

## Electroreflectance in hydrogenated amorphous silicon

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Electroreflectance (ER) measurements have been performed on a number of sputtered hydrogenated amorphous silicon films in the vicinity of the absorption edge. The results confirm features seen in unmodulated spectra but do not show any new details. The usefulness of ER is assessed, and a model is advanced to explain the occurrence and spectral dependence of the phenomenon in amorphous silicon.

### I. INTRODUCTION

The electroreflectance (ER) technique has been used extensively in the study of the band structure of crystalline semiconductors.<sup>1</sup> Features in ER are seen at energies at which critical points occur in the interband joint density-of-states function. Comparison of these energies with those calculated theoretically for various direct transitions, aided by the exploitation of fine structure, such as spin-orbit splittings, yields an iterative procedure leading to the establishment of the band structure. The ER and other modulation techniques possess the distinct advantage of providing sharp features at precise energies by comparison with the weak and poorly resolved corresponding features in the unmodulated spectra. However, interpretation of the amplitude of the ER signal requires not only more careful experimentation than that for the ER frequencies, but also a theory to disentangle the effects of matrix elements and densities-of-states functions.

Comparatively little has been reported on ER in amorphous materials, the only studies in the literature being of amorphous selenium,<sup>2</sup> amorphous germanium,<sup>3</sup> and recently, some work on hydrogenated amorphous silicon (*a*-Si:H).<sup>4,5</sup> There have also been some recent measurements<sup>6</sup> on electroabsorption in *a*-Si:H which are related to the data reported here.

The density of states in an amorphous material is unlikely to show any sharp features because of the disorder inherent in the structure. However, it is known that the introduction of hydrogen into amorphous semiconductors such as Si, Ge, and GaAs has the effect of reducing the density of states in the gap region by several orders of magnitude. The effect on the absorption edge is to make it steeper and shift it to higher energies.<sup>7</sup> The steeper edge makes the observation of an ER signal at that energy much more probable and, if such a signal were obtained, it could be used as a much more convenient definition of optical gap than we have at present.

The great current interest in *a*-Si:H as a solar cell material has focused attention on the details of the

state distribution in the band gap, an energy range which is extremely difficult to probe using conventional optical-absorption measurements in a thin-film sample. Any well-defined structure in the gap might be expected to give rise to an additional ER feature and so this technique could in principle be used as a sensitive, although only qualitative, indicator of the state density in the gap.

There are important difficulties of interpretation in the study of ER in thin films which are basic in nature but appear to have received very little discussion in the literature. In this paper we discuss these problems in detail and show how they can seriously affect the interpretation of all ER data on thin films and in the present case limit the usefulness of ER as a tool for the characterization of *a*-Si:H.

### II. EXPERIMENTAL PROCEDURE

Electroreflectance is the fractional change in reflectivity,  $\Delta R/R$ , induced by an applied electric field. A number of configurations can be used to apply the field to the sample. A convenient approach, which requires only small voltages for thin films, is to use a sandwich electrode configuration and bring the light in through an electrolyte<sup>8</sup> or a semitransparent metal layer<sup>9</sup> which forms the top contact. The field inside the sample surface can be enhanced by using a metal known to form a large Schottky barrier. This method suffers from the disadvantage that the field inside the sample is both nonuniform and unknown but, since little information can be obtained from the magnitude of the ER, this is not a serious problem.

As we show in Fig. 1, we deposited samples for ER on either (a) glass which had a conducting chromium or nichrome layer evaporated on top of it, or (b) a roughened 3- $\Omega$  cm phosphorus-doped crystalline-silicon substrate. Some of the samples on glass were prepared as Schottky-barrier photovoltaic devices and therefore had a 300- $\text{\AA}$ -thick phosphorus-doped layer deposited first on the substrate to provide a more ohmic contact. This, however, had little influence on

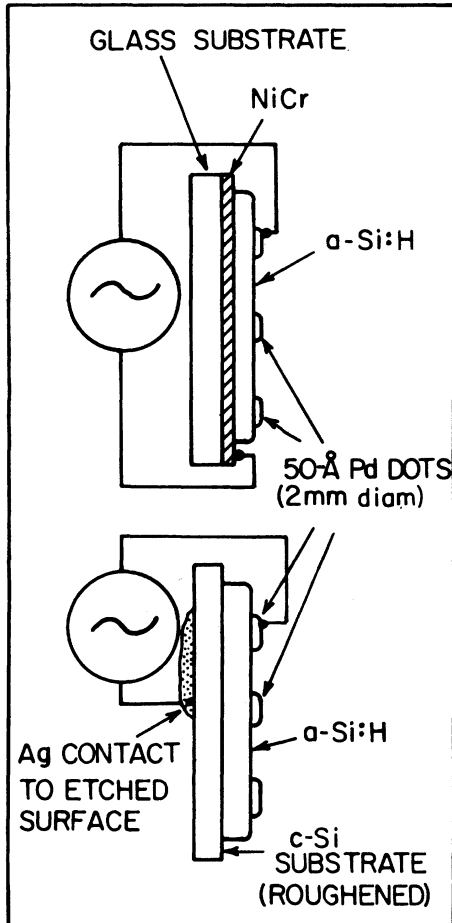


FIG. 1. Sample configuration for ER.

the ER signal, which is predominantly a front surface effect.

A 50-Å semitransparent layer of Pd was evaporated on top of the *a*-Si:H to make a top electrode. Palladium was used because of its low reflectivity and because it is known to form a large barrier<sup>10</sup> at the *a*-Si:H interface. Several Pd dots (2-mm diameter) were deposited on each sample to check for reproducibility of results.

The optical arrangement, shown in Fig. 2, consisted of a 1000-watt continuous tungsten-halogen source, a Perkin-Elmer 12G prism monochromator, and an E G & G SND 140 silicon photodiode. We applied a 200-Hz sinusoidal voltage to the sample and detected the output of the photodiode synchronously with a Princeton Applied Research HR-8 lock-in amplifier. For a 1- $\mu$ m-thick sample, a peak-to-peak voltage of up to 20 volts was used. We divided the 200-Hz part of the signal by the total output of the detector to find the relative change in the reflectance,  $\Delta R/R$ .

The Si photodiode is an ideal detector for this par-

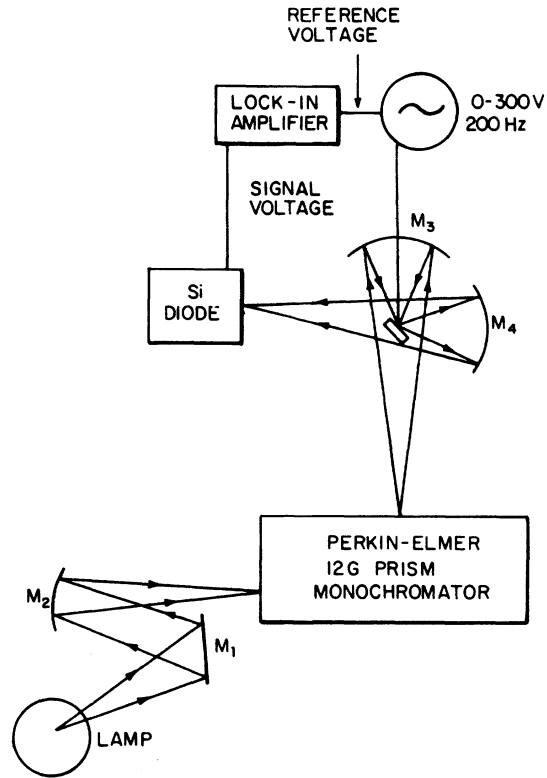


FIG. 2. Optical layout used for ER measurements.

ticular experiment since the ER features might be expected to lie in the region of the optical gap which, for *a*-Si:H, occurs between 1.4 and 2.1 eV, where the Si photodiode is particularly sensitive. It is interesting to note that unless one is willing to signal average for a long time, a photomultiplier cannot be used for the levels of ER we were measuring, typically one part in  $10^6$ . Assuming that the noise goes roughly as the square root of the signal and that one is averaging over about one second, one finds that a photon flux of about  $10^{12}$  photons/sec is necessary for the ER signal to be distinguished from the noise. This is much higher than a photomultiplier tube can tolerate. Our actual photon flux was about  $5 \times 10^{13}$  photons/sec.

Details of the preparation of our samples by rf sputtering in a plasma of argon and hydrogen have been published elsewhere.<sup>11</sup> In the 16 samples used for this study, the substrate temperature  $T_s$ , the partial pressures of hydrogen and phosphine,  $p_H$  and  $p_{PH_3}$ , respectively, and the thickness  $t$ , were varied. The hydrogen concentration in our samples varied from 0 to 25 at. %.

### III. RESULTS

Figure 3 is a typical ER spectrum for a sample deposited on glass [Fig. 1(a)]. The most striking

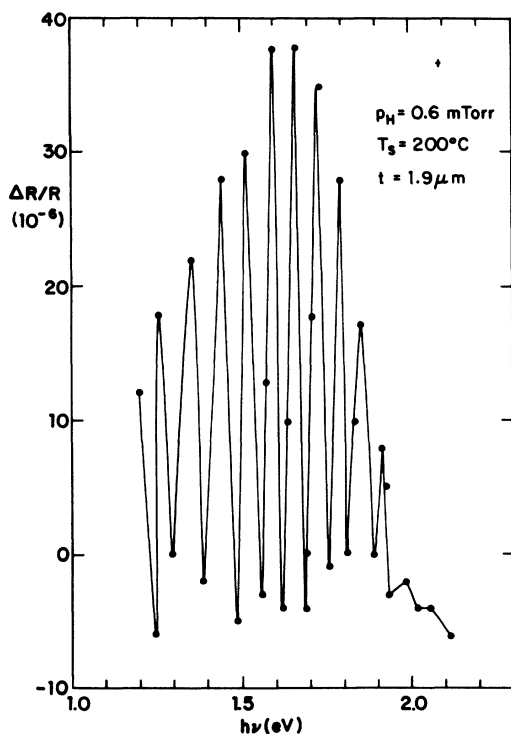


FIG. 3. ER spectrum as a function of photon energy of a typical sample deposited on nichrome. The cross in the upper right-hand corner indicates the uncertainty in the ER and in the photon energy.

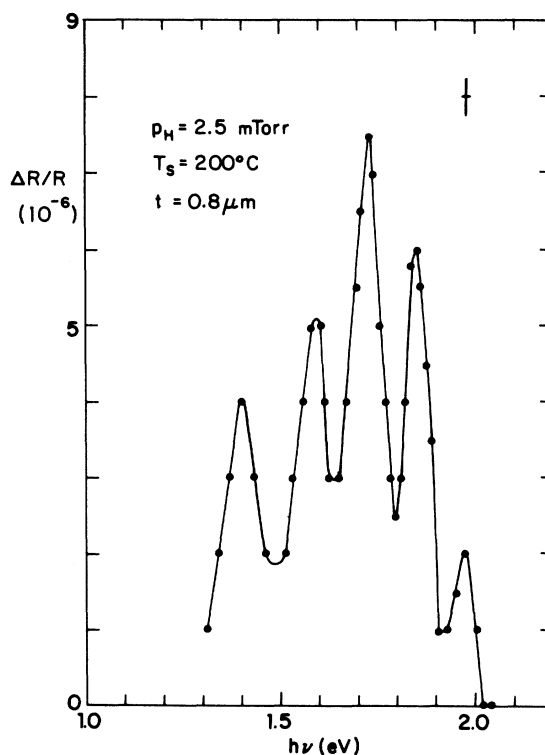


FIG. 4. Electroreflectance spectrum of a sample deposited on roughened crystalline silicon.

features are the oscillations which we can identify as interference fringes whose spacing in energy is consistent with the known thickness of the sample and its refractive index. Underlying the fringes is what appears to be a single broad feature centered about 1.6 eV of  $2 \times 10^{-5}$  in magnitude with some broadening towards low energies.

Figures 4 and 5 show ER spectra for two other samples. The sample of Fig. 4 was deposited on a roughened piece of crystalline silicon [Fig. 1(b)]. The roughening decreases the intensity of the interference fringes and the close match in the refractive indices of crystalline Si and *a*-Si:H aids further in this effort. Although the interference fringes are diminished, they are not eliminated. The intensity of the signal is also decreased considerably, probably due to some of the voltage being dropped across the substrate-sample interface and the back contact to the substrate. In Fig. 5, we show the ER spectrum of a 2.6- $\mu$ m-thick sample deposited on glass. Comparing Figs. 3 and 5, we see that increasing the film thickness also reduces the intensity of the interference fringes, but the appearance of the spectrum has now changed. The peak is shifted to higher energy and is much sharper.

Spectra similar to Figs. 3–5 were observed in all

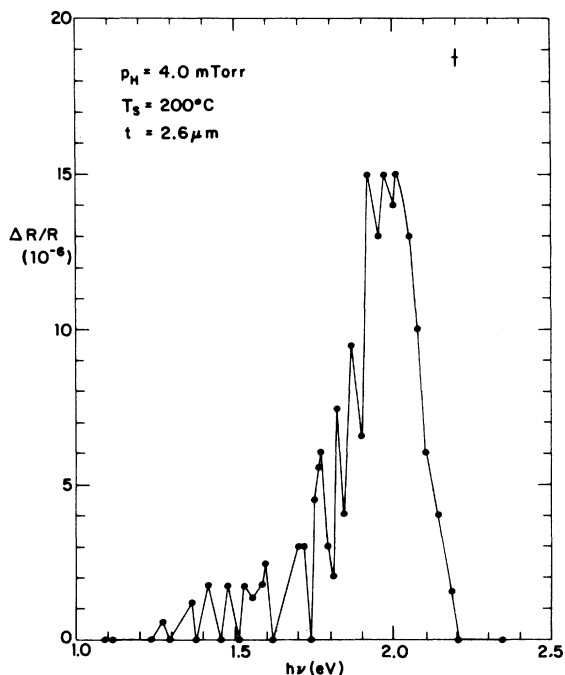


FIG. 5. ER spectrum of a thicker sample deposited on nichrome.

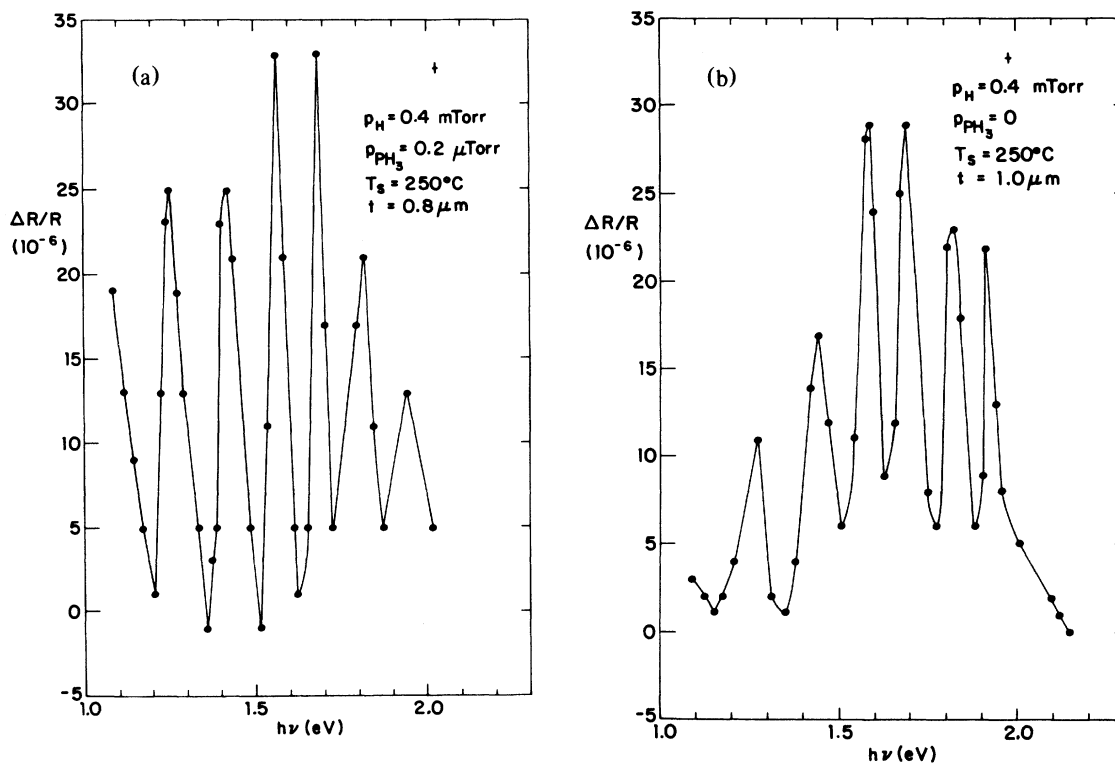


FIG. 6. ER spectra of (a) phosphorus-doped sample and (b) undoped sample.

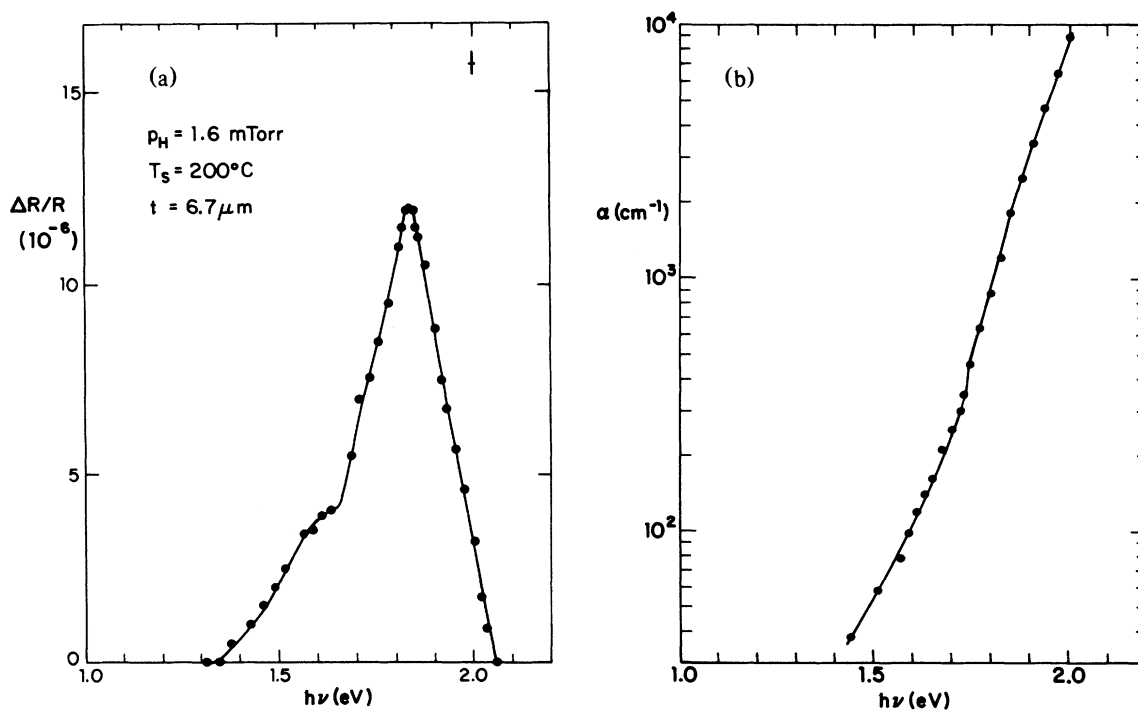


FIG. 7. (a) ER spectrum and (b) absorption spectrum of sample with structure near 1.7 eV.

samples studied. Rather surprisingly, the peak in the ER spectrum shifted only about 0.3 eV, compared with the shift of the optical gap of 0.7 eV upon increasing  $p_H$ .<sup>7</sup> The full width at half maximum of the feature did however appear to decrease from 0.75 to 0.35 eV as the hydrogen content increased.

In two samples, we observed differently shaped spectra and these are shown in Figs. 6 and 7. In both samples, optical-absorption measurements indicated some structure in the edge.

Figures 6(a) and 6(b) compare ER spectra of two films prepared under the same conditions, except that the sample of Fig. 6(a) had phosphine added to the sputtering gas. It has been reported earlier<sup>7,12</sup> that the incorporation of phosphorus introduces a shoulder in the absorption edge at about 1.4 eV. Due to the wide spacing of the interference fringes in the ER spectra, we cannot resolve a feature at 1.4 eV, but it is evident that the ER spectrum of the doped sample is more broadened to lower energies than that of the undoped sample.

The sample whose ER spectrum is shown in Fig. 7(a) also has a bump in its absorption edge displayed in Fig. 7(b). The thickness of this sample was such that no interference fringes were observed in the ER spectrum and this allowed a second lower energy feature to be resolved. The energy at which this feature occurs can be closely correlated with the bump in the optical-absorption edge. Although the origin of this absorption is not known, this sample had been deliberately doped with oxygen. At this stage, however, it is premature to assume any direct link between oxygen and states in the gap.

The electric field dependence of the ER signal could be fitted by a relation of the form

$$\Delta R/R = AV^B, \quad (1)$$

where  $V$  is the applied voltage and  $A$  and  $B$  are constants. Using a least-squares fit, we found the exponent was usually about 1 but values between 0.5 and 2.5 were obtained. In this geometry, as mentioned earlier, the voltage is mostly dropped across the depletion region, whose width is itself a function of the voltage. The field inside the semiconductor is therefore unknown and so no significance can be attached to the voltage dependence of the signal.

#### IV. DISCUSSION OF RESULTS

##### A. Origin of the effect

A change in either the real ( $n$ ) or the imaginary ( $k$ ) part of the refractive index due to an applied field could change the reflectance of a film. Although, as we shall discuss, there are several possible causes of ER, they all require that the optical gap become smaller with the applied field. Correspondingly,

$n$  and  $k$  must increase with an applied field in the region of the absorption edge.

The reflectance (averaged through the interference fringes) of a thin film of given  $n$  and  $k$  deposited on a reflecting metal can be expressed as

$$R = \frac{R_1 + R_2 e^{-8\pi kt/\lambda} (1 - 2R_1)}{1 - R_1 R_2 e^{-8\pi kt/\lambda}}, \quad (2)$$

where  $t$  is the thickness of the film,  $\lambda$  the wavelength of the incident light,

$$R_1 = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (3)$$

is the reflectance of the  $a$ -Si:H—air interface<sup>13</sup> and  $R_2$  is the reflectance of the  $a$ -Si:H—metal interface. Multiple reflections within the metal film can be ignored because a thick metallic layer absorbs the light not reflected.

Using Eq. (2), one sees that as  $n$  increases,  $R$  increases, but that as  $k$  increases,  $R$  first decreases because the exponential factor outweighs the increase in  $R_1$ . When  $kt/\lambda$  is large  $R \rightarrow R_1$  and then  $R$  increases with increasing  $k$ , as shown in Eq. (3).

We can make use of this difference in the behavior of  $R$  in a weakly absorbing region to determine whether the ER signal is caused primarily by a field-induced change in  $k$  or in  $n$ . Experimentally, there is a 180° phase difference between the ER signal and the applied voltage, implying that the reflectance decreases with applied field. Thus the effect of increase in  $k$  dominates and the ER is really electroabsorption. In fact, our spectra are very similar to electroabsorption spectra obtained by Weiser and Braun<sup>6</sup> on  $a$ -Si:H prepared from SiH<sub>4</sub>.

There are at least three possible explanations for the shift in the absorption edge with electric field. One model is based on the Franz-Keldysh effect.<sup>14</sup> In the presence of a large field, the optical transitions can be assisted by a tunneling contribution. In the case of an exponential edge this results in a parallel shift of the edge to lower energy and in the vicinity of critical points this will create an ER signal. Although an amorphous material has no critical points, we expect there should be an ER signal at the bottom of the absorption edge. The energy derivative of the absorption coefficient is at a maximum and constant in the region of the absorption edge, so since we are studying  $\Delta k/k$ , the ER signal will be largest when  $k$  is smallest, which occurs near the bottom of the absorption edge. This model is consistent with our finding only one ER peak in the spectrum.

A second model is the one put forward by Dow and Redfield.<sup>15</sup> They used the idea that the exponential part of the absorption edge is caused by absorption into excitonic states and showed that an applied field would cause a Stark shift, which would result in an edge broadened to lower energies.

A third possibility was suggested recently by Brodsky and Leary.<sup>16</sup> They point out that the modulated reflectance might be due to heating from the current passing through the sample, so that this would actually be a thermoreflectance measurement. We tested this possibility by depositing a semitransparent nichrome strip on a sample and running a 200-Hz ac current through the nichrome. A milliwatt of power was used, which is the same as the electrical power developed in the sample during the ER measurement. We saw no modulation in the reflectance with this technique of direct heating. In addition, solving the heat diffusion equation for the geometry of our samples indicated that the temperature rise with a milliwatt applied to the sample is so small that thermoreflectance can be only a small fraction of the total effect.

We found the ER signal appeared only for reverse bias. This is to be expected in our Schottky-barrier geometry, because in forward bias the barrier collapses, so the field necessary for ER is not present. With nichrome as our top contact instead of palladium, we saw no ER signal in forward or reverse bias because the Schottky barrier is not as high.

The observation of the effect only in reverse bias, when the current is less than in forward bias lends further support to our contention that the effect is caused directly by the electric field and not by heating. We should remember that the power put into the sample is the product of the voltage and the current and that the voltage drop across the depletion layer in the reverse biased sample is greater than in the forward biased sample. This means that all the power in reverse bias would be developed in the depletion region. However, since the current, as we show in Fig. 8, is much larger in the forward biased sample and since the effect is below the experimental limit of detection in forward bias, we again doubt that

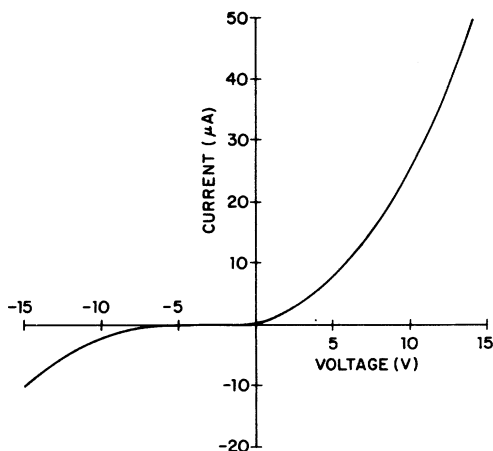


FIG. 8. Current-voltage characteristics of typical ER sample.

thermoreflectance is a large part of the effect observed.

From our data, we cannot distinguish between the Franz-Keldysh effect and the Dow-Redfield model, but there is little doubt that we are observing the influence of an electric field on the optical constants of  $\alpha$ -Si:H. The data suggest that the principal effect of the field is to decrease  $k$  and that the presence of a large built-in field below the Schottky contact is essential for its observation.

### B. Interpretation of ER in thin films

In thick samples, in the region of the absorption edge, there is little or no contribution to  $R$  from multiple reflections. From Eqs. (2) and (3),  $R = R_1$ , which increases with  $k$  and  $n$  near the edge. In thin films, the contributions to  $R$  from multiple reflections are significant and may introduce structure in the ER spectra  $\Delta R/R$  in the absence of any structure in  $\Delta R$ . In particular, an examination of Eq. (2) shows that for a film of a given thickness  $t$ ,  $R$  will be approximately constant with energy in a weakly absorbing regime, then begin to decrease as  $k$  increases even though  $n$  is increasing. As the edge is approached, the exponential term approaches zero and  $R$  tends to  $R_1$ , which is increasing monotonically with energy. Thus the measured  $R$  has a minimum whose position depends on the thickness of the sample and the position of the absorption edge.

The reflectance spectra of the samples whose ER spectra were given in Figs. 4 and 5 are given in Fig. 9. The curves were obtained by averaging through the interference fringes. For the thin sample,  $R$  is relatively flat up to about 1.7 eV and then begins to decrease. For the thick sample,  $R$  also decreases above about 1.7 eV, but then goes through a minimum as discussed above. The significant fact is that the minimum in  $R$  corresponds exactly with the maximum in ER shown in Fig. 5. We conclude therefore that the position and shape of the ER spec-

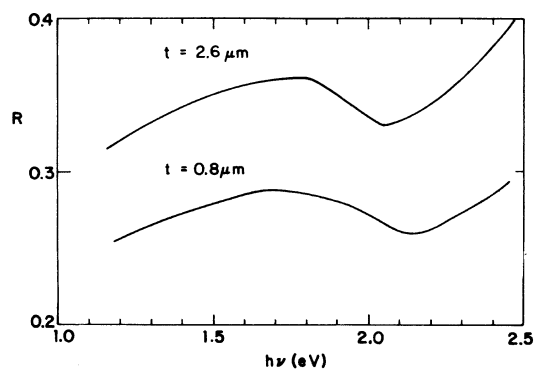


FIG. 9. Reflectance spectra (averaged through the interference fringes) of samples of different thickness.

trum  $\Delta R/R$  in that sample are solely a function of the position of the minimum and shape of the reflectance spectrum  $R$  and that this is the origin of the peculiarities of the spectrum shown in Fig. 5.

In order to determine  $R$  accurately, free from distortions produced by thickness-dependent structure in  $R$ , samples thinner than one micron or thicker than  $100\ \mu\text{m}$  are required. Unfortunately, a sample less than  $1\ \mu\text{m}$  thick has interference fringes spaced so far apart that it is impossible to locate the peak with any great accuracy and  $100\ \mu\text{m}$  is thicker than is normally feasible for a homogeneous, low-strain, sputtered film.

The above analysis also helps to explain the observation of fringes in the ER spectra which are exactly  $180^\circ$  out of phase with the fringes in  $R$ . This is undoubtedly part of the reason but other models have been given. Fischer<sup>3</sup> suggested that electrostriction could be causing the thickness to vary so that  $t$  would be a function of the applied field. Subashiev<sup>17</sup> calculated the change in reflectivity if  $n$  changed slightly because of an applied electric field and showed that this also led to interference fringes.

#### C. Usefulness of ER as a characterization tool

For the reasons discussed above, the position of the ER maximum is a function of the film thickness as well as the position of the absorption edge. Thus, although we do indeed observe an electroreflectance signal in the region of the absorption edge, caution must be exercised in using the position of the peak as a measure of the optical gap. This, in part, explains the apparent insensitivity of the position of the peak to the hydrogen content of the film, which we know to result in shifts of the optical edge of more than  $0.5\ \text{eV}$ . Our statistics are simply not good enough to be sure that the narrowing observed as the hydrogen content increased was real, but it would certainly be consistent with other optical measurements.

The data of Figs. 6 and 7 suggest that ER might be used to detect structure in the joint density of states below band-gap energies, but in the case of these two

samples this structure was also observed with less ambiguity in an unmodulated measurement. It is not clear that we would have the sensitivity to detect a weaker structure.

#### V. CONCLUSIONS

We have demonstrated that an electroreflectance signal can be obtained in  $a\text{-Si:H}$  thin films by using a sandwich electrode configuration making use of the field below a Pd contact. We have demonstrated that the effect is not a thermal one and that it takes place predominantly in the depletion region of the Schottky contact.

The usefulness of this technique as a tool in the characterization of  $a\text{-Si:H}$  thin films is limited by two factors, each of which can be traced to the thin-film geometry. The first is that the unmodulated  $R(h\nu)$  goes through a minimum in the neighborhood of the edge giving rise to a maximum in  $\Delta R/R$  which seriously distorts the true electroreflectance signal. The second is the presence of large interference fringes in the spectrum unless special precautions are taken to reduce them. In thin samples, the interference fringes can be confused with real electroreflectance features.

As a result of these difficulties, we were unable to use the ER peak position as a measure of the optical gap, but we have shown that ER can detect structures below the band edge and may therefore have some usefulness in the study of gap states.

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