Electrolyte Electroreflectance Investigation of Microcrystalline Silicon Semiconductors

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The sharp features in the optical properties of crystalline semiconductors are determined by the long range order and hence are quite sensitive to disorder. In order to get information about the nature of disorder in hydrogenated amorphous silicon (a-Si:F:H) we have investigated electrolyte electroreflectance (EER) spectra of (a) high temperature thermal annealing (HTA) a-Si:H (B), as well as unannealed a-si:F:H (B) and a-Si:F:H (P), (b) heavily doped n-type *a*-Si:F:H and (c) lightly doped type a-Si:F:H alloy. For comparison we also studied the modulated optical spectra of crystalline silicon (c-Si) and laser-annealing on ion-damaged silicon.

No distinct features of the EER spectra are found in unannealed a-Si:H (B) and lightly doped n-type a-Si:F:H samples. We found 3.4 eV and 4.5 eV features in the EER spectra of heavily doped n-type (P or As) Si:F:H alloy. Those samples showed a microcrystalline structure between amorphous and crystalline phase. HTA a-Si:H (B) samples present EER features. Both high temperature annealing and laser annealing processes indicate the increase of crystallinity.

I. INTRODUCTION

WITHIN the past few years several group[1~4] have reported the observation of the micro-crystalline (μC) phase in the films of the a-Si:H and a-Si:F: H alloy systems. Recently, the c-Si has received considerable attention because of its possible application as contact interlayers in solar cells[2~3].

Tsu et *al*[4] have reported, in heavily As- or P- doped Si:F:H alloy systems, the appearance of a Raman peak lying intermediate between 522 cm^{-1} for c-Si, and 480 cm^{-1} for amorphous silicon. Whenever such Raman peak is observed, EER peaks appear around 2 eV, together with those associated with c-Si at 3.4 eV and 4.5 eV. They interpreted these observations in terms of an intermediate range order or a "microcrystalline phase". They also indicated that the size of micocrystallite of Si:F:H (P) sample is in the range of 20 Å to 60 Å.

It is of considerable interest to investigate the modulated optical properties of n-type doped a-Si:F: H alloy as well as boron doped a-Si: H alloy. In order to understand the electronic properties of a-Si, μc-Si and c-Si alloy systems we have measured the EER spectra of (a) HTA a-Si:H (B) as well as unannealed a-Si:H (B), (b) lightly doped n-type Si:F:H alloy, (c) heavily

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doped n-type Si:F:H alloy, and (d) laser annealing on ion-damaged silicon specimens with different laser energy densities.

This paper reports work on the modulated optical spectra of those samples. We have observed sharp features in EER spectra of heavily doped n-type Si:F:H samples as well as HTA-a-Si: H (B) samples. The features in EER spectra for the as-grown n-type doped Si:F:H samples indicate that the degree of crystallization is not as good as for the high-temperature materials. The EER results are consistent with the observations reflectivity measurement[6]

II. THIORETICAL CONSIDERATIONS

The relative modulation AR/R of the reflected beam is the basic quantity in electric field modulation spectroscopy. In order to understand EER spectra connection must be made between the experimentally observed quantities, AR/R, and the optical parameters of the material.

The fundamental quantity which describes the optical response of the material is the complex dielectric function $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$. We assume that this complex dielectric function is uniformly changed by the electric field modulation by amounts $\Delta\epsilon_1$ and $\Delta\epsilon_2$. We also assume that ϵ and $\Delta\epsilon$ are scalar quantities in the material.

For near-normal incident light the reflectivity can be expressed in terms of the index of refraction as following form

$$R=\left|\frac{(n-n_a)}{(n+n_a)}\right|^2 \qquad (1)$$

$$n^2=\epsilon,\ n_a^2=\epsilon_a$$

where n_a is the real refractive index of the ambient. It has been shown:[7~10]

$$\frac{AR}{R}=\alpha(\epsilon_1,\epsilon_2,\epsilon_a)\Delta\epsilon_1+\beta(\epsilon_1,\epsilon_2,\epsilon_a)\Delta\epsilon_2 \qquad (2)$$

where α and β are the Serahpin coefficients.

Aspenes showed that under low field limit the EER signal is given by[10]

$$\frac{\Delta R}{R}=-\frac{2q}{\epsilon_0}VNL(\hbar\omega) \qquad (3)$$

where q is the element charge, ϵ_0 is the static dielectric constant, V the amplitude of the applied modulating voltage (at frequency Ω_m) in the space-charge region, N the carrier concentration and $L(\hbar\omega)$ is a spectral line shape function characteristics of a particular material.

III. EXPERIMENTAL DETAILS

All doped and undoped a-Si:F:H samples have been prepared by the plasma glow-discharge decomposition technique as well as a-Si:H samples. Most of the specimens were prepared at Energy Conversion Devices (ECD) Inc. in Michigan. The a-Si:F:H samples studied were made by the capacitance discharge method using an RF power of 30 Watt decomposite a gas mixture of $SiF_4:H_2$ of 5:1. Normally the sample substrate electrode was bias at approximately 100 V. A gas flow rate around 0.05 liter/min at 0.5 torr was normally used.

Doping was accomplished by the introduction of PH_3 (for P-doped) or AsH_3 (for As- doped). The temperature of the substrate was held at 300°C. Corning 7059 glass was used as a substrate. boron- doped was performed by the introduction of B_2H_6 gas. HTA-Si:H(B) samples have been annealed at temperature of -1000°C for about 10 min.

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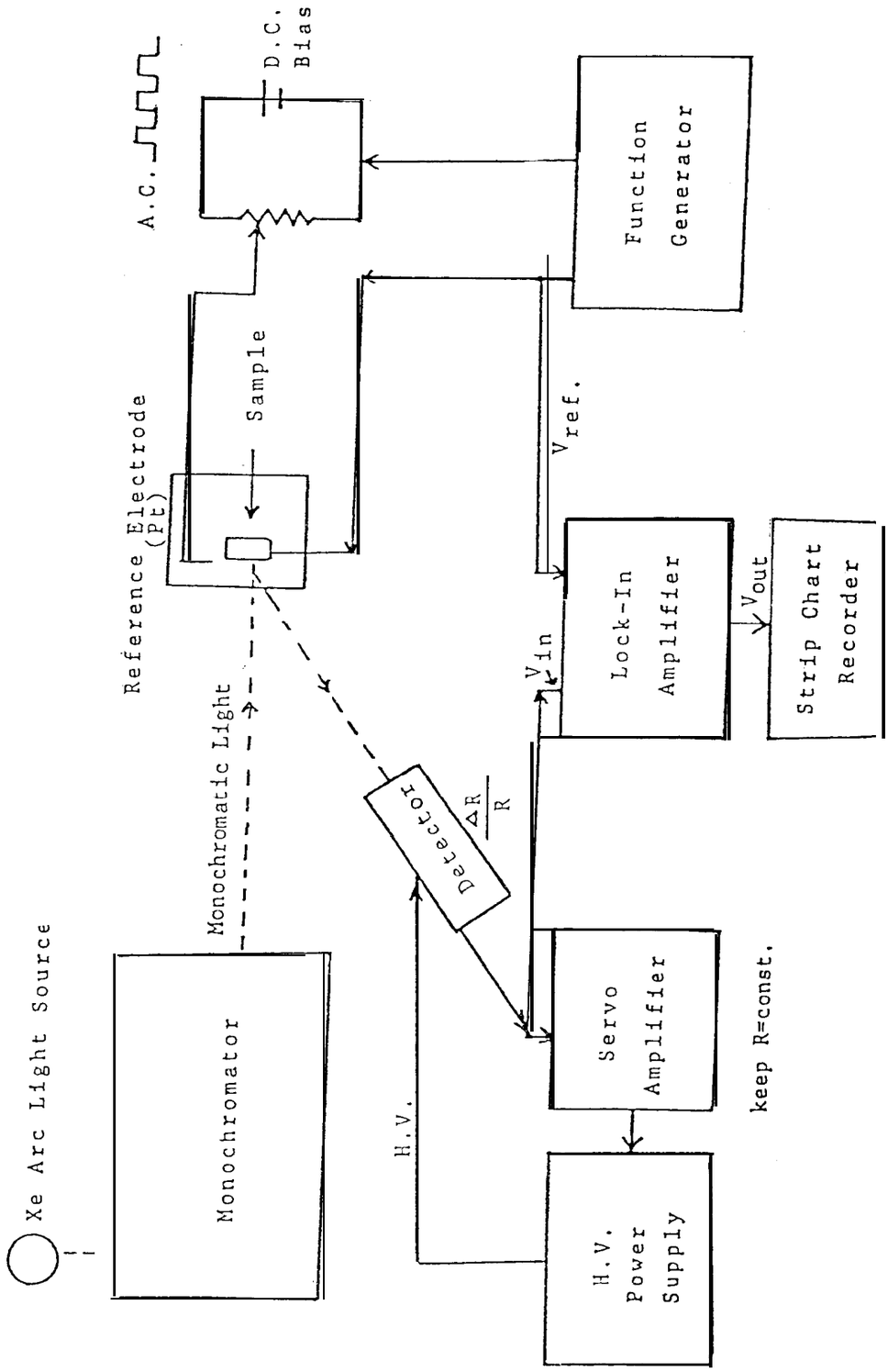

Fig. 1. The experimental arrangement for the EER measurement.

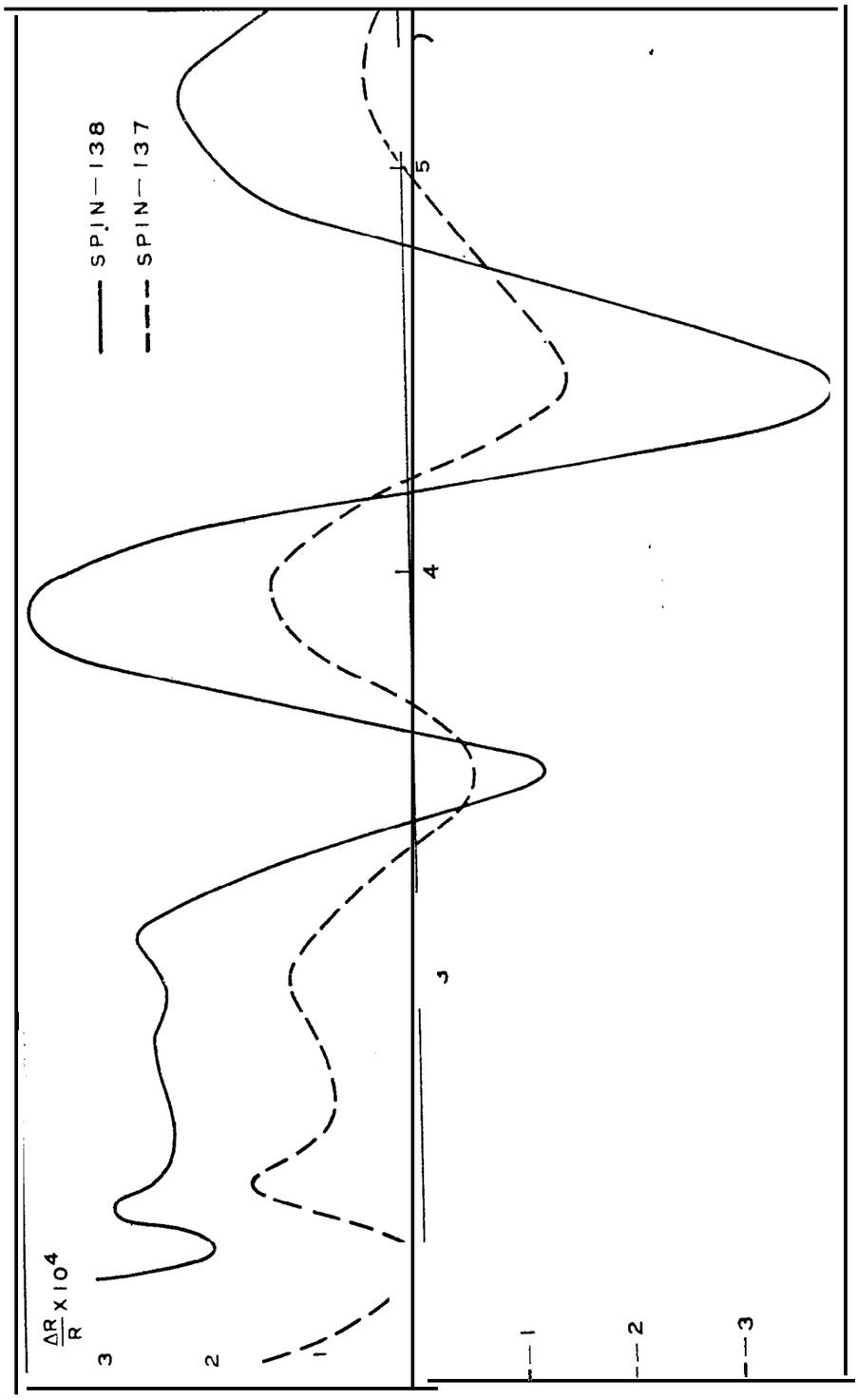

Fig. 2. EER spectra for heavily phosphorus doped Si:F:H alloy.

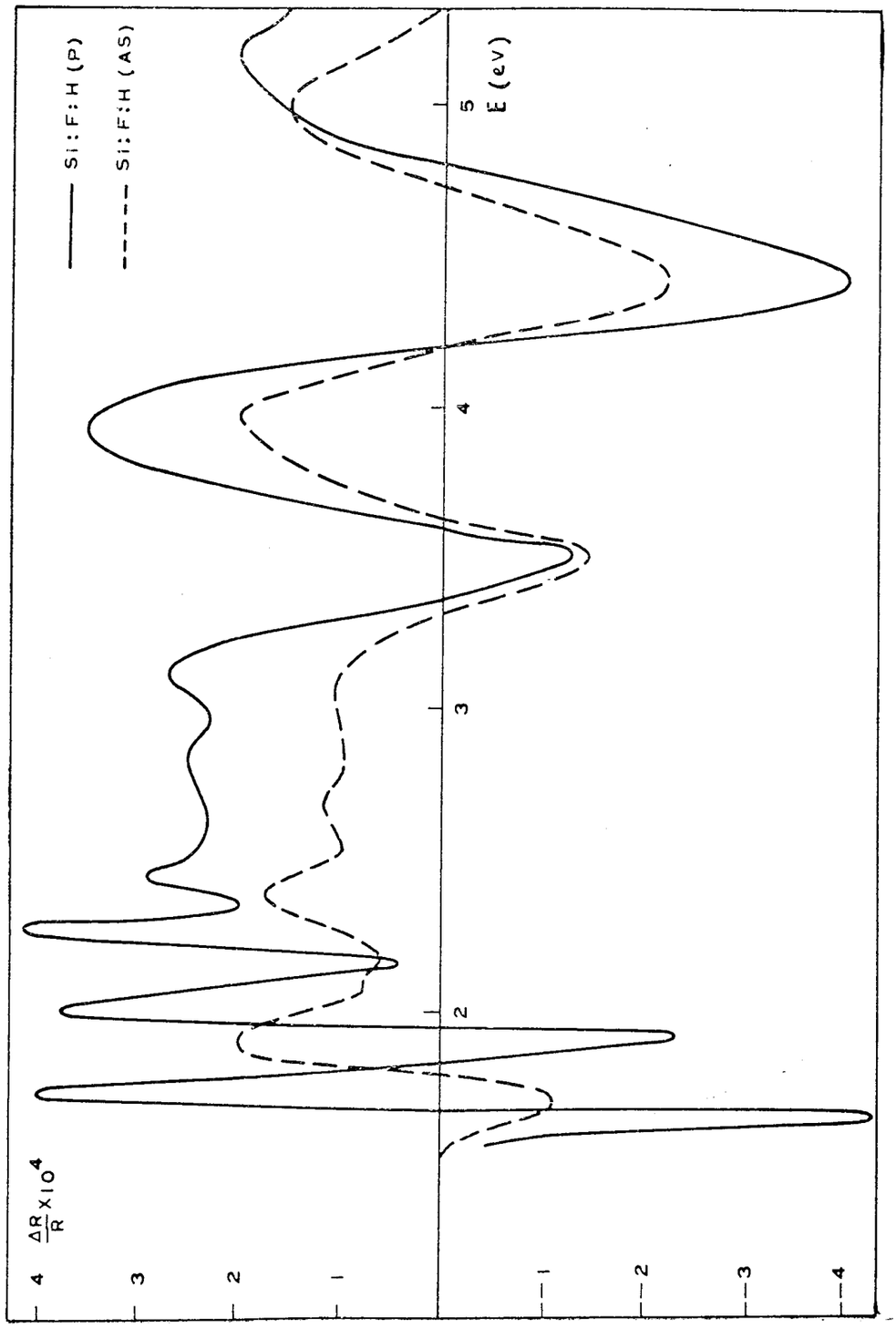

Fig. 3. EER spectra for heavily P- or As- doped Si:F:H alloy.

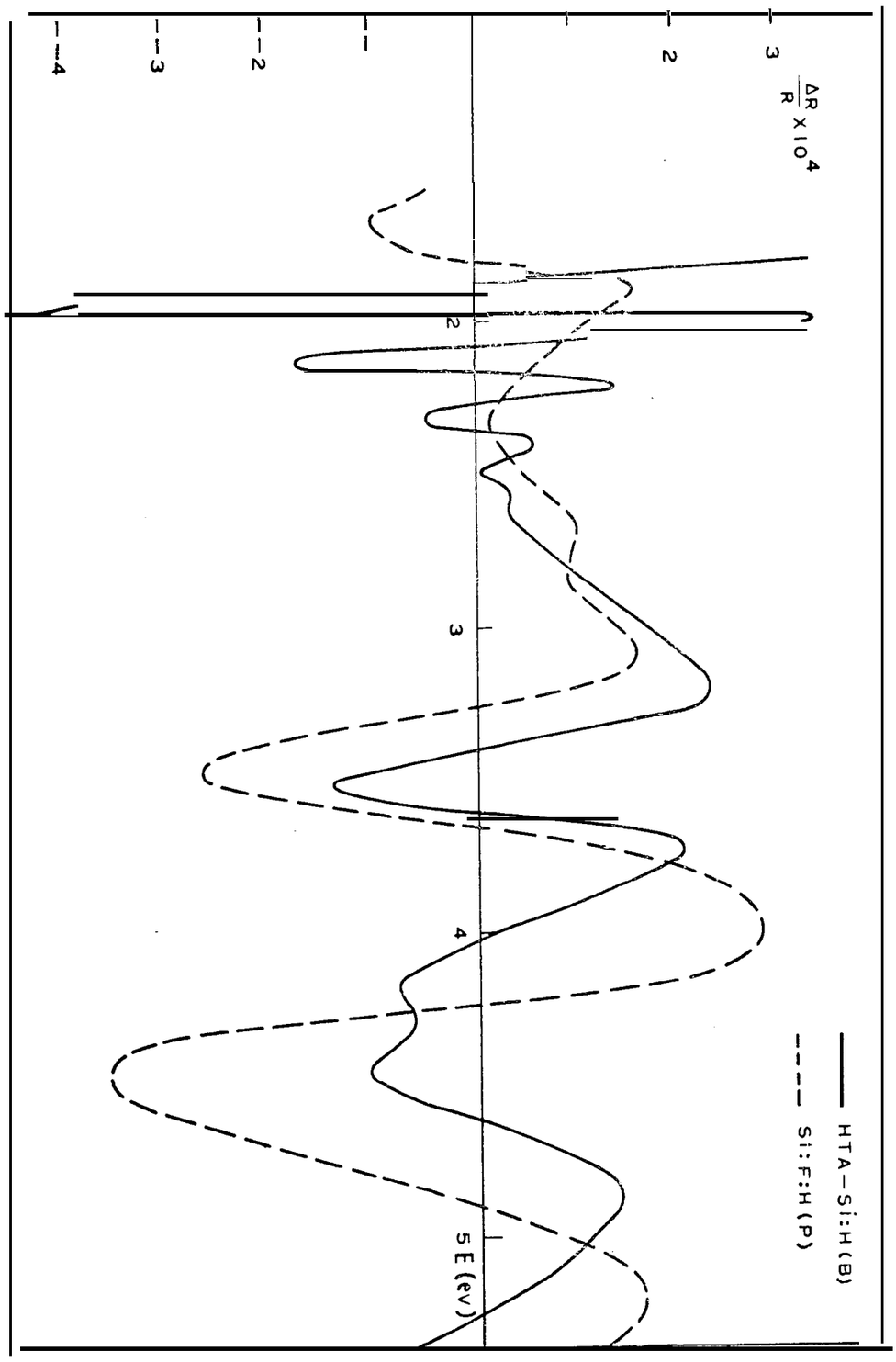

Fig. 4. EER spectra for unannealed heavily P- doped Si:F:H alloy and high temperature thermal annealed boron-doped a-Si:H alloy.

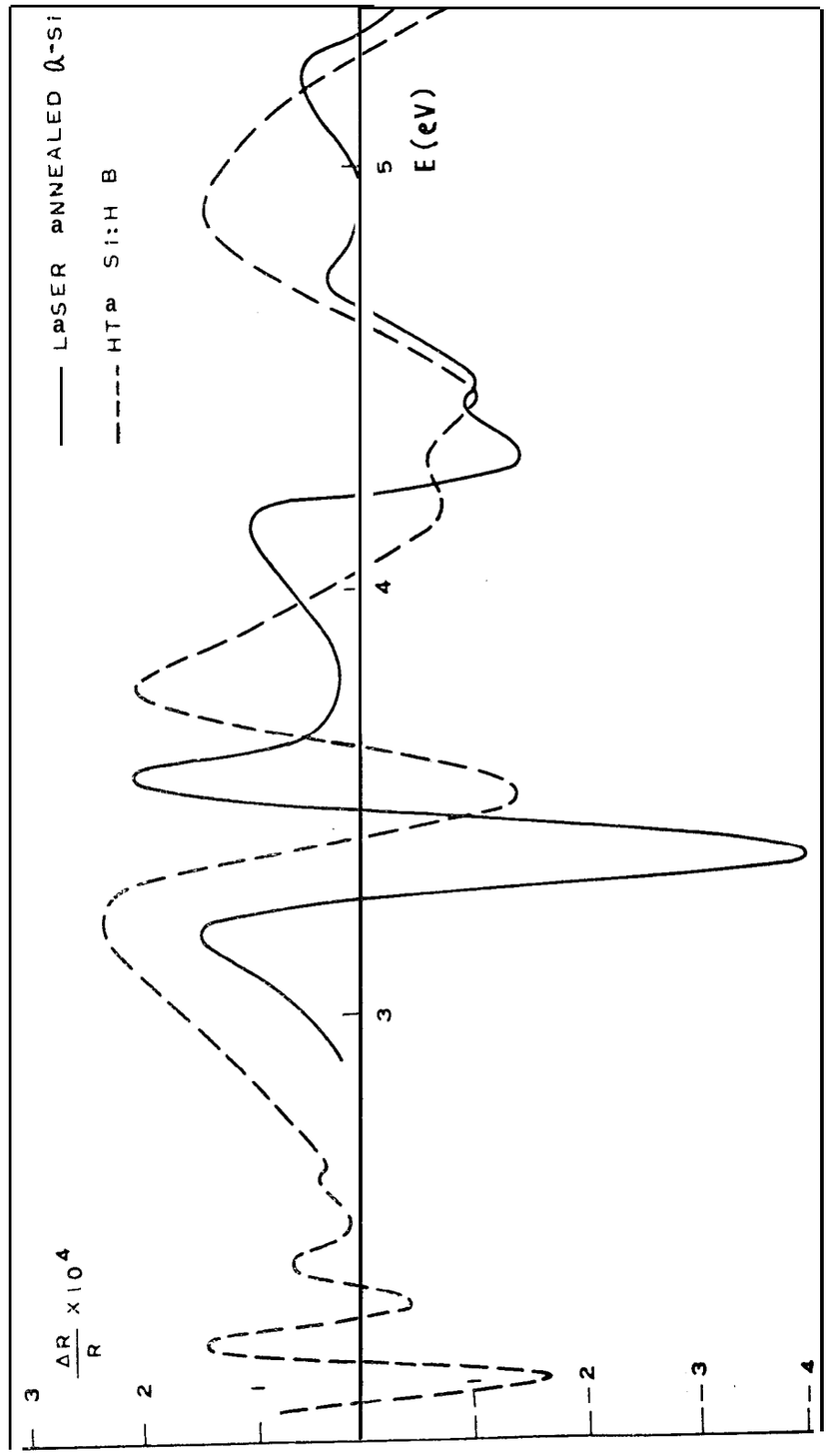

Fig. 5. Comparison of EER spectra for ion-damaged, laser-annealed *a*-Si and high temperature thermal annealing *a*-Si:H (B).

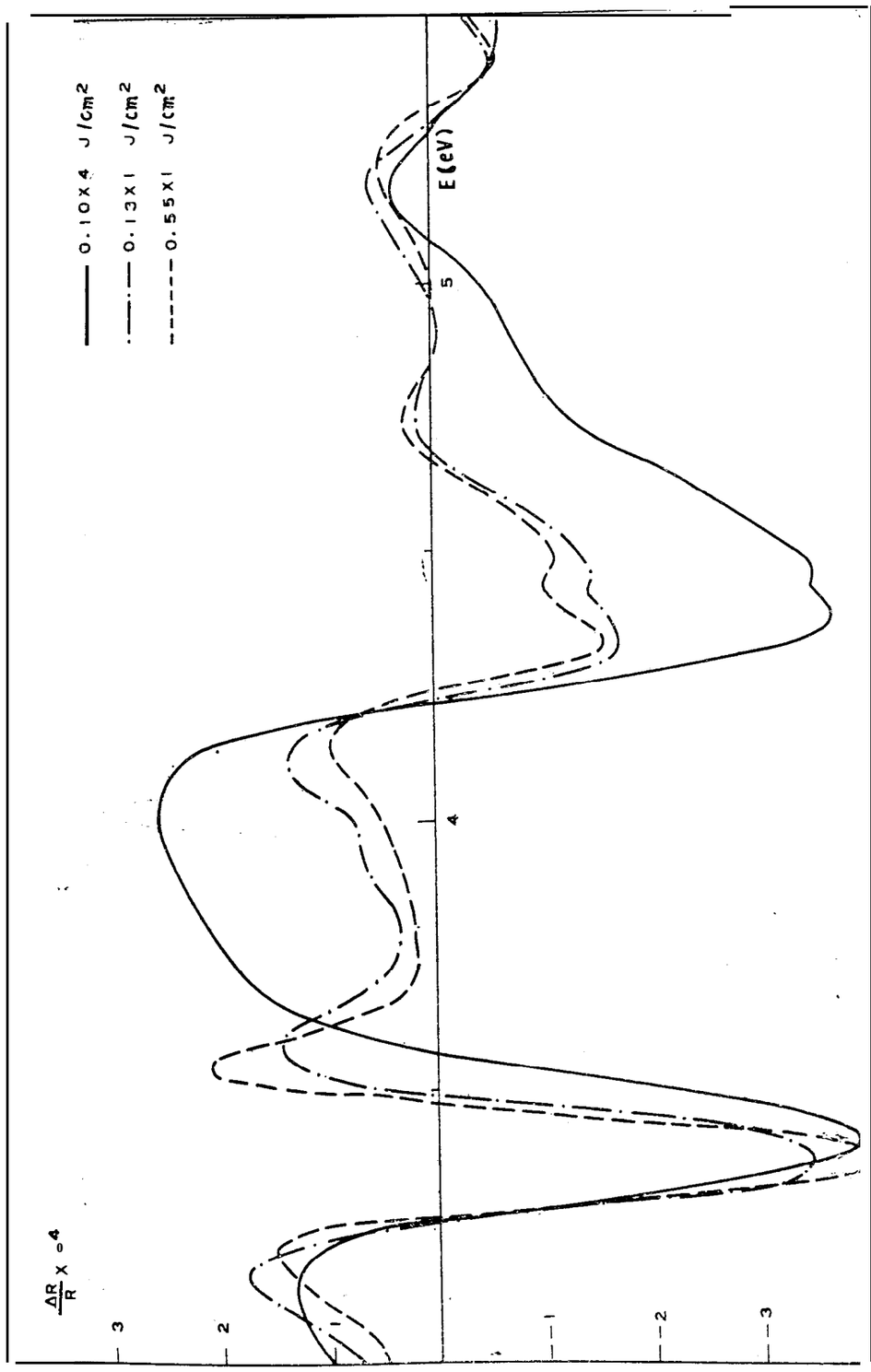

Fig. 6. EER spectra for ion-damaged, laser-annealed silicon for different energy densities.

Laser annealing, ion damaged on silicon sample was a piece of (100) polished c-Si wafer that has been bombarded with 100 keV silicon ions at a flux of 10^{16} ions/cm^2. A frequency-doubled Nd:YAG laser with 15 nanosecond pulse was used to anneal the ion-damaged silicon sample. The sample was annealed at laser power densities of (a) 0.1 (X4) (b) 0.13 (X 1) and 0.55 (×1) J/cm^2 The numbers in the parathesis indicate the repeated exposures at that energy density.

Shown in Fig. 1 is a schematic drawing of the experimental arrangement for the EER measurement. Light from an appropriate source passed through the monochromator. The exit intensity I, is focused onto the sample by means of the focusing lense. The sample is immersed in an elecrolyte that is contained in a quartz cell. The electroyte used was a 0.001N KC1 solution. The modulating voltage was in the form of a square wave, 1 V peak to peak at 220 Hz. The *ac* bias was applied to the platinum counter-electrode and to the sample. The EER technique has been described extensively in the literature[7~10].

IV. EXPERIMENTAL RESULTS

The EER spectra of two heavily P-doped Si:F:H samples (SPIN-137 and SPIN-138) are shown in Fig. 2. Doping concentration of phosphorous are also shown in this figure. The two spectra are quite similar with pronounce peaks around 3.4 eV and 4.5 eV. The 3.4 eV and 4.5 eV features are associated with *c*-Si[11~12].

The EER spectra of heavily P-doped Si:F:H samples (55 ppm) and highly As-doped Si:F:H samples are shown in Fig. 3. The doping concentration of As impurity are 20 ppm. Both samples also show the EER features around 3.4 eV and 4.5 eV. No fine structure is found in the feature around 4.5 eV. It indicates the lineshape of the EER feature of Si:F:H sample is much broader than that of c-Si. The interference fringes are observed at the photon energy below 2.5 eV.

Fig. 4 shows the EER spectra for Si:F:H alloy with 0.3% phosphorous doping and HTA-Si:H (B) alloy. We found that the EER peak of 3.4 eV of HTA Si:H (B) sample is much narrower than that of Si:F:H (P).

In order to compare the EER spectra of the HTA Si:H (B) with laser-annealing, ion-damaged on silicon samples, the EER spectra of HTA Si:H (B) and laser annealing, ion-damaged on silicon with laser energy density 0.55 (x 1) are shown in Fig. 5.

The EER spectra of laser-annealing, ion-damaged on silicon samples with different laser energy densities are shown in Fig. 6. The general features of the spectra at 3.4 eV that similar to those observed of c-Si, although the lineshapes are much broader. The observed features show fine structures around 4.5 eV, two peaks are resolved in this experiment. These 4.5 eV features are similar to that of c-Si but the lineshapes are broader.

V. DISCUSSION AND CONCLUSIONS

The structures we observed at 3.4 eV and 4.5 eV correspond to the interband transition in *c*-Si[10,11]. It has been established that the main contribution of the 3.4 eV peak in Si is due to transition along (111) regions ($L_3'-L_1$) of the Brillouin zone. It is identified as a E_1 transition in diamond- and zinc-blend type crystal structure materials. It has been reported that it is related to the short range order[13]. On the other hand, the 4.5 eV feature (E_2) in c-Si is due to transitions at the X-point (X_4-X_1) and Σ regions ($\Sigma_2-\Sigma_3$) of the Brillouin zone. Based on the theoretical calculations, the E_2 feature is associated with long rang order. Thus the observation of the E_2 feature is associated with long range order. Thus the observation of the E_2 structure in EER spectra suggests &c-structure in heavily doped n-type (P- or As-doped) Si:F:H alloy.

No EER energy feature has been observed in low doping n-type concentration Si: F: H and

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boron-doped Si : H specimens. It means that those samples are still in amorphous phase. However, HTA-Si:H (B) samples show very similar features in EER spectra with ion-damaged, laser-annealed silicon. Those features around 3.4 eV and 4.5 eV are associated with the degree of crystallinity of Si. Therefore, high temperature thermal annealing process will increase the degree of crystallinity as well as laser annealing. But heavily n-type doped Si:F:H alloy will build the microcrystalline structure.

In conclusion we found heavily doped n-type Si:F:H formed a microcrystal structure and the EER method also provides a very sensitive tool to trace crystallinity.

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