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## ANNEALING STUDIES ON LOW OPTICAL ABSORPTION OF GD a-Si:H USING PHOTO-ACOUSTIC SPECTROSCOPY

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**Abstract.-** We have performed photoacoustic spectroscopy (PAS), ESR and ir absorption measurements on undoped GD a-Si:H film before and after isochronal annealings, from which absorption coefficient (down to  $\alpha = 1 \text{ cm}^{-1}$ ), spin density ( $N_S$ ) and bonded H content ( $C_H$ ) were determined. It has been found out that the extrapolated spectrum of spin-free a-Si:H shows a long exponential tail, and that additional broad absorption is strongly correlated with  $N_S$ . The origin of  $\alpha$  below  $E_0$  is discussed.

**Introduction.-** In many amorphous compound semiconductors the absorption edge spectrum can be roughly divided into three regions; the high absorption region *A* ( $10^3 < \alpha < 10^4 \text{ cm}^{-1}$ ), the exponential part *B* extending over 4 orders of magnitude of  $\alpha$  and the weak absorption tail *C*. There has been reported less data on the optical absorption of a-Si:H in the regions *B* and *C* compared with *A*, although an important information on gap states near the mobility edge is involved in these regions below the optical gap. Crandall and Abeles et al. determined independently the optical absorption coefficient down to  $\alpha = 10^{-1} \text{ cm}^{-1}$  using the photocurrent method [1][2], but their photoelectric measurements are inherently accompanied by the ambiguities originated in surface states and/or photon-energy dependence of  $\mu\tau$  product. In earlier work we have demonstrated that photoacoustic spectroscopy (PAS) is a powerful tool for determining the low absorption coefficient of a thin film below the optical gap (region *B*) and free from any problems accompanied by the transport phenomena of the photo-generated carriers [3].

In this report we present the first data on the below-gap absorption (region *B*) of GD a-Si:H as a function of annealing temperature, and discuss them in relation to the ESR spin density and the bonded hydrogen content of the specimen prepared and annealed under the identical condition.

**Experimental.-** Used samples in the present work were deposited in a glass substrate (Tempax) in a 13.56-MHz induction plasma chamber at a low power density from pure SiH<sub>4</sub>. A flow rate of 5 SCCM, a gas pressure of 100 mTorr and a substrate temperature ( $T_S$ ) of 100°C were maintained.

The PAS data are collected as follows: The thin film sample to be studied is placed inside a closed cell containing air and a sensitive microphone, and then illuminated with a modulated monochromatic light. The periodic heating caused by the nonradiative processes associated with optical absorption gives a periodic heat flow to the air gas and the resultant acoustic signal is detected by the microphone as a function of the photon energy of the incident light. Actual PAS signals of the samples (9  $\mu\text{m}$  in thickness) were traced using the PAR model 6001 photoacoustic spectrometer. PAS, ESR and ir absorption measurements were systematically carried out on the samples after each 3-hour isochronal annealing at different temperatures elevated at 50°C intervals in the flowing H<sub>2</sub>, from which absorption coefficient (down to  $\alpha = 1 \text{ cm}^{-1}$ ), spin density ( $N_S$ ) and bonded H content ( $C_H$ ) were determined.

**Results and discussion.**— Figure 1 shows the optical absorption spectra extending down to  $\alpha = 1 \text{ cm}^{-1}$  of the undoped a-Si:H ( $T_s = 100^\circ\text{C}$ ) before and after the isochronal annealings at  $T_a = 300, 450$  and  $550^\circ\text{C}$ , respectively. The data for the specimen deposited at  $T_s = 300^\circ\text{C}$  are also shown in the figure for comparison [3]. These data were obtained from the PAS data using the exact relation between PAS signal and  $\alpha$  of a thin film sample which we derived from the thermal diffusion equations taking into account the multiple reflection [4]. In a low  $\alpha$  region the normalized PAS signal  $q$  is approximated as

$$q = Q(\alpha)/Q_s = (1+r_2^2)\alpha\ell/(1-r_1^2r_2^2), \quad (1)$$

where  $Q(\alpha)$  is the PAS signal from the sample,  $Q_s$  the saturated value of  $Q(\alpha)$  in high  $\alpha$  region,  $\ell$  the thickness of the sample ( $9 \mu\text{m}$ ),  $r_1^2$  and  $r_2^2$  the reflectivities for the normal incidence of a light from the sample to the gas and the sample to the backing material, respectively. The detailed procedure was described earlier [3].

As shown in the figure, a-Si:H film deposited at  $T_s = 300^\circ\text{C}$  shows a long exponential tail in its spectrum, while the specimen deposited at  $T_s = 100^\circ\text{C}$  has an additional optical absorption over a wide energy range below  $1.7 \text{ eV}$  independent of whether as-deposited or annealed. But the broad optical absorption band below  $1.7 \text{ eV}$  decreases by nearly one order of magnitude according as  $T_a$  increases up to  $300^\circ\text{C}$ , and increases again for  $T_a > 300^\circ\text{C}$ . This characteristic behaviour of low  $\alpha$  region caused by annealing is, to our knowledge, the first observation in a-Si:H. Tsai and Fritzsche have observed in their annealing study of GD a-Si:H that the structure sensitive absorption tail, its onset around at  $\alpha = 10^3 \text{ cm}^{-1}$ , does not diminish with annealing [5], which is likely due to scattering losses or the lack of data accuracy inherent to the direct transmission method in a thin film structure.

We determined the optical gap  $E_0$  using the empirical relation

$$\sqrt{\alpha h\nu} \propto (h\nu - E_0) \quad (2)$$

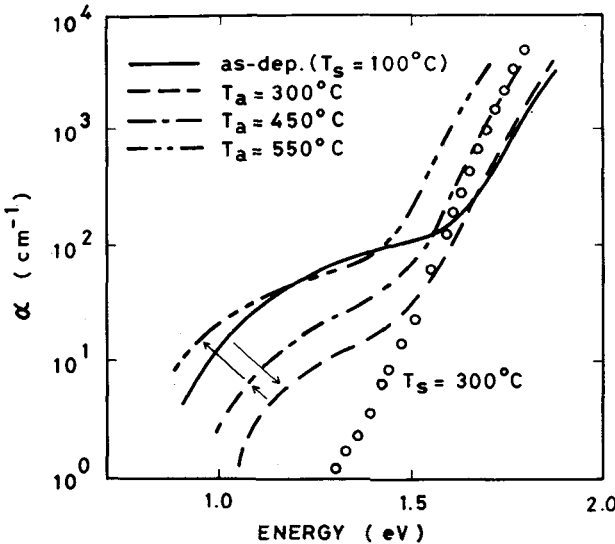


Fig. 1 : Optical absorption spectra of GD a-Si:H ( $T_s = 100^\circ\text{C}$ ) before and after each isochronal annealing, which were obtained by analyzing the PAS data. The result of a-Si:H ( $T_s = 300^\circ\text{C}$ ) is also plotted.

from the spectra in the range  $10^3 \text{ cm}^{-1} < \alpha < 10^4 \text{ cm}^{-1}$  (region A), and the energy  $E_c$  characterizing the slope of the exponential part B from the formula

$$\alpha = \alpha_0 \exp(h\nu/E_c), \quad (3)$$

being fitted to the spectra in the range of  $10^2 \text{ cm}^{-1} < \alpha < 10^3 \text{ cm}^{-1}$ , respectively. The results are shown in Fig. 2.  $E_0$  (top of the figure) increases first up to  $T_a \approx 200^\circ\text{C}$  and afterwards decreases rapidly according as the bonded hydrogen content  $\text{CH}$  decreases due to thermal effusion (see Fig. 3), being a widely observed tendency [5][6][7]. The increase in  $E_0$  with  $T_a$  in low  $T_a$  range should mainly be attributed to the thermal reconstruction of the local structure because  $\text{CH}$  remains constant in this  $T_a$  range (see Fig. 3), which has also been pointed out by several

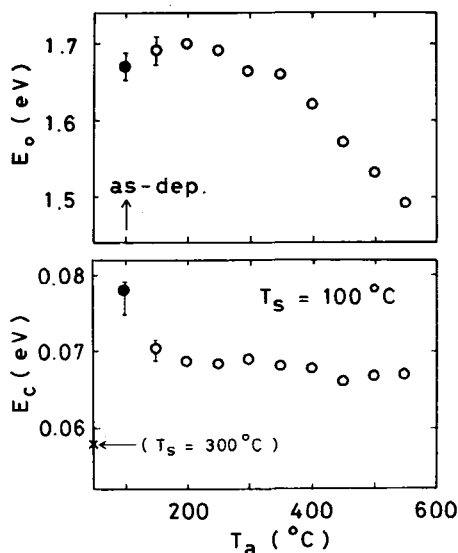


Fig. 2 : The optical gap  $E_o$  (top) and the energy  $E_c$  characterizing the slope (bottom) of a-Si:H ( $T_s = 100^\circ\text{C}$ ) as functions of  $T_a$ .

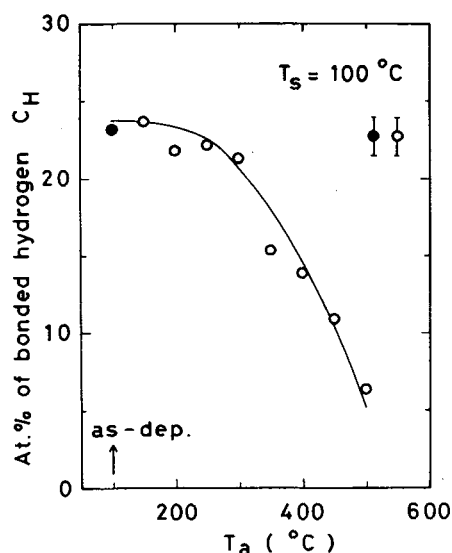


Fig. 3 : Atomic % of bonded H content ( $C_H$ ) in a-Si:H ( $T_s = 100^\circ\text{C}$ ) as a function of  $T_a$ .

groups [5][6][7]. On the other hand, different from  $E_o$ , the energy  $E_c$  associated with the slope of the exponential tail does not show a drastic change over a wide  $T_a$  range from  $150^\circ\text{C}$  up to  $550^\circ\text{C}$ , as shown in the bottom of Fig. 2. The value of  $E_c$  nearly remains at  $0.07\text{ eV}$ , surprisingly, being close to those of chalcogenide glasses [8]. The specimen deposited at  $T_s = 300^\circ\text{C}$  has an  $E_c$  smaller than  $0.06\text{ eV}$  (denoted by x in the figure) [3].

In order to get more detailed information on the nature of the broad absorption band below  $E_o$ , we correlate the integrated absorption  $A$  with the ESR spin density  $N_s$ , which is defined as

$$A = \int \frac{\Delta\alpha}{\nu} d\nu, \quad (4)$$

where  $\Delta\alpha$  is a difference between the observed value and the value determined by the fitted exponential relation of eq.(3), i.e.,

$$\Delta\alpha(h\nu) = \alpha(h\nu)_{ob} - \alpha_0 \exp(h\nu/E_c). \quad (5)$$

Fig. 4 shows integrated absorption  $A$  and the ESR spin density  $N_s$  at room temperature as functions of  $T_a$ . Both quantities show quite a similar behaviour, i.e., decrease rapidly as  $T_a$  increases, taking a minimum around at  $T_a = 250 - 300^\circ\text{C}$ , and increase again for  $T_a > 300^\circ\text{C}$ . It means that the broad optical absorption below  $E_o$ ,  $A$  defined by eqs.(4) and (5), has a strong correlation with  $N_s$ , in other words, the concentration of dangling bonds involved in amorphous Si-H network. The data indicate within experimental errors that  $A$  and  $N_s$ , to a first approximation, are connected by a linear relation,

$$A \propto N_s. \quad (6)$$

From eqs. (4), (5) and (6) it is concluded that the absorption spectrum of spin-free a-Si:H should have a long exponential tail extending to low photon energies independent of  $E_o$ . This conclusion is compatible with the data for a-Si:H deposited at  $T_s = 300^\circ\text{C}$  showing the long exponential part in its spectrum in Fig. 1.

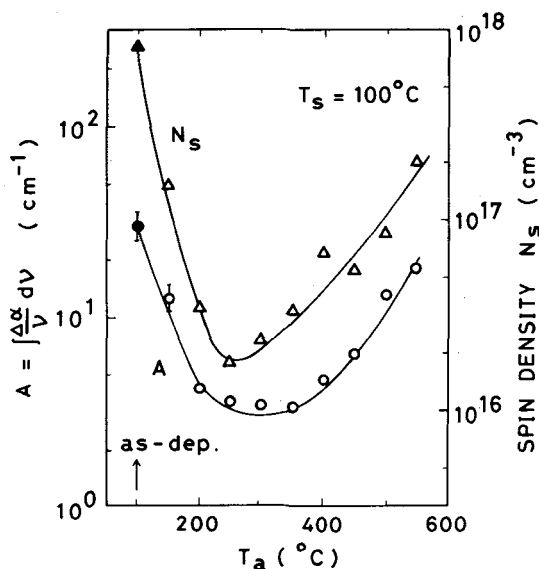


Fig. 4 : Excess optical absorption  $A$  defined in the text and corresponding ESR spin density  $N_s$  of a-Si:H ( $T_s = 100^\circ\text{C}$ ) as functions of  $T_a$ .

Brodsky and his coworkers have made an initial effort to correlate the optical absorption with the ESR spin density in evaporated amorphous Si films which are non-hydrogenated, and estimated the optical absorption spectrum of a-Si free from the effects of voids and broken bonds by extrapolating the results to zero spin concentration [9]. According to their estimation the extrapolated spectrum of spin-free a-Si falls sharply at 1.8 eV and does not obey the exponential relation, which is not the present case as mentioned above. Concerning the quantitative relation between  $A$  and  $N_s$ , for example the ratio of  $A$  to  $N_s$ , there exists no substantial difference between the present data and those of Brodsky et al.

On the other hand, Bishop et al. observed the optically induced ESR and absorption at  $T = 6\text{ K}$  due to localized paramagnetic states in the forbidden gap in several chalcogenide glasses [10]. For  $\text{As}_2\text{Se}_3$  glass, according to their data, the induced absorption amounting to  $\alpha = 15\text{ cm}^{-1}$

has been observed corresponding to  $N_s \approx 10^{18}\text{ cm}^{-3}$ . It should be noted that the ratio of the induced absorption to  $N_s$  takes a value of the same order as that of  $A/N_s$  in the present work, in spite of the substantial difference in the structure of the materials, a-Si:H vs. amorphous chalcogenides.

One is tempted to attribute directly the origin of the broad absorption  $A$  to dangling bonds, but more detailed information will be required for further discussion.

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