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Project Title: EXPLORATORY STUDY ON MICROANALYSIS OF THIN

FILMS BY BACKSCATTERING TECHNIQUES

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July 22 - 25, 1975.

OVERALL OBJECTIVES

1. To use backscattering spectrometry in the 1-2 MeV range
    for the determination of the composition and the detection
    of interdiffusion in thin film structures of interest to
    photovoltaic conversion.

2. To investigate the solid-phase epitaxial growth (SPEG) of
    Si layers at low temperatures obtained by interdiffusion
    processes.

3. To investigate backscattering spectrometry in the sub-MeV
    range and to assess its possibilities and problems.

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PLANNED ACTIVITY FOR LAST SIX MONTHS

1. Investigate electrical properties of the SPEG layer.

2. Investigate the possibility of SPEG with metal films other
    than Pd as transport medium.

3. Investigate BS below 1 .IeV

EXPLORATORY STUDY ON MICROANALYSIS
OF THIN FILMS BY BACKSCATTERING TECHNIQUES

by

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ABSTRACT

I. SPEG

To be potentially useful, SPEG layers must have controllable electrical characteristics, particularly with regards to conductivity type and resistivity value. Efforts were therefore undertaken to establish that such a control is possible.

We added one processing step to the standard sample fabrication procedure by vacuum-depositing a thin layer (nominally 5Å) of Sb before the deposition of the amorphous Si layer, as shown in diagram labelled Caltech 4 (C4). Anneal steps remained unchanged. The resulting SPEG layer was analyzed in four different ways: (a) Auger Electron Spectroscopy (see C5),performed after the uppermost Pd_xSi_y layer was removed, confirmed that Sb was present within the SPEG layer of Si. (b) The I(V) characteristics of the SPEG layer against the Si substrate (<100>, 1-10 Ωcm p-type) was rectifying, and the layer itself afforded good electrical conductivity and easy ohmic contacting with W wires via the Pd_xSi_y layer (see C6). (c) A scanning microprobe picture of a cleaved sampled taken in the electron-beam-induced current mode established the presence of a depletion region more than 1 µ below the surface (see C7 and C3). (d) Hall effect data indicated that the SPEG layer was n-type, had an average free carrier concentration of about 10^{13} cm^{-3} and an average electron mobility $\bar{\mu}_n$ of about 40 cm^2/Vs (see C9). These results apply to a typical sample obtained with initial layers of about 1000Å Pd, 5 Å Sb and 1 µ of amorphous Si annealed in vacuum, first at 280° for 30 min and then under slowly increasing temperatures ($\gtrsim$ 0.2 °C/min) up to 525 °C. The evidence that the layer is n type and well doped is convincing. We plan to determine the properties of the doped SPEG

layers more accurately, and to try other methods of intro-
ducing the dopant species of various kinds. The main problems
are inadequate process control and marginal sensitivity of
analytical tools.

SPEG with Pd_2Si as transport layer has two stages (see
C10): (a) Initial fast (~10 Å/s at 500°C) transient regime. The
growth starts with islands which ultimately join to form a
layer (C11). The final thickness is equal to that of the
initial Pd_2Si layer (C12). (b) Steady state regime. The
growth is much slower (~ 1 Å/s), linear, and independent of
the thickness of the transport medium (C13). The rate is thus
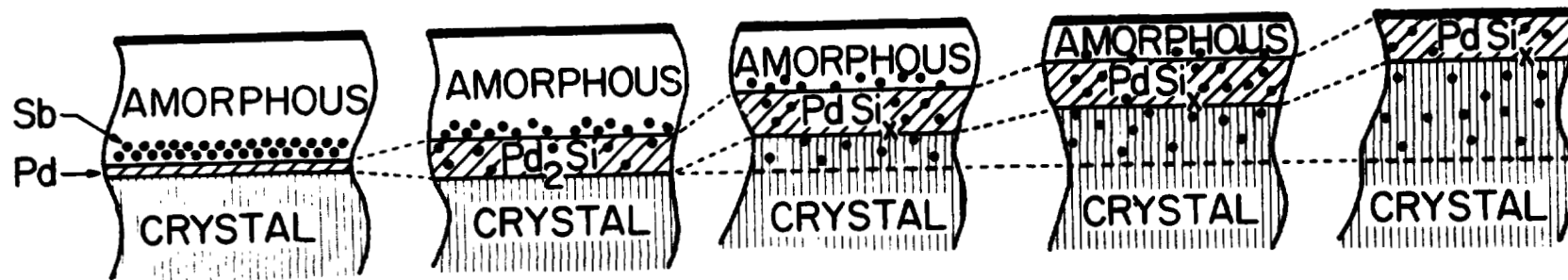not diffusion-limited.

SPEG with Ni silicide in lieu of Pd silicide as
transport medium has been demonstrated by backscattering spec-
trometry (C14). As a whole, Ni SPEG is quite similar to that
cf Pd SPEG (C15). The transient is less distinct, because
slower, and in the steady state regime, the boundaries of the
transport medium lose their definition as the growth proceeds,
which indicates poorer quality of the grown layer. Reactions
require temperatures which are typically 90°C above the corres-
ponding temperatures of Pd SPEG.

II. BACKSCATTERING SPECTROMETRY (BS)

To develope BS at energies below 1 MeV, depth calib-
ration must be provided first by absolute measurements of stop-
ping cross sections. Typical past errors of ± 10% are unde-
sirably large. We have compared various methods of data
evaluation and their errors with computer programs tested against
real ^{4}He spectra. All methods can attain a few %, but values
derived from films of known mass per unit area are generally
most reliable. Main sources of errors are caused by detector
noise and background signals. Absolute measurements are planned
next.

Summaries of main results, major problems, planned
activity and renewal proposal are given in C16 to C19.
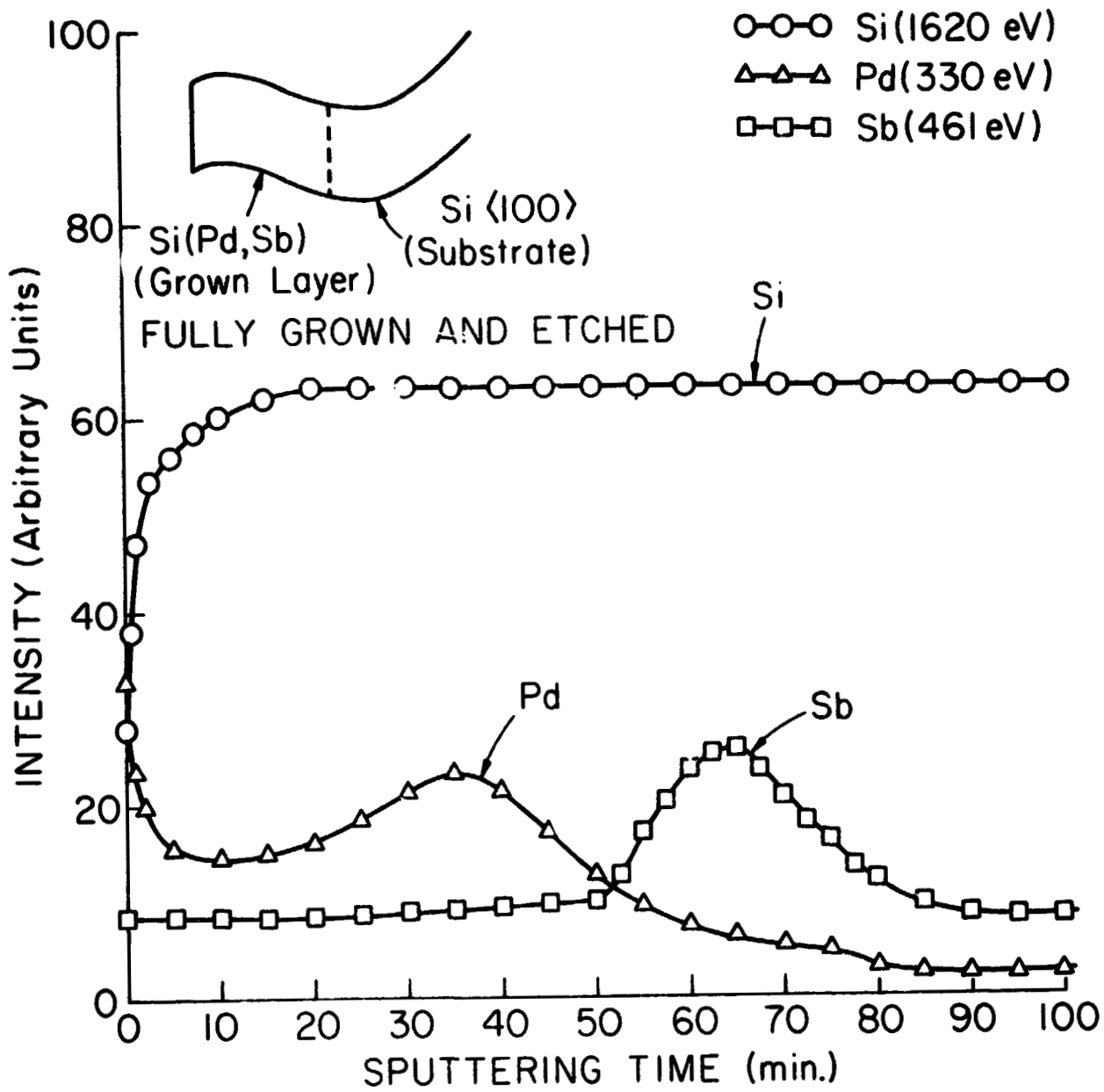
ROOM TEMP. → ~200° C → ~400° C →

Sb
Pd

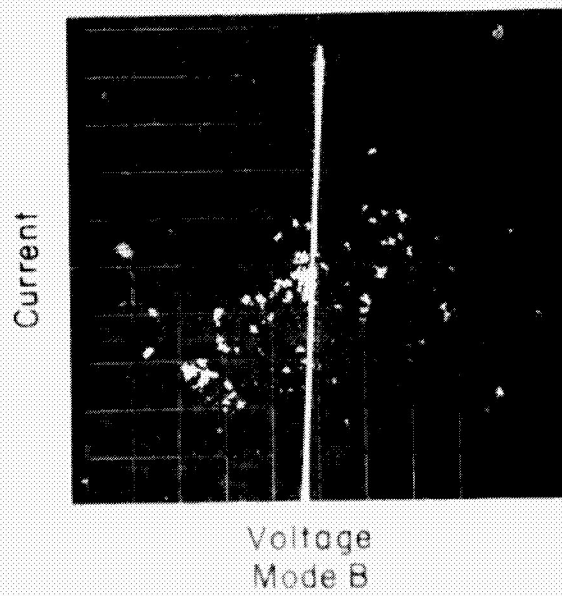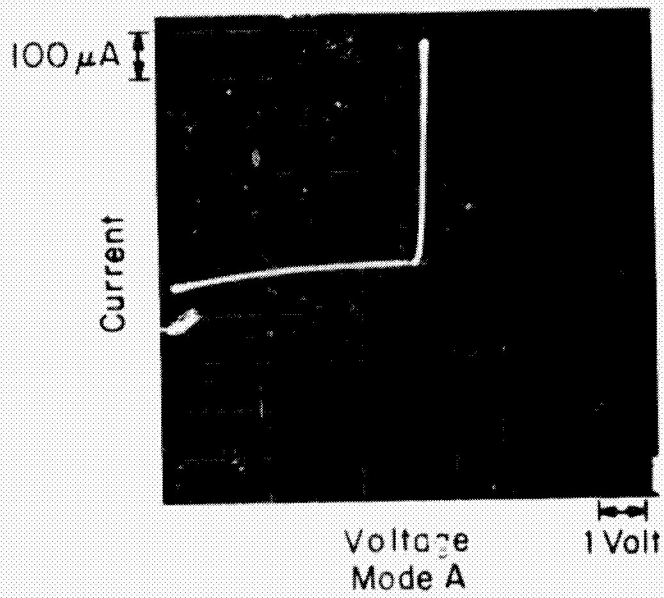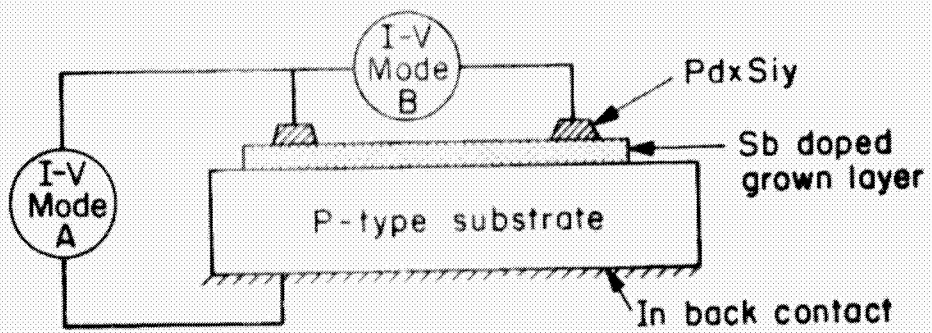| AMORPHOUS | | AMORPHOUS | | AMORPHOUS | | AMORPHOUS | |
| Pd | | Pd₂Si | | PdSi | | PdSi | | PdSi |
| CRYSTAL | | CRYSTAL | | CRYSTAL | | CRYSTAL | | CRYSTAL |

INITIAL STATE   EXPOSURE OF VIRGIN SURFACE   EPITAXIAL GROWTH
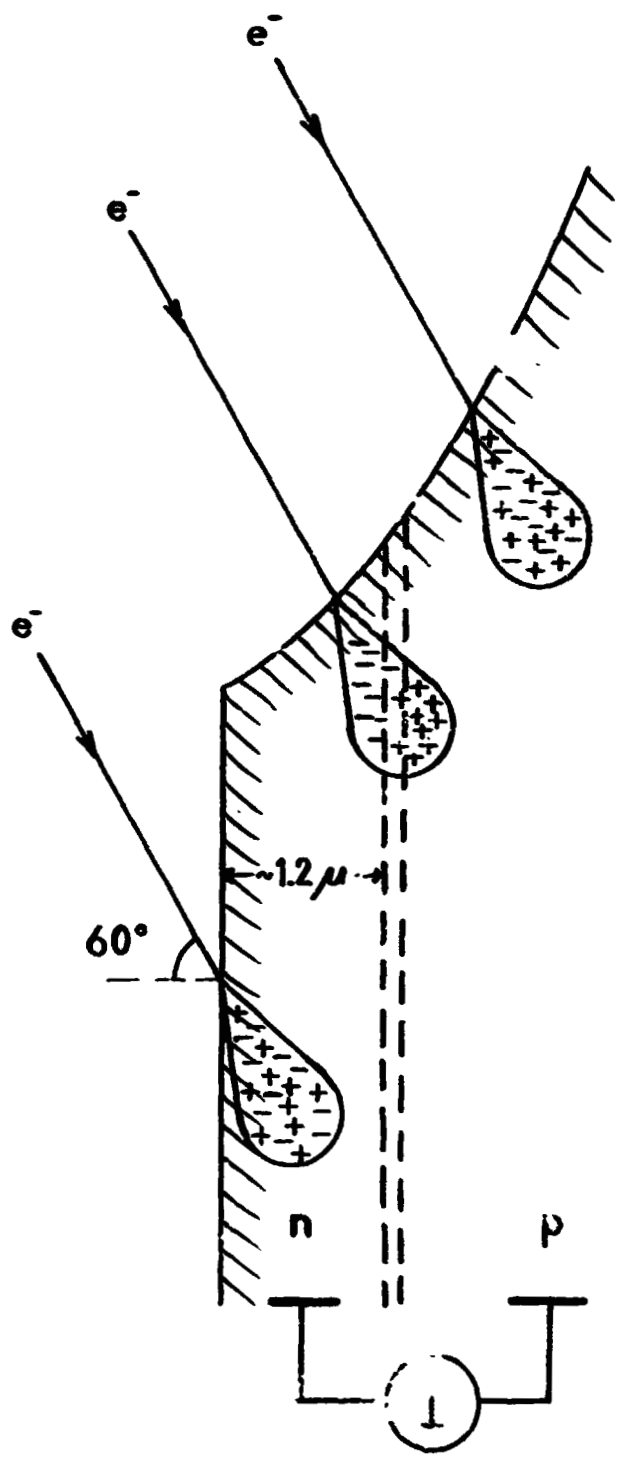
SPEG

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FULLY GROWN AND ETCHED

Legend:
- O–O–O Si(1620 eV)
- △–△–△ Pd(330 eV)
- □–□–□ Sb(461 eV)

Y-axis: INTENSITY (Arbitrary Units)
X-axis: SPUTTERING TIME (min.)

Si(Pd,Sb) (Grown Layer)
Si ⟨100⟩ (Substrate)

I-V Mode B

I-V Mode A

PdxSiy

Sb doped grown layer

P-type substrate

In back contact

100 μA

Current

Voltage
Mode A

1 Volt

Current

Voltage
Mode B

Substrate

Top of epitaxial
layer
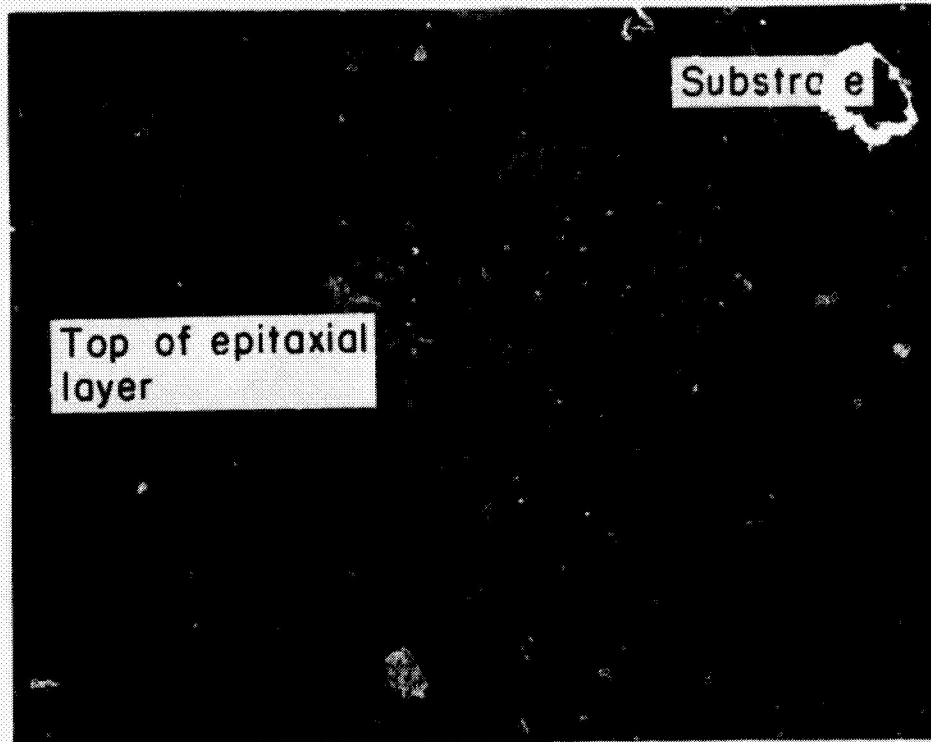
2nd electron Mode

20μ
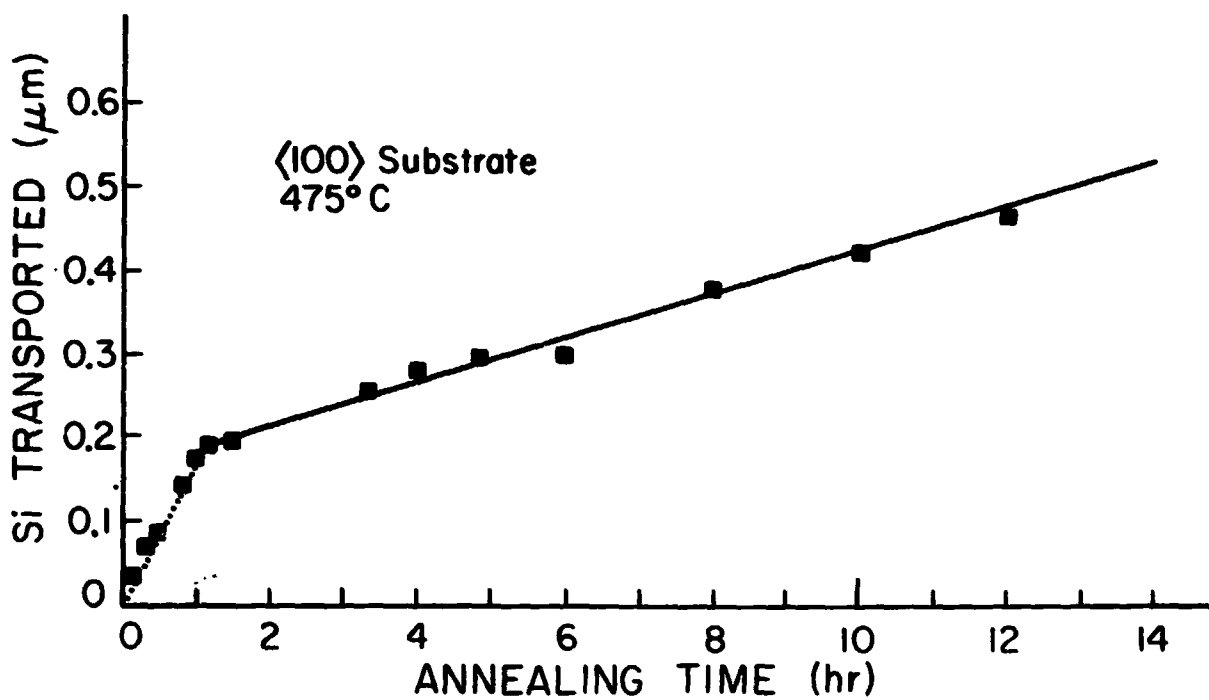
EBIC Mode

520

e⁻

e⁻

e⁻

e⁻

~1.2 μ

60°

n   p
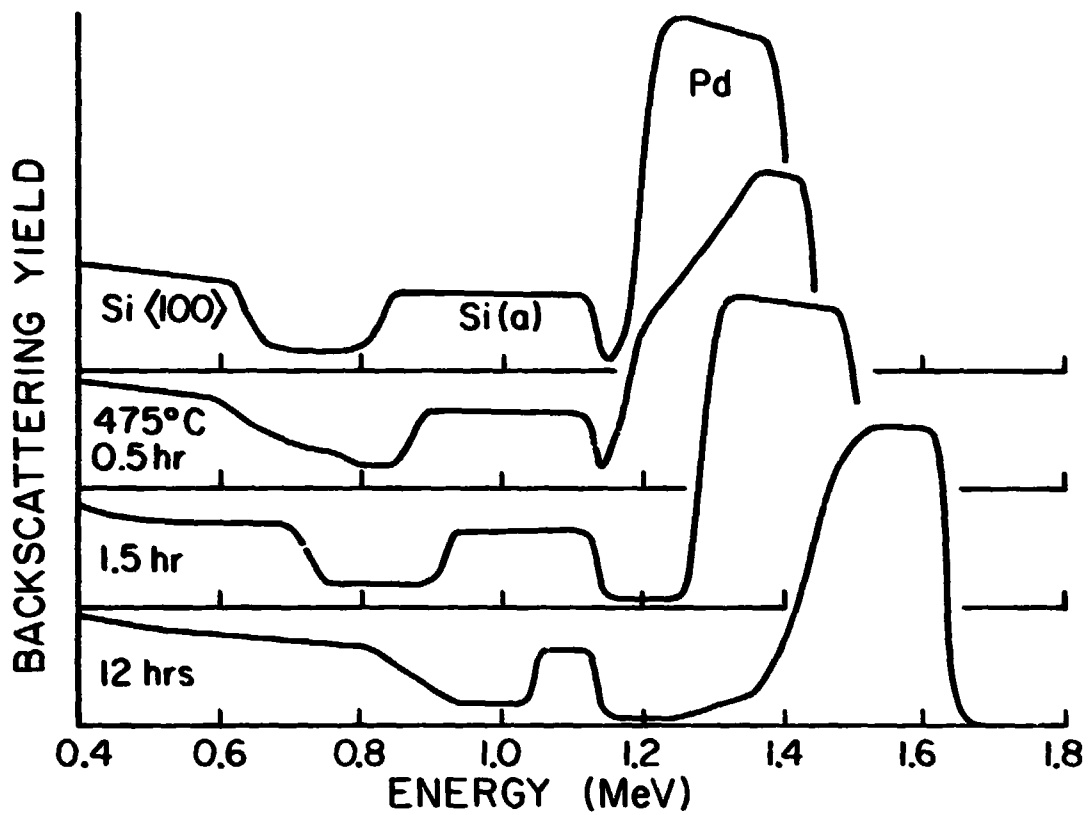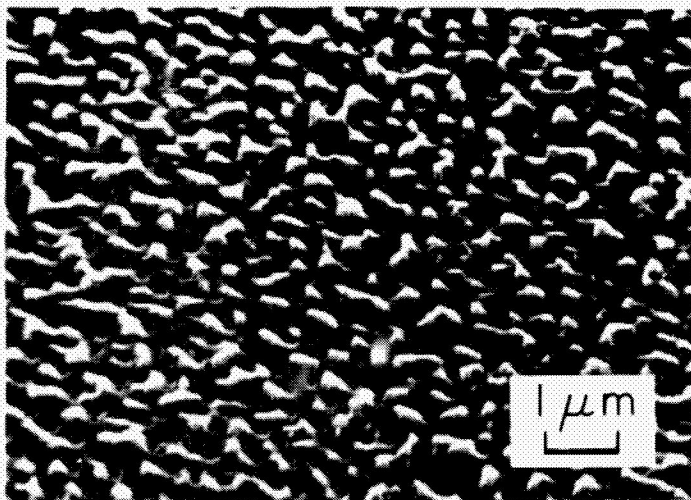
EBIC

521

HALL EFFECT

Data obtained at room temperature with van der Pauw patterns. Values are averages over the whole thickness ($\sim$ 1 μm) of the SPEG layer.

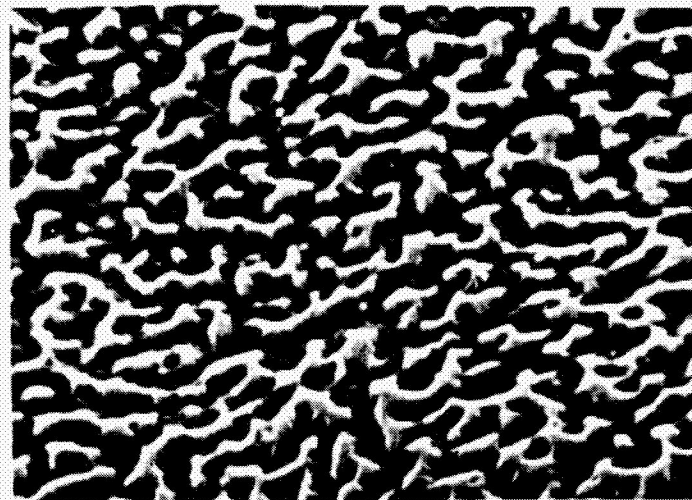|	SPEG Layer	Comparison with bulk single crystal	
Conductivity type	n	n	
Mobility μ_n	$\sim$ 40-50	140	cm^2/Vs
Carrier Concentration	10^{19}	10^{19}	cm^{-3}
Resistivity	$\sim$ .02	. J04	Ωcm

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475°C   30 min

50 min

70 min

90 min

2.0 MeV ^{4}He$^+$

Si <100>   NiSi   Si(a)

Si <100>   Si(a)

Ni

Si

N$_i$

350°C 30 min

Si (<100>)   Si(a)

590°C   5 min

10 min

20 min

50 min

BACKSCATTERING YIELD

ENERGY (MeV)

0.2   0.4   0.6   0.8   1.0   1.2   1.4   1.6   1.8
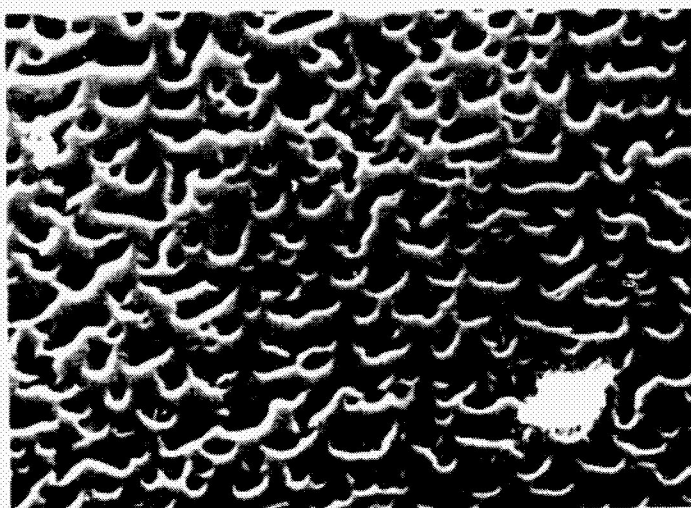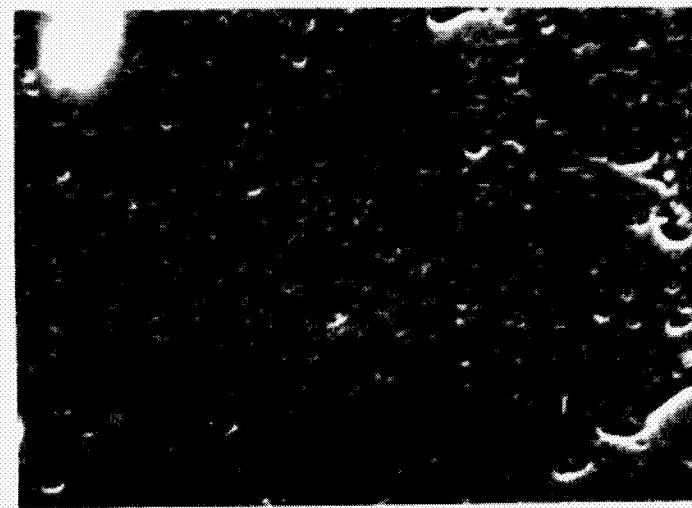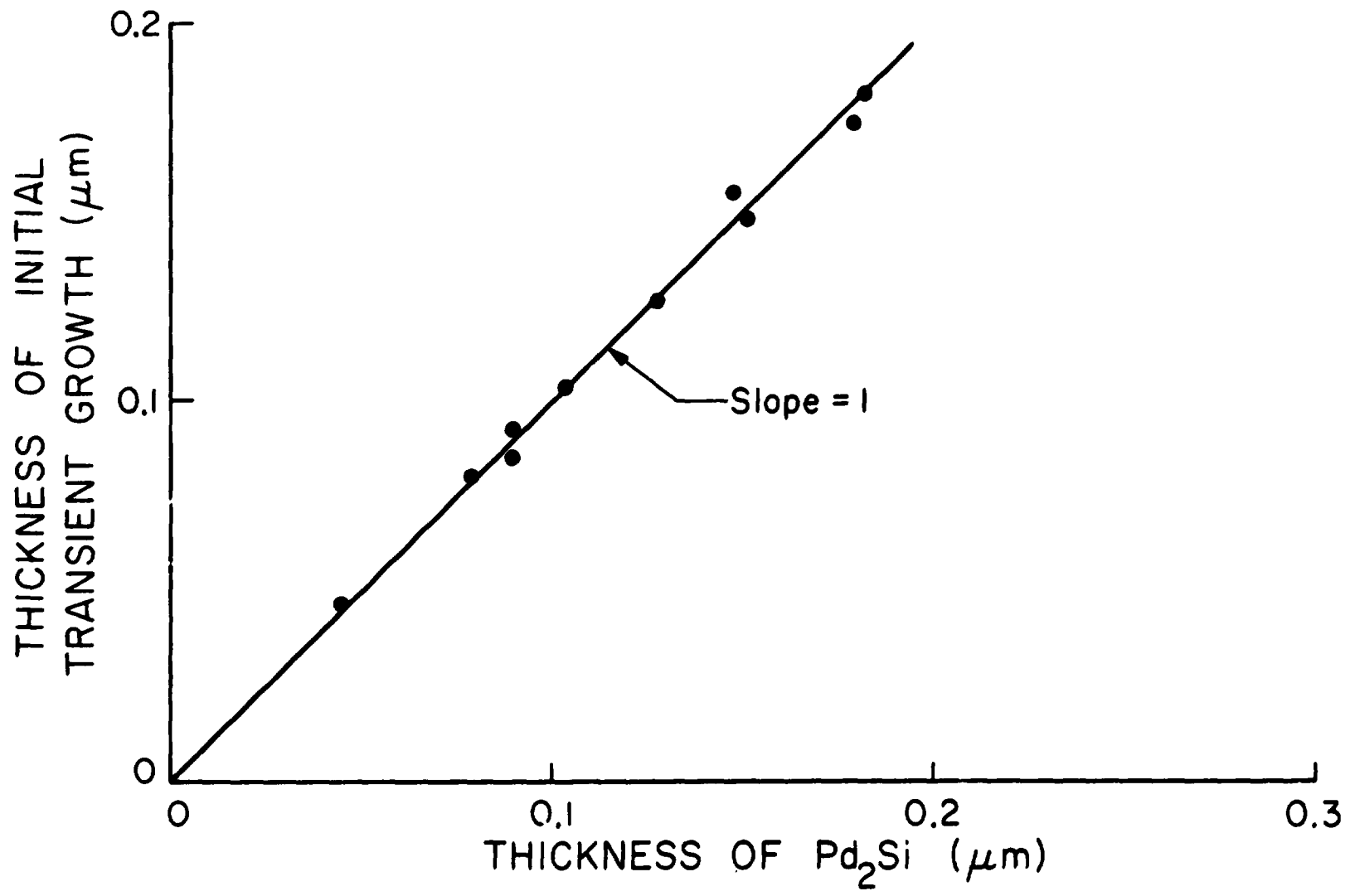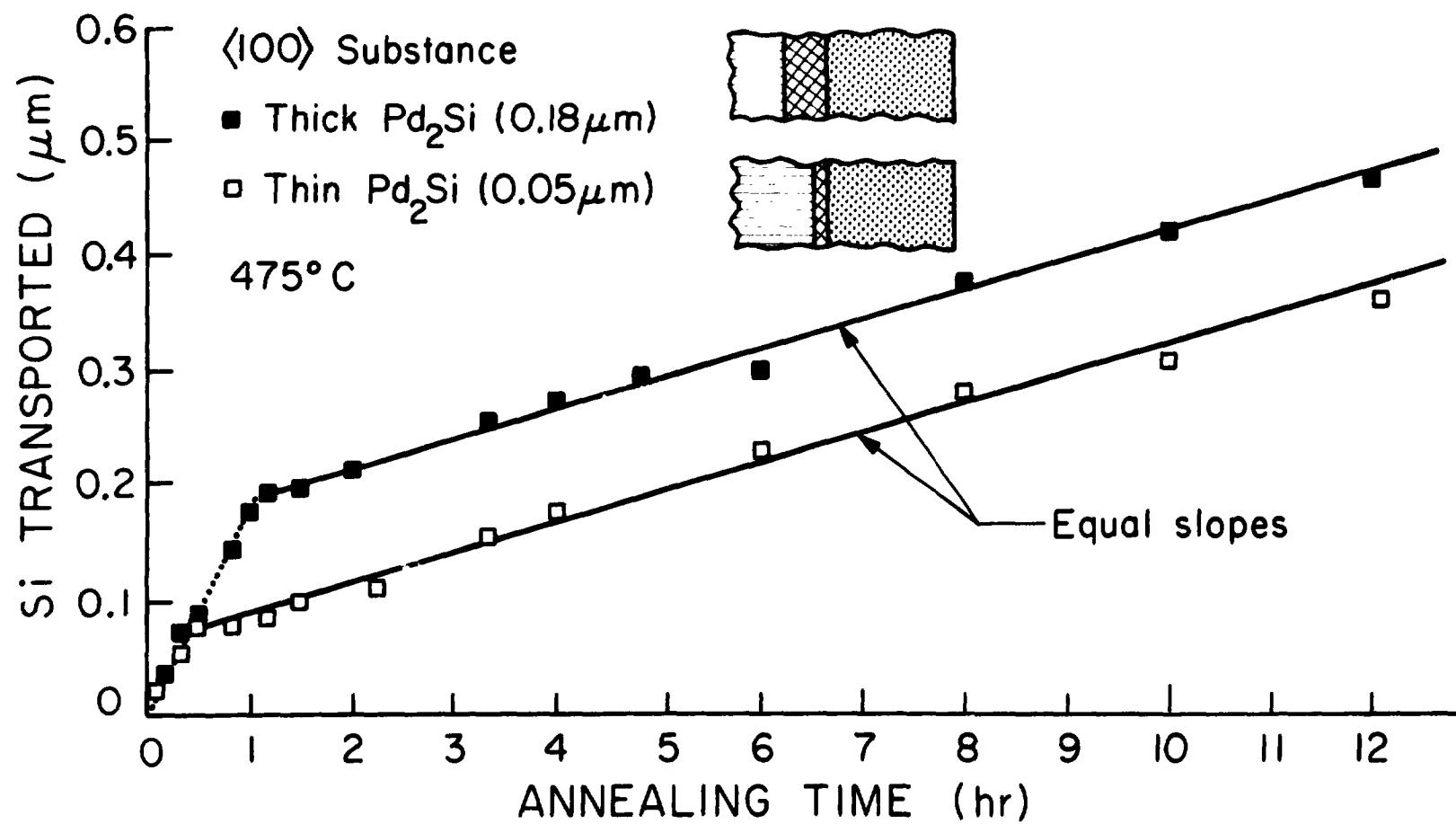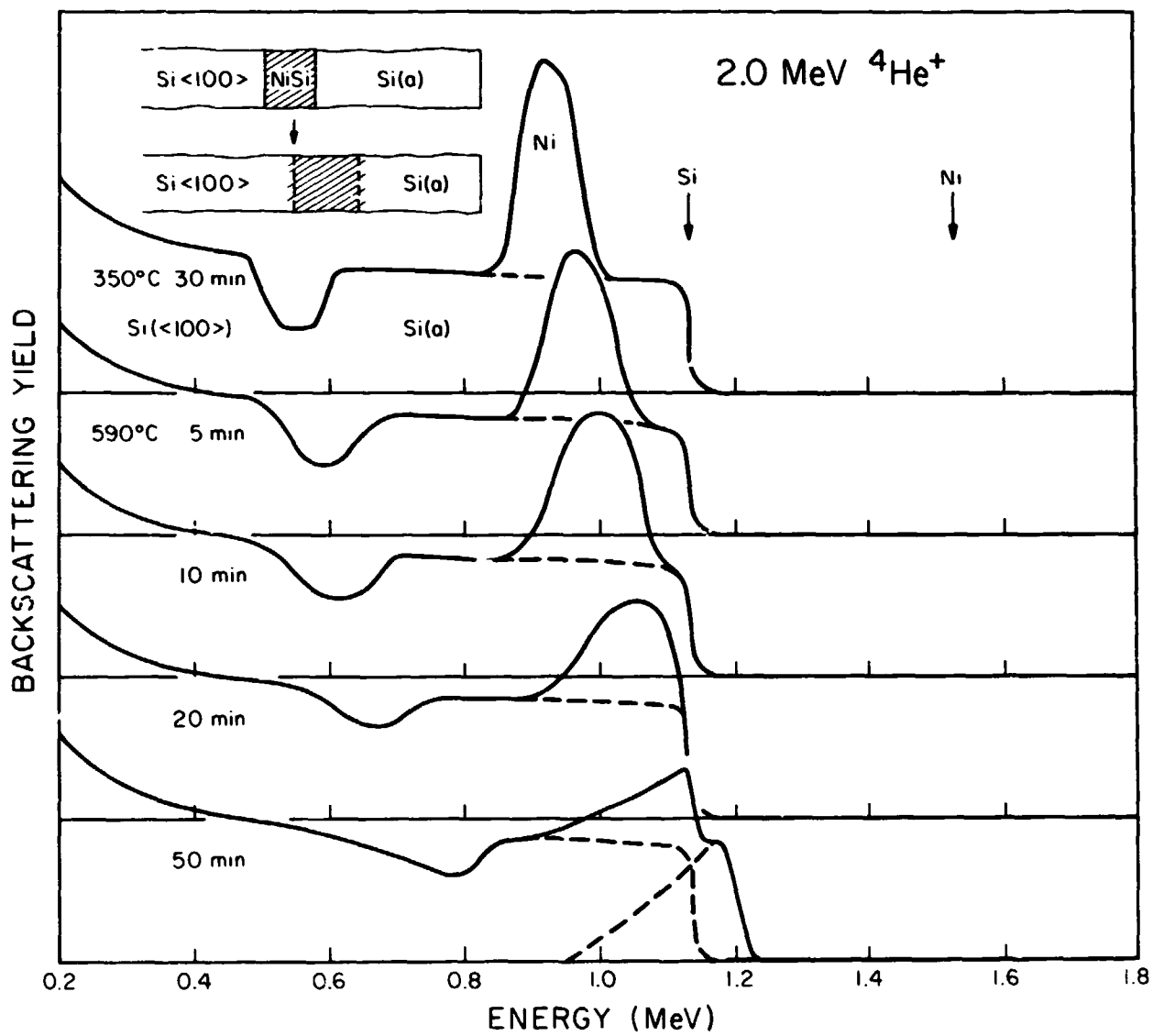
COMPARISON OF SPEG WITH Pd AND Ni

	Pd	Ni	
SAMPLE			
Substrate	<100>	<100>	
Metal Film	~1000	~1000	$\overset{o}{A}$
Si(a) Film	~1	~1	μm
FORMATION OF TRANSPORT MEDIUM			
Typical Temperature	280	350	°C
Typical Time	30	30	min
Composition by BS	$\frac{Pd}{Si} = \frac{2}{1}$	$\frac{Ni}{Si} = \frac{1}{1}$	
by x-rays	Pd_2Si	NiSi	
TRANSPORT OF Si			
Typical Temperature	~500	~590	°C
Transient Rate	~10	~2	$\overset{o}{A}/s$
Form	island	no island	
Steady State Rate	~1	~1	$\overset{o}{A}/s$
Structure	epitaxial	epitaxial (poor)	
Apparent Activation Energy	~4	~4	eV

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SUMMARY OF KEY RESULTS

1. Doping of SPEG layers is possible; proof obtained with Sb
   and established via:
   - I(V) characteristics
   - Hall effect measurements
   - EBIC μ-probe pictures
   - AES

2. SPEG with Pd_2Si has two stages:
   Initial transient regime
   - 10 A°/s rate
   - island growth
   - thickness = that of Pd_2Si layer
   Steady State regime
   - 1 A°/s rate, independent of Pd_xSi_y layer thickness
   - continuous film growth

3. SPEG with NiSi also works; generally similar to SPEG with
   Pd_2Si:
   - Corresponding process temperatures are typically
     ~ 90°C higher for Ni
   - Layer quality presently inferior to obtained with
     Pd_2Si

4. Identified best methods for stopping power measurements
   below 1 MeV from backscattering spectra.

MAJOR PROBLEMS

SPEG

Control of fabrication processes

- cleanliness of interfaces

- purity of deposited layers

- amount of doping

- annealing ambient

Characterization of final product

- limitations of analytical tools

BS

Limitations in system

- detector noise

- preamplifier noise

Limitations in target

- purity

- thickness $\left.\begin{array}{l}\end{array}\right\}$ density
- mass/cm^2

PLANNED ACTIVITY FOR NEXT SIX MONTHS

1. Characterization of doped SPEG layers.

2. Doping of SPEG layers by other dopants or other incorporation methods.

3. Compare SPEG with regrowth of amorphous Si layers on single crystal Si substrates.

4. Obtain stopping cross sections in 0.3 - 1.0 MeV range.

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PLANNED RENEWAL REQUEST

Major Goals

    Investigate SPEG

    Assess practical potential of SPEG to solar cell, and to
        semiconductor devices generally

    Liberate SPEG from single crystal substrate

    Develop sub-MeV backscattering spectrometry

Estimated Dates and Costs

    August, 1976 to August, 1978 (24 Months) $150,000.00

<div align="right">Caltech 19</div>