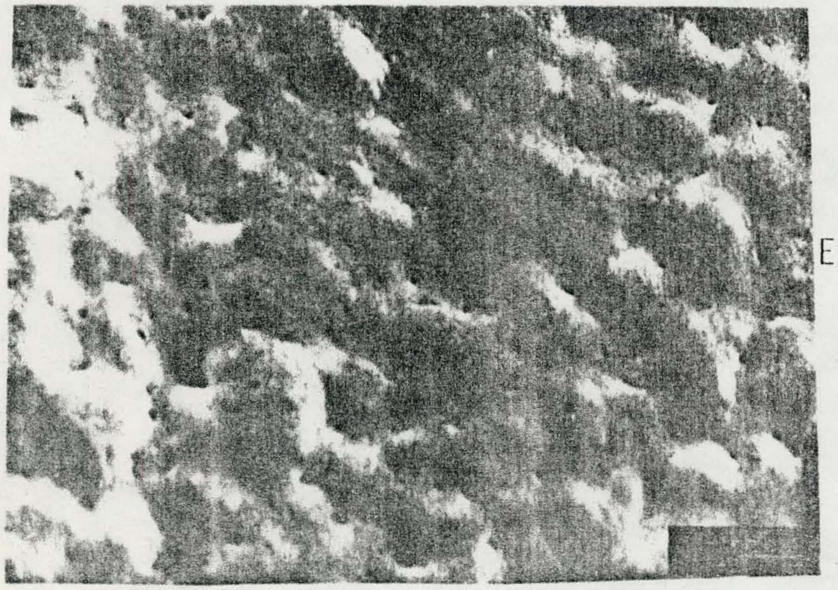
$\lesssim 1\mu m$ GRAIN SIZE

$\gtrsim 5\mu m$ GRAIN SIZE



$E_\ell = 0$

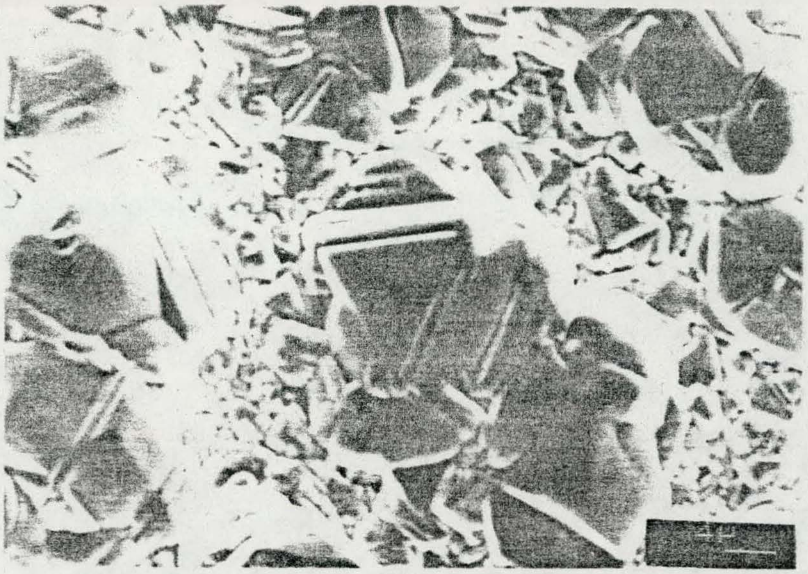




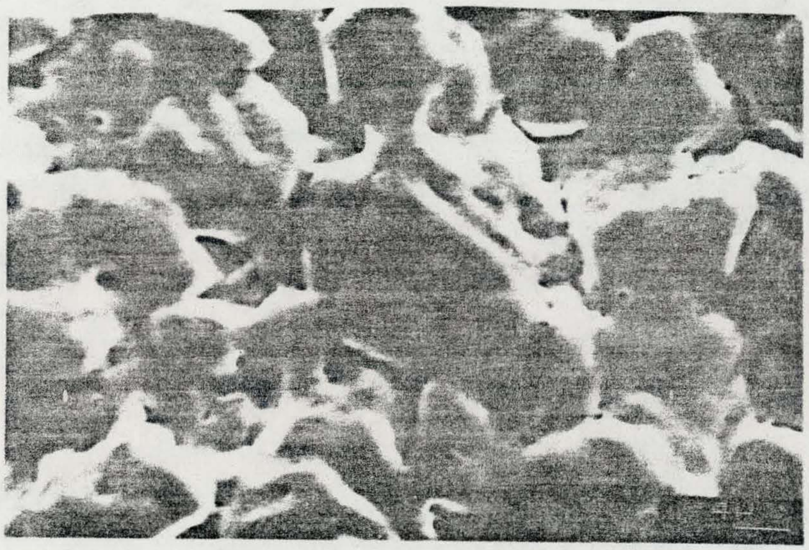
$E_\ell = 0.5\ J/cm^2$

PULSED LASER RECRYSTALLIZATION OF CVD POLY-GaAs

$T_{SUB} \sim 20°C$, $\gtrsim 5\mu m$ GRAIN SIZE



$E_\ell = 0$

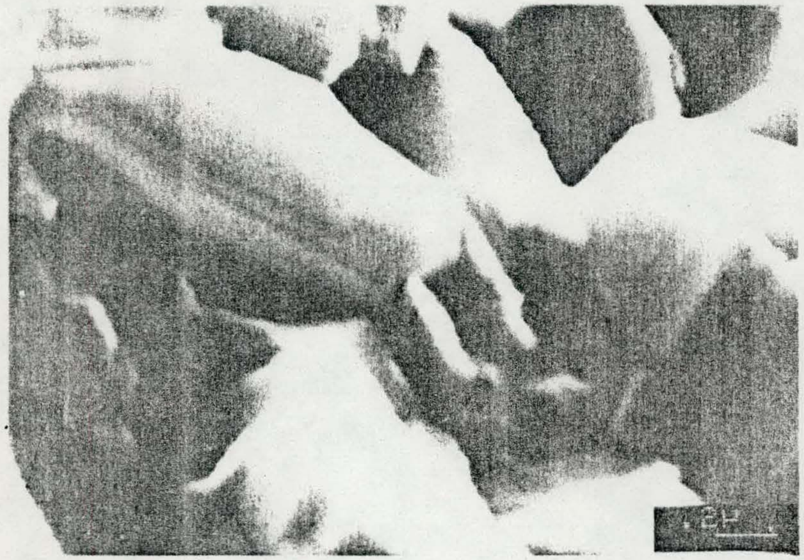


$E_\ell = 0.5\ J/cm^2$

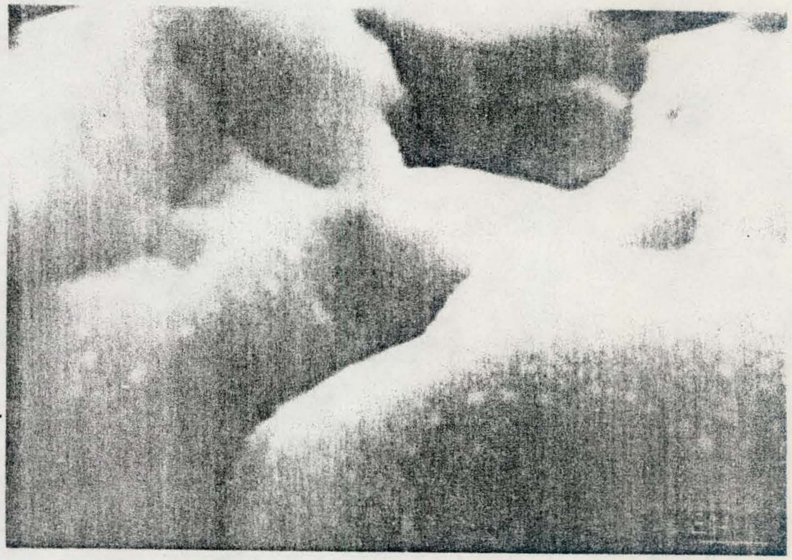
$E_\ell = 0.9\ J/cm^2$

PULSED LASER RECRYSTALLIZATION OF CVD POLY-GaAs

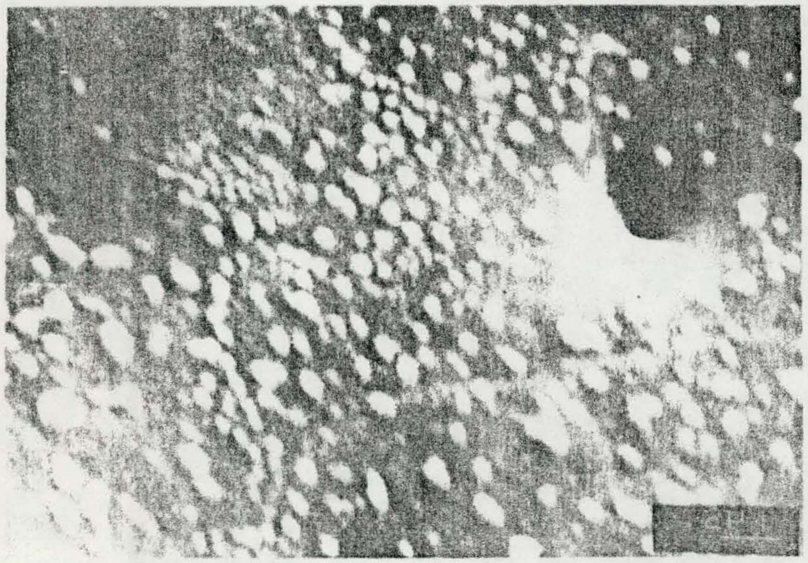
$T_{SUB} \sim 20°C$, $\lesssim 1\ \mu m$ GRAIN SIZE



$E_\ell = 0$



$E_\ell = 0.2\ J/cm^2$



$E_\ell = 0.5\ J/cm^2$

$E_\ell = 0.7\ J/cm^2$

PLANNED ACTIVITIES

(CONTINGENT ON ADDITIONAL FUNDING FOR GaAs RESEARCH)

SOLAR CELL FABRICATION

1. EXPLORE MO-CVD FILM GROWTH

2. FORM THIN FILM GaAs SOLAR CELLS BY CVD ON LATTICE-MATCHED LASER-PROCESSED SUBSTRATES. (FOCUS LASER PROCESSING ON SUBSTRATE PREPARATION AND RECRYSTALLIZATION).

BASIC STUDIES

3. PULSED LASER ANNEALING OF ION IMPLANTED GaAs

   EXPLORE CONSEQUENCES OF { ENCAPSULATION / SUBSTRATE HEATING }

4. ELECTRICAL/OPTICAL PROPERTIES OF LASER INDUCED DEFECTS (I-V, C-V; DLTS; ELLIPSOMETRY)

5. COMPARISON OF PULSED AND CW LASER ANNEALING OF GaAs.