Thermal modulation of the optical properties of amorphous semiconducting films

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Modulation spectroscopy was performed on amorphous semiconducting films of a-Si:H and a-As_2Se_3 (of thickness ~ 3 μm), using a chopped Ar^+-ion laser beam as the modulating source. The results show that oscillation fringes in the modulated reflection (ΔR) and transmission (ΔT) are due to the thermal modulation of the index of refraction through the thermal modulation of the band gap E_g. Therefore the (peak-to-peak) signal amplitude $\Delta R_{\mathrm{p.p.}}$ in the ΔR spectrum gives a measure of the quantity $\partial E_g/\partial T$. The temperature dependence of $\Delta R_{\mathrm{p.p.}}$ in a-Si:H between 1.8 and 300 K is found to be consistent with the known behavior of $\partial E_g/\partial T$.

INTRODUCTION

One of the more useful experimental techniques for probing the electronic states within the gap of amorphous semiconductors has been the optical modulation technique. In experiments of this type various optical quantities, such as transmission or reflection, are monitored in phase with the application of a modulated optical pump. It is assumed, sometimes implicitly, in these experiments that the modulated changes are entirely optically driven and in particular that none of the changes are thermally generated.[1–5] These optically induced changes are commonly attributed to changes in the imaginary part of the index of refraction.

In this paper we quantify the thermally induced changes which can be generated in amorphous semiconducting films and show that thermal effects on the order of those reported in the optical modulation experiments can sometimes be observed. We also show that the thermally modulated changes in the optical properties can be explained quantitatively by changes in the real part of the index of refraction via the well-known variations of the electronic band gaps with temperature.

The optical properties of a material are determined by the energy-dependent complex index of refraction $n_c(E)=n(E)+ik(E)$. The imaginary part $k(E)$, which is related to the absorption coefficient $\alpha=4\pi k/\lambda$, where λ is the wavelength, has been of considerable interest in a-Si:H and the chalcogenide glasses, especially in the subgap region. The real part of the index in this spectral region has received much less attention because the spectrum is thought to be featureless. However, as a consequence of its relation to the band gap, $n(E)$ has interesting thermal properties. In this paper we discuss thermally modulated reflectivity (and transmission) measurements on films of a-Si:H and As_2Se_3 on glass substrates. The aims of the present work are to show that the modulation of the reflectivity (or transmission) is primarily thermal in origin, rather than electronic and is a result of the sensitive temperature dependence of the real part of the index n. We also comment on the effect the modulation of n has on the modulated transmission spectrum.

EXPERIMENTAL DETAILS

The temperature modulation was accomplished by a chopped Ar^+ cw laser beam (5145 Å) incident on the sample. The experimental arrangement is shown schematically in Fig. 1. The sample surface in the illuminated region was blackened with paint to separate temperature effects from electronic effects and to avoid an extraneous signal caused by luminescence in the low temperature measurements. A broadband tungsten lamp source was employed and the spectra were analyzed by a 0.75 m grating spectrometer and detected with an S1 or S20 photomultiplier tube. Reflection spectra were usually taken from the substrate side, although this geometry is not critical to observe the thermal effects. The modulated spectrum is measured using standard lock-in techniques.

RESULTS AND DISCUSSION

The thin film is a Fabry-Perot cavity and the reflectivity spectrum consists of fringes given by the Airy sum[6]

$$R=\frac{r_1^2+2r_1r_2\cos(2\delta)+r_2^2}{1+2r_1r_2\cos(2\delta)+r_1^2r_2^2}\ , \tag{1}$$

where $\delta=2\pi nd/\lambda$ (d is the film thickness) and r_1 and r_2 are the Fresnel coefficients given by

$$r_1=\frac{n_0-n}{n_0+n}\ ,$$
$$r_2=\frac{n-n_2}{n+n_2}\ .$$

n_0, n, and n_2 are the indices of refraction as shown in Fig. 1. Equation (1) assumes that the absorption is negligible.

Figure 2(a) shows a typical room temperature spectrum of the modulated reflectivity, ΔR, for a 3-μm-thick film of a-Si:H on a glass substrate. The signal remained unchanged on moving the modulating laser spot to a region of the sample which was not blackened at the surface.

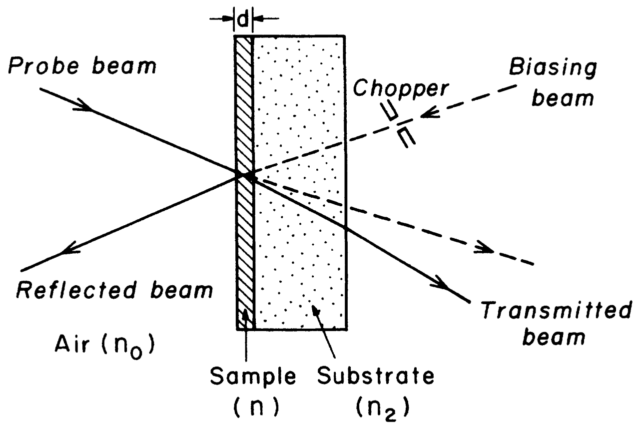

FIG. 1. Experimental arrangement for measuring the modulated reflection (transmission).

This procedure illustrates that the effect is thermal and can be generated by the absorption of light in the sample itself. Therefore, the measured change in reflectivity, ΔR, is given by

$$\Delta R = \left[\frac{dR}{dn}\right]\left[\frac{dn}{dT}\right]\Delta T , \tag{2}$$

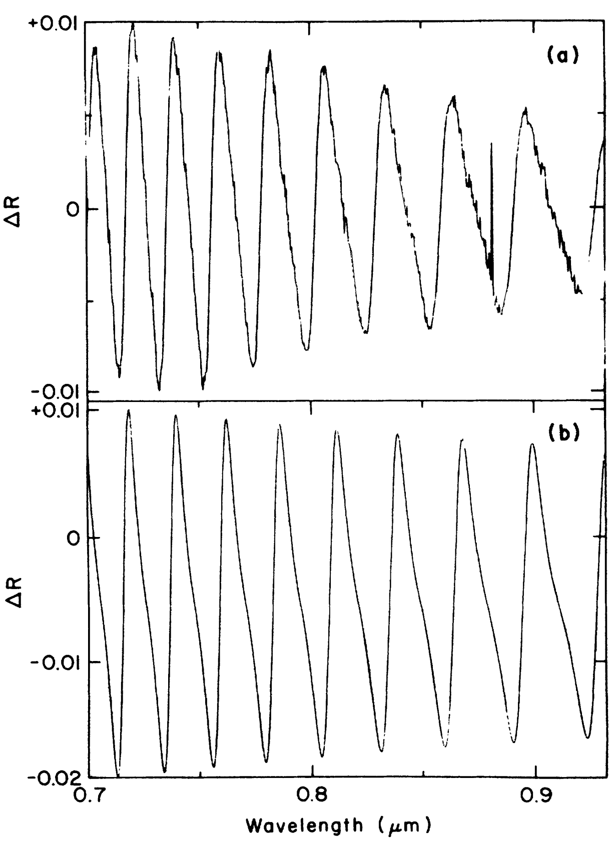

FIG. 2. (a) Modulated reflectivity, ΔR, spectrum at 40 Hz and 300 K, of a 3 μm a-Si:H film on glass. (b) Calculated spectrum with $n=3.5$.

where R is the reflectivity, n is the real part of the index, and ΔT is the rise in temperature due to the modulation. From (1) and (2) it can be seen that the derivative spectrum will also consist of fringes whose amplitude is proportional to $\Delta n = (dn/dT)\Delta T$. Figure 2(b) shows the calculated spectrum of ΔR according to Eq. (2) using Eq. (1), with $n=3.5$ for a-Si:H. Good agreement was obtained for $\Delta n = 1\times 10^{-3}$ for this measurement where the average modulation intensity was 500 mW/cm^2. In writing down Eq. (2), it is implicitly assumed that there are no thermally induced changes in absorption or at least that $\Delta k \ll \Delta n$. We now proceed to show that this is indeed the case.

In a semiconductor the contribution to the real part of the dielectric constant ($\epsilon_r = n^2$) at energies below the optical band gap is a complicated function of the band structure. In many semiconductors, however, the index is approximately proportional to a power of the optical gap, $n \propto E_g^{\alpha}$, where E_g is the band gap (often $\alpha \approx 2$).[7] Through dn/dT the temperature dependence of the amplitude of the ΔR spectrum [Eq. (2)] should be proportional to the temperature derivative of E_g. The comparison for the thin film of a-Si:H is shown in Fig. 3 where the quantity dE_g/dT for a-Si:H was obtained from the expression[8]

$$E_g = E_g^0 - \frac{0.220}{\exp(400/T)-1} , \tag{3}$$

where E_g^0 is the optical gap in eV at 0 K. The good agreement provides confirmation for the presence of a thermal modulation of n through a modulation of the band gap. The average modulation intensity for this measurement was 70 mW/cm^2 and the modulation frequency was 40 Hz. The expression for the modulated reflectance spectrum in a-Si:H [from Eqs. (1) and (2)] depends only on the temperature dependence of the optical band gap [Eq. (3)] and should thus apply to any thin semiconducting film at energies below the band gap. We have obtained similar results on thin films of glassy As_2Se_3 which will be discussed below.

In general, the modulated intensity can be expressed as

$$I = I_a[1+\cos(\omega t)] , \tag{4}$$

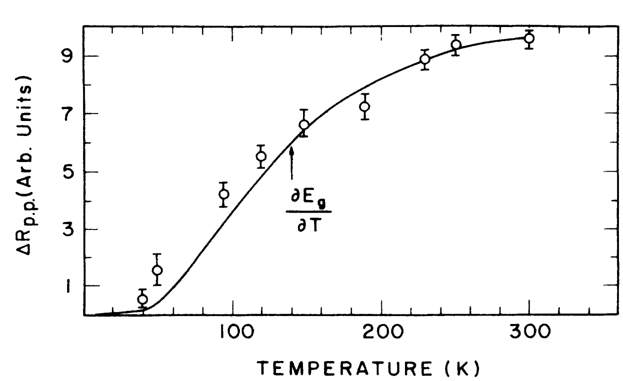

FIG. 3. Temperature dependence of the peak-to-peak amplitude of ΔR. The solid line is dE_g/dT calculated from Eq. (3) and the circles are data points for the average intensity of the biasing beam. These data were taken at 40 Hz modulation.

where ω is the chopping frequency and I_a is the average value of the modulation intensity. The average local dc temperature rise $(\Delta t)_{dc}$ due to this modulation can be estimated from a simple one dimensional model of heat conduction through the substrate. For thin films, the temperature rise is controlled by the thermal conductivity of the substrate. The heat flux from the heated spot on the sample is then

$$-\kappa\left[\frac{dT}{dx}\right]\pi r^2=P_a \; , \tag{5}$$

where P_a is the power absorbed, κ is thermal conductivity for glass, and r is the radius of the laser beam spot on the sample. Assuming that the back of the substrate is at ambient temperature,

$$(\Delta T)_{dc}=\frac{P_a d}{\pi r^2\kappa} \; . \tag{6}$$

The amplitude of the temperature oscillations due to a modulated incident intensity of the form of Eq. (4) is given by[9]

$$(\Delta T)_{max}=\left[\frac{P_a d}{\pi r^2\kappa}\right]\left[1+\frac{1}{[1+(\omega\tau)^2]^{1/2}}\right] , \tag{7}$$

where τ is the effective thermal time constant given approximately by

$$\tau=d^2\frac{c\rho}{\pi^2\kappa} \; , \tag{8}$$

where c is the heat capacity and ρ is the density. For a low modulation intensity, $I_a=70$ mW/cm^2, $(\Delta T)_{dc}$ was estimated to be ≈ 2 K near room temperature, increasing to ≈ 15 K at about 5 K. This dc component is therefore relatively unimportant in the fit to the data in Fig. 3. $(\Delta T)_{dc}$ increases with I_a and its effect can be seen in the data of Fig. 4, for three values of I_a. With increasing I_a, there is a deviation from the behavior of dE_g/dT. The reason can be traced to the local temperature which is essentially $T+(\Delta T)_{dc}$, where T is the ambient temperature. The signal should then be compared with dE_g/dT at $T+(\Delta T)_{dc}$. The dashed line in Fig. 4 is a plot of $(dE_g/dT)_{T+(\Delta T)_{dc}}(\Delta T)_{ac}$, where $(\Delta T)_{dc}$ is computed from (5) based on the 1D model for $I_a=490$ mW/cm^2.

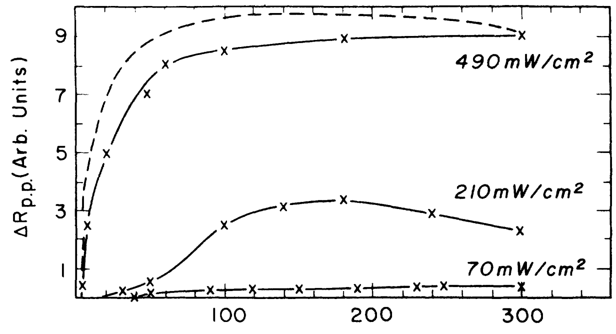

FIG. 4. Temperature dependence of the peak-to-peak amplitude of ΔR for three different values of the biasing light intensity. The dashed line is the result of a calculation for 1D heat flow for the average intensity of the biasing beam $I_a=490$ mW/cm^2.

By painting the sample black, we have shown that the modulated reflectivity is the result of a thermal effect. In addition, the good agreement of Eqs. (2) and (3) with the data shown in Fig. 3 indicates that $\Delta k \ll \Delta n$, i.e., the absorptive effect is negligible.

With our present knowledge of the thermal effects, we now examine the implications for modulated transmission (ΔT) measurements. The transmission of a thin film of index n and absorption coefficient α, expressed by the ratio of the transmitted to incident intensity is

$$T=\frac{n_2}{n_0}\frac{[(1+g_1)^2+h_1^2][(1+g_2)^2+h_2^2]}{e^{\alpha d}+(g_1^2+h_1^2)(g_2^2+h_2^2)e^{-\alpha d}+C\cos(2\delta)+D\sin(2\delta)} ,$$
$$g_1=\frac{n_0^2-n^2-k^2}{(n_0+n)^2+k^2},\quad h_1=\frac{2n_0k}{(n_0+n)^2+k^2},\quad g_2=\frac{n^2-n_2^2+k^2}{(n+n_2)^2+k^2},\quad h_2=\frac{-2n_2k}{(n+n_2)^2+k^2} , \tag{9}$$
$$k=\frac{\alpha\lambda}{4\pi},\quad C=2(g_1g_2-h_1h_2),\quad D=2(g_1h_2+g_2h_1) .$$

The expression for $\Delta T/T$ can be written as

$$\frac{\Delta T}{T}=a\,\Delta n+b\,\Delta\alpha \tag{10}$$

with

$$a=\frac{1}{T}\frac{\partial T}{\partial n},\quad b=\frac{1}{T}\frac{\partial T}{\partial \alpha} .$$

Photoinduced absorption contributes to the second term. It is clear that if Δn were zero, the $\Delta T/T$ spectrum would be essentially that of $\Delta\alpha$, but from our reflectivity data we know that $\Delta n=10^{-3}$ cm^2/W. The expression for T in Eq. (9) is rather complex, as it stands, for calculating ΔT. However, for the situation when $k \ll n$ and $\Delta k \ll \Delta n$, a simplified form of T, namely

$$T=\frac{n_2}{n_0}\frac{t_1^2t_2^2e^{-\alpha d}}{1+r_1^2r_2^2e^{-2\alpha d}+2r_1r_2e^{-\alpha d}\cos(2\delta)} \tag{11}$$

with

$$t_1 = \frac{2n_0}{n_0+n}, \quad t_2 = \frac{2n}{n+n_2}$$

and r_1 and r_2 as defined immediately following Eq. (1), may be used.

Using Eq. (11), we have calculated $\Delta T = [(\partial T/\partial n)\Delta n + (\partial T/\partial \alpha)\Delta\alpha]$ for the two cases of (a) $\Delta n = 10^{-3}$, $\Delta\alpha = 0$ and (b) $\Delta n = 10^{-3}$, $\Delta\alpha = 10$ cm^{-1} and the corresponding plots are shown in Figs. 5(a) and 5(b). Note that the amplitudes of the fringes are essentially the same in both cases but the position where $\Delta T = 0$ is shifted in case (b) so that the spectrum is no longer as symmetric about zero as in (a) ($\Delta\alpha = 0$). In Fig. 6(a) we present the experimental ΔT measured for the 3 μm *a*-Si:H films. In sample with low defect density, as is ours, the induced absorption $\Delta\alpha$ is usually never greater than 10 cm^{-1}.[10] So we can compare Fig. 6(a) with Fig. 5. Although the values are not exactly the same one can see the clear similarities between Figs. 6(a) and 5(a), which are both symmetric about zero. So in our samples photo-induced absorption is indeed negligible. Even in samples with higher defect densities $\Delta\alpha$ has been inferred to be at most about 50 cm^{-1} from measurements of ΔT.[10]

Reliable values of $\Delta\alpha$ can be obtained only when $\Delta n = 0$—a situation that is possible in our samples and our substrates only at low temperatures and low excitation intensities. From the data of Fig. 3, $\Delta n \simeq 0$ when $I_a < 70$ mW/cm^2 and $T < 50$ K.

Analysis of Eq. (10) together with Eq. (9) yields another important point. For the situation when $k\,\Delta k \ll n\,\Delta n$, to a good approximation

$$b\,\Delta\alpha = \frac{1}{T}\frac{\partial T}{\partial \alpha}\Delta\alpha \approx -2d\,\Delta\alpha$$

so that

$$\frac{\Delta T}{T} = a\,\Delta n - 2d\,\Delta\alpha\ .$$

The above expression may be used in extracting $\Delta\alpha$.

In Fig. 6(b) we show the measured ΔT spectrum at 300 K for a thin film of As_2Se_3. Ordinary transmission spectra indicated that thickness variations were more important in the glassy As_2Se_3 film. These variations result in the fringe pattern being less sharp than would be expected for the ideal case. Although the qualitative features of the ΔT spectra in Fig. 6 are very similar for these two samples, the spectrum for As_2Se_3 exhibits features due to variations in sample thickness.

The signals in Fig. 6 decay as one approaches the band gaps of *a*-Si:H and As_2Se_3 where a significant fraction of the incident light is absorbed in one pass through the film. The band gap of the *a*-Si:H is typical for a material

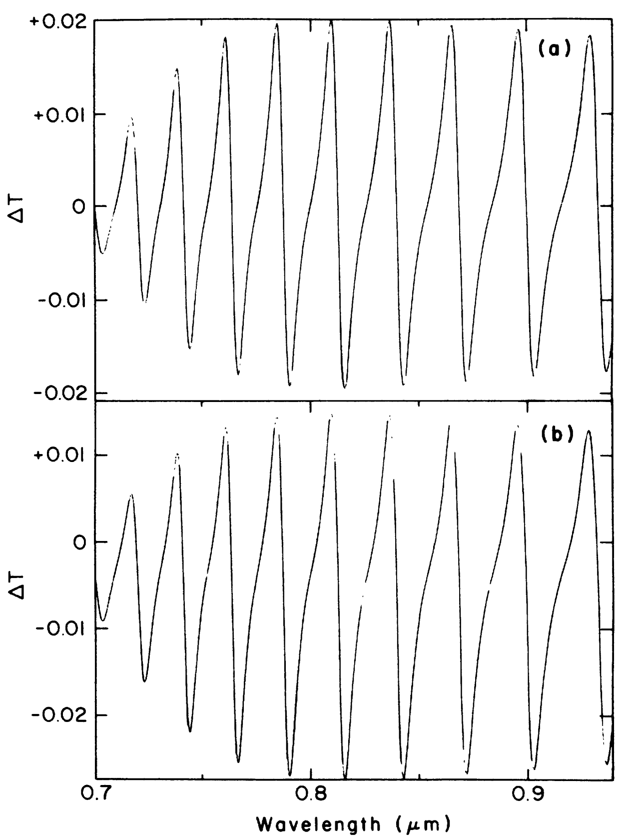

FIG. 5. Comparison of ΔT with (a) $\Delta n = 10^{-3}$, $\Delta\alpha = 0$, and (b) $\Delta n = 10^{-3}$, $\Delta\alpha = 10$ cm^{-1} for $n = 3.5$ and a film thickness of 3 μm.

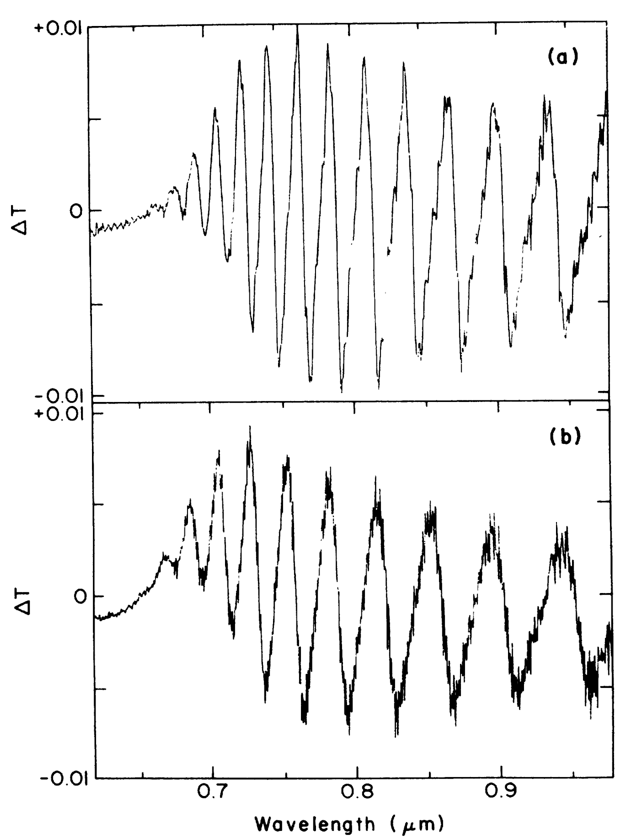

FIG. 6. ΔT as a function of wavelength for (a) a 3-μm-thick film of *a*-Si:H on glass and (b) a 3-μm-thick film of glassy As_2Se_3 on glass.

which has low defect density, but the band gap for the As_2Se_3 is not typical of the bulk glass because the film was made by rapid deposition on a 300-K substrate.

Modulation spectroscopy techniques have been applied to *a*-Si:H and the chalcogenide glasses to study the defect states and the modulation of the transmission has been attributed to a purely electronic effect which produces photoinduced absorption.[1–5] Our results show that the thermal modulation of n in these materials can make a significant contribution to the modulation spectrum in some cases.

Note added in proof. Brodsky and Leary[11] have measured the temperature dependence of the refractive index of *a*-Si:H and also calculated the modulated thermoreflectance.

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