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Optical Characterization of Undoped a-Si:H Prepared by Photo-CVD and GD Techniques

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We have optically characterized undoped a-Si:H films prepared by photo-CVD and GD techniques under various deposition conditions. Photoluminescence(PL) and transmission spectra were measured at 77 K, from which the peak energy E_p of the main PL band and the optical absorption edge E_{gopt} could be deduced. We have obtained the Urbach energy E_0 by means of photothermal deflection spectroscopy(PDS) at room temperature. The differences ΔE between E_p and E_{gopt} were plotted against E_0 for films prepared under various conditions, from which it was found that the same linear relation holds between ΔE and E_0 commonly for films prepared by both techniques. We conclude that the increase of ΔE in films deposited at a low substrate temperature is mainly caused by a broadening of the tail states owing to disorder in the amorphous network.

§1. Introduction

Hydrogenated amorphous silicon (a-Si:H) shows a strong photoluminescence (PL) band at low temperatures. The peak-energy position of the main PL band (located around 1.3 eV) varies with the preparation condition.[1] Although there are unresolved details regarding the mechanism, there is general agreement that this luminescence arises from transitions between band-tail states.[2]

The most remarkable feature of this luminescence is a large shift between the optical band gap (E_{gopt}) and the luminescence peak energy (E_p), the origin of which is still under dispute. The purpose of the present study was to obtain some information regarding this problem through optical studies on amorphous silicon films prepared under various preparation conditions.

It has also been known that the peak energy E_p varies with the preparation condition of film. The variation of E_p occurs mainly due to the E_{gopt} introduced by a difference in the hydrogen concentration. However, the observed variation of E_p is not as simple as was expected from only considering E_{gopt}; the difference $\Delta E = E_{gopt} - E_p$ increases in films deposited at low substrate temperatures (T_{sub}). Two mechanisms are suspected to be involved: one is a difference in the electron-phonon interaction (so-called Stokes shift) and the other is a difference in the energy distribution of tail states. Information on the latter effect can be estimated by using the Urbach energy E_0, the inverse of the slope of the exponential tail in the subgap absorption spectrum.

We have, therefore, studied the quantitative relations between $\Delta E = E_{gopt} - E_p$ and E_0 through photoluminescence, transmission and photothermal deflection spectroscopy (PDS).

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§2. Experimental

Undoped amorphous Si:H films were deposited on Corning 7059 substrates by mercury-sensitized photo-CVD and conventional capacitively coupled rf-glow discharge techniques. Details of the deposition conditions are summarized in Table I. Sample thicknesses ranged from 0.7 to 3 μm. Samples for PL were deposited on ground-glass substrates in order to remove interference effects.

The optical bandgap was determined from a Tauc plot of the absorption coefficients obtained by using conventional optical transmission spectroscopy with appropriate corrections for multiple-reflection effects.

The absorption spectra for the exponential absorption tail region were measured by PDS.[3-5] The excitation source was a 500 W xenon arc lamp chopped at 10 Hz. The periodic beam deflection was detected by a position-sensitive photodiode. The samples were immersed in CCl_4 in order to increase the deflection. The amplitudes of photothermal signals were normalized to the incident-light intensity monitored simultaneously with a thermopile detector.

The PL measurements were performed at 77 K. The excitation source was the 5145 Å line of an argon-ion laser. The excitation power was 25 mW/cm^2. A PbS cell cooled by dry ice was used as a detector. The PL spectra were

Table I. Summary of preparation conditions of a-Si:H used in this study.

Technique	photo-CVD	GD	Unit
T_{sub}	100–275	130–262	°C
P_{ch}	2	0.4	Torr
SiH_4 flow rate	20	7–20	SCCM
RF power	—	5–14	W
Hg temp.	20	—	°C

T_{sub}: substrate temperature
P_{ch}: pressure in the reaction chamber
Hg temp: temperature of the mercury reservoir

corrected for the response of the detection system, determined using a tungsten lamp of known color temperature.

§3. Results

We observed a broad featureless emission band around 1.3 eV for each sample. Figure 1 shows the peak energy E_p, peak intensity I_p of the main band of PL, together with the hydrogen content C_H as a function of the deposition temperature. C_H was determined by infrared absorption spectroscopy.

The emission intensity I_p of both photo-CVD and GD films decreased as T_{sub} was lowered. However, photo-CVD films showed higher photoluminescence intensities than GD films for T_{sub} below 200°C. As is well known, the PL intensity is highly correlated with the dangling bond density. Therefore, the difference in I_p can be attributed to the difference in the dangling bond density.

The most significant difference between photo-CVD and GD a-Si:H is the behavior of the peak energy (E_p). The peak energy for photo-CVD films increased with a decrease in T_{sub}. On the other hand, the E_p for GD films decreased for T_{sub} below 200°C. Figure 2 shows the energy difference ΔE between E_{gopt} and E_p at 77 K as a function of T_{sub}. As shown in the figure, the difference ΔE increases, especially, for T_{sub} below 200°C.

Figure 3 illustrates the typical absorption spectra of photo-CVD films obtained by connecting those measured by transmission spectroscopy and those by PDS. It can be seen in this figure that E_{gopt} shifts toward higher energies and the slope of the exponential tail becomes less steep as the substrate temperature is lowered.

Figure 4 shows the Urbach energy E_0 as a function of T_{sub}, while Fig. 5 illustrates the T_{sub}-dependence of the ratio of $Si–H_2$ bonding to Si–H bonding as determined from infrared spectroscopy. A similar dependence on T_{sub} can be observed in both figures.

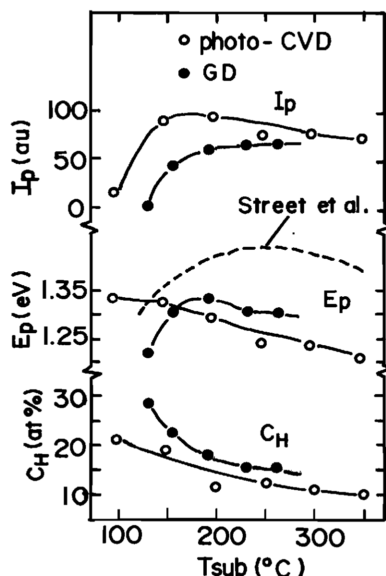

Fig. 1. Peak energy E_p, peak intensity I_p of the main band of the photoluminescence spectrum at 77 K, together with the hydrogen content C_H as a function of the deposition temperature. Open circle denotes photo-CVD film and closed circles GD film.

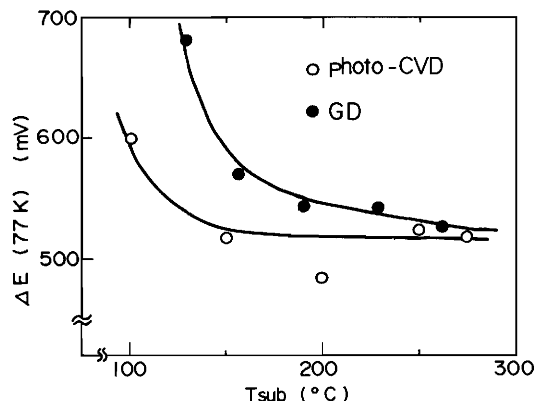

Fig. 2. Energy difference ΔE between E_{gopt} (optical band gap) and E_p (photoluminescence peak energy) as plotted against the deposition temperature T_{sub}. Open circle denotes photo-CVD film and closed circle GD film.

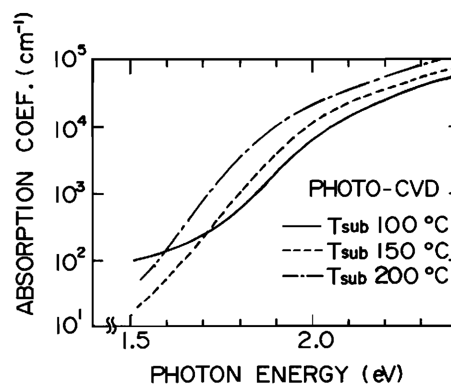

Fig. 3. Typical absorption spectra of photo-CVD a-Si:H films for several deposition temperatures, as obtained by associating those measured by transmission spectroscopy and those by PDS.

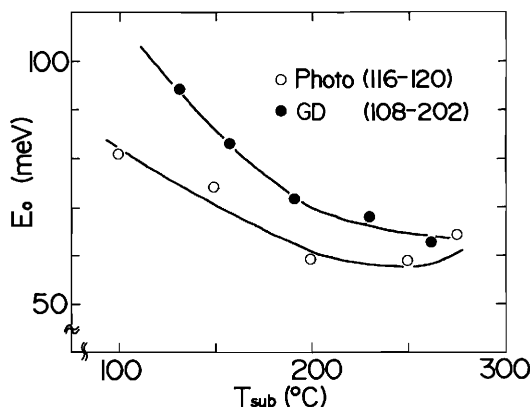

Fig. 4. Dependence of the Urbach energy E_0 on deposition temperature T_{sub}. Open circle denotes photo-CVD film and closed circle GD film.

§4. Discussion

It has been pointed out that the optical and electrical properties in both photo-CVD and GD a-Si:H might not be so different if an appropriate optimization of the deposition conditions is performed. Since the two techniques are based on quite different deposition mechanisms, the substrate temperature is not always a suitable parameter for representing the deposition condi-

tions of these films. Nevertheless, T_{sub} is important for industrial applications. It has been found that the optical properties of photo-CVD films in our work (Figs. 3 and 4) have a weaker dependence on the substrate temperature than those of GD films. As far as our films are concerned, the photo-CVD technique has a better capability for low-temperature processing than the GD technique.

The increase in the Urbach energy E_0 means an increase in the structural disorder in an amorphous network, resulting in a broadening of the tail states. Comparing Figs. 2 and 4 indicates that the shift of E_p with deposition temperatures is due to variations in both E_{gopt} and the widths of the tail states.

Figure 5 indicates that the Si–H_2 bonding increases relative to the Si–H bonding according to the decreases in the deposition temperature. The similarity of the E_0 vs T_{sub} plot and the Si–H_2/Si–H vs T_{sub} plot seems to indicate that the increase in Si–H_2 bonding is responsible for the disorder in the network.

Figure 6 shows a plot of ΔE against E_0 for a number of a-Si:H films prepared under various deposition conditions. Both films show a similar tendency, as described in the following formula:

$$\Delta E = 5.25E_0 + 200 \text{ [meV]}. \quad (1)$$

Here, we use the room-temperature value for E_0. However, since ΔE was measured at 77 K, we should use 77 K for E_0 as well. E_0 consists of thermal as well as structural disorders. Recently, Yamasaki showed that the contribution of the thermal disorder to E_0 (by means of PAS (photoacoustic spectroscopy)) is not more than 6 meV.[6] Provided that the contribution of the thermal disorder is not sensitive to the preparation method of the films, eq. (1) can be rewritten as

$$\Delta E = 5.25E_0 + 230 \text{ [meV] at 77 K}. \quad (2)$$

According to the simplified model by Street,[2] the difference ΔE between E_{gopt} and E_p consists of a sum of the width of the valence band tail E_{VT} and that of the conduction band E_{CT} and the electron phonon coupling energy E_{ep}. We believe that $5.25E_0$, the first term in eq. (2), represents the total width, $E_{CT}+E_{VT}$, that contributes to the photoluminescence process, although E_0 has been known to provide a measure of the width of the valence band tail[7] introduced by the disorder in the amorphous network of Si–Si bonding. The remaining constant value in eq. (2), (230 meV) can then be assigned to the Frank-Condon shift due to electron phonon coupling.

The above-mentioned treatment may be somewhat too simplified; there have been a number of experiments reported that support the involvement of some center like the "A-center" introduced by Morigaki[8] through ODMR in the PL process. However, no details are known concerning the origin of the center. We, therefore, merely point out that the value of $5.25E_0$ observed in the present study is very close to the reported position of the A-center measured from the valence band edge.

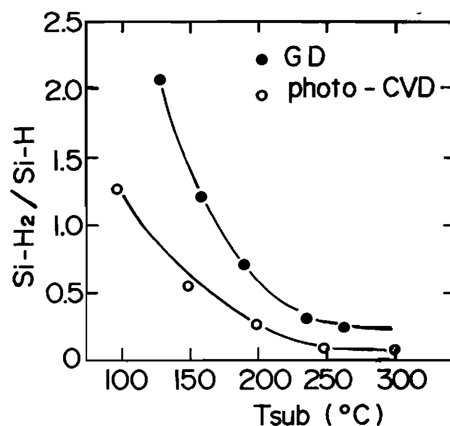

Fig. 5. The ratio of Si–H_2 bonding to Si–H bonding as plotted against the deposition temperatures. Open circle denotes photo-CVD film and closed circle Gd film.

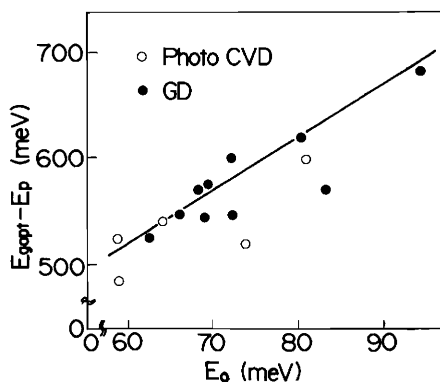

Fig. 6. The difference $\Delta E = E_{gopt} - E_p$ as plotted against the Urbach energy E_0 for films prepared under various deposition conditions. Open circle denotes photo-CVD film and closed circle GD film.

§5. Conclusions

We have investigated the photoluminescence and optical absorption properties in undoped a-Si:H produced by photo-CVD and GD techniques. It has been found that the optical properties of our photo-CVD films have a weaker dependence on the substrate temperature than those of our GD films. We consider that photo-CVD techniques have capabilities for lower-temperature processing. The dependence of the peak energy of the main luminescence band on the preparation conditions could be explained as being due to a variation in both the band-gap and widths of the tail states.

For a further discussion, more detailed experimental information on the tail states is required.

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