STATES IN THE GAP OF DOPED AND UNDOPED a-Si:H STUDIED BY PHOTOMODULATION SPECTROSCOPY

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ABSTRACT

The steady state photomodulation spectrum, its temperature and excitation intensity dependences have been studied in phosphorous doped and undoped a-Si:H. The spectra are analyzed in terms of photocarriers trapped in band-tail states and dangling bonds (DB) defects in undoped samples and impurities and charged DB states introduced by doping in P-doped samples. In undoped a-Si:H we found that the two DB energy levels $D^{\pm}$ are symmetrically located about midgap with an effective correlation energy U_{eff} of 0.6±0.2eV. In P-doped a-Si:H D^- is pushed toward midgap by about 0.25 eV and U_{eff}=0.4±0.2eV.

INTRODUCTION

The photomodulation (PM) spectroscopy is a powerful optical technique for studying localized states in the mobility gap, trapping and recombination processes of photogenerated carriers in amorphous materials [1]. We have extended the PM energy range from 0.1 to 1.8 eV and applied it to P-doped (a-Si:H:P) and undoped a-Si:H. From the temperature and excitation intensity dependences in undoped a-Si:H, we found that the PM spectra contain two distinctive photoinduced absorption (PA) bands. We associate the low energy band to carriers trapped at band-tail states whereas the high energy band is due to carriers trapped at DB defects; this enables us to determine the two DB levels $D^{\pm}$. We found that D^- is 0.6±0.1eV from the conduction band (CB), and D^+ is 0.6±0.2eV from the valence band (VB). The PM spectrum of a-Si:H:P also contains two distinctive PA bands, however, their relative intensities in the spectrum do not change much with temperature or with excitation intensity. We assign the PA bands to carriers trapped in charged defects introduced by doping, namely, shallow impurities and D^- states. We found that D^- is 0.85±0.1eV from the CB so that the state is pushed by about 0.25 eV relative to D^- in undoped material, while U_{eff} remains positive (≈0.4eV).

EXPERIMENTAL

Two light sources are needed for the PM spectroscopy [1,2]: a pump beam for photogeneration of carriers and a probe beam for measuring the photo-induced changes in transmission. The pump was a chopped (75 Hz) Ar^+ laser beam with an adjustable intensity from 1 to 100 mW/cm^2 , whereas the probe beam was an incandescent light source dispersed by a monochromator. The transmission T and its modulation ΔT were recorded simultaneously using InSb, Ge or Si detectors and lock-in amplifier; the system response was accounted for by taking the ratio $\Delta T/T$ which is proportional to the induced changes $\Delta\alpha$ in the absorption coefficient α. The samples were heavily (10^{-3}) doped a-Si:H:P and undoped a-Si:H thin films (thickness≈3μm) deposited on sapphire substrates by the glow discharge technique.

UNDOPED a-Si:H

The steady state PM spectra of undoped a-Si:H at 10K and 240K are shown in

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Figs 1 and 2. Both spectra show a pronounced onset of photoinduced absorption (PA, $\Delta\alpha > o$) followed by a reduction of $\Delta\alpha$ at higher energies. The broad maximum

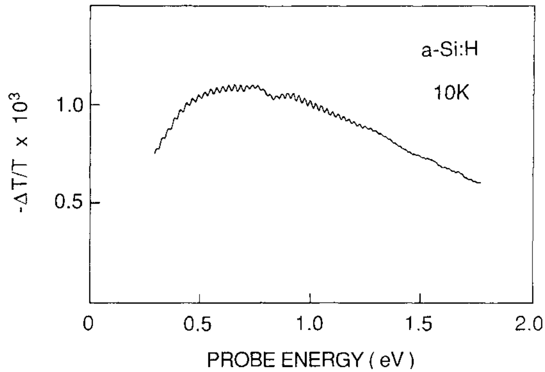

Fig. 1 PM spectrum of a-Si:H at 10K.

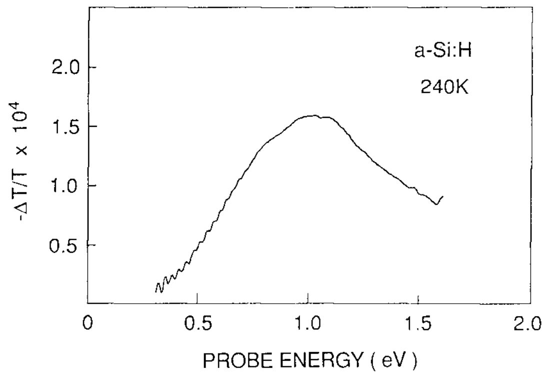

Fig. 2 PM spectrum of a -Si:H at 240K.

of the PA band shifts from 0.5 eV at 10K to 1.0 eV at 240K. This shift may result either from a shift in the PA onset or from two distinct PA bands whose strengths have different dependencies on temperature. The former interpretation was used in previous studies [1,2] to derive the hole quasi-Fermi energy as a function of temperature. To examine which interpretation is correct we have measured the temperature dependence and pump intensity dependence at two different probe energies: $\hbar\omega$=o.4eV which is the PA peak at low temperatures and $\hbar\omega$=1.0eV which is the peak at high temperatures.

The temperature dependence is shown in Fig. 3. The photoinduced change in absorption $\Delta\alpha$ at both 0.4 and 1.0 eV decays exponentially [1,2] with temperature $[\Delta\alpha \sim \exp(-T/T_1)]$ with T_1 = 70K for $\hbar\omega$=0.4eV and T_1 = 130K for $\hbar\omega$=1.0eV. The different temperature dependence for the two probe energies is a clear manifestation of the trend seen in the PM spectra of Figs. 1 and 2, however, it can still result from a shift in the PA onset with temperature. A more crucial test is the pump intensity (I) dependence at a constant temperature. At 10K, we found that $\Delta\alpha$ at 0.4 and 1.0 eV increase as $I^{0.4}$ and this shows that a single PA band dominates the PM spectrum at 10K. However, at 240K, we found that $\Delta\alpha$ increases differently at 0.4 and at 1.0 eV. As shown in Fig 4, $\Delta\alpha \sim I^{0.4}$ at $\hbar\omega$=0.4eV whereas at $\hbar\omega$=1.0eV $\Delta\alpha \sim I^{0.65}$. This conclusively demonstrates that two PA bands are involved in the PM spectrum of a-Si:H.

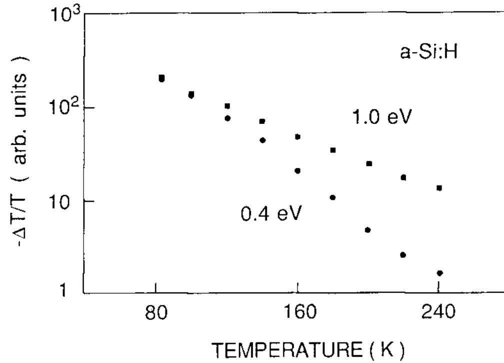

Fig. 3 Temperature dependence of $\Delta\alpha$ in a-Si:H at $\hbar\omega$ = 0.4 (dots) and 1.0 eV (squares).

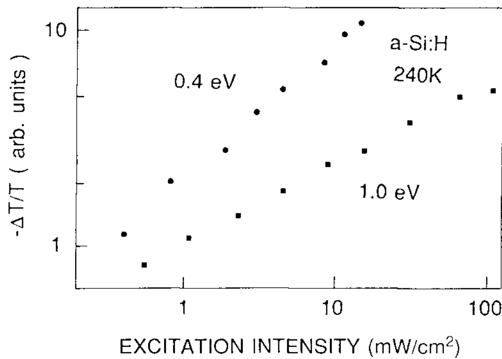

Fig. 4 Excitation intensity dependence of $\Delta\alpha$ in a-Si:H at 240K at $\hbar\omega$ = 0.4 (dots) and 0.9 eV (squares).

The first PA band with low energy onset has a strong temperature dependence whereas the second PA band with a high energy onset has a moderate temperature dependence (Fig. 3). Based on the PA onsets at low and high energies, we attribute the first PA band to photocarriers trapped in band-tail states [1,2] whereas the second PA band is due to photocarriers trapped in DB defects [3]. Only carriers trapped in DB defects survive at elevated temperatures; on the other hand the band-tail carriers quickly recombine [4] so that their contribution to the steady state PM spectrum measured at 75 Hz is negligibly small. Therefore, the PM spectrum at 240K (Fig. 2) is dominated by the DB contribution [4] and we can use it to extract valuable information about the DB energy levels.

The trapping process of photocarriers in DB defects ($e+D^o \rightarrow D^-$ and $h+D^o \rightarrow D^+$) can be summarized [3] by the reaction $2D^0 \rightarrow D^+ + D^-$. Therefore, optical transitions associated with D^o are photo-bleached [5] (PB, $\Delta\alpha<o$) whereas optical transitions associated with $D^\pm$ are enhanced (PA, $\Delta\alpha>o$). Fig. 2 contains only one PA band and thus we conclude that D^+ ,D^- are symmetrically displaced around midgap. The PB contribution is observed in Fig 2. as a reduction in $\Delta\alpha$ starting at 1.0 eV. We have successfully fitted the DB PM spectrum of Fig 2 using two group of states in the gap with Gaussian distributions [6]. The PA is due to states centered at 0.6±0.1eV from the adjacent band; it is associated with electron transition from (into) $D^-(D^+)$. PB is due to states centered at 1.2±0.1eV from the CB and is associated with electron transition from D^o into the CB. From the DB levels D^- and D^o we can directly calculate the effective correlation energy $U_{eff}=1.2-0.6=0.6\pm0.2$eV. This is in good agreement with U_{eff} extracted previously from magnetic studies of lightly doped and undoped a-Si:H [7]. However, $D^\pm$ levels measured by the PM technique are in disagreement with the results of deep level transient spectroscopy (DLTS) [8] which have placed D^- at 0.85 eV from the CB. This disagreement is due to different materials rather than systematic errors in the experimental techniques. Our measurements are done on undoped a-Si:H whereas the DLTS measurements have been carried out on P-doped a-Si:H. In the following we show that the PM studies of a-Si:H:P are in agreement with the results of DLTS.

P-DOPED a-Si:H

The steady state PM spectrum of 10^{-3} P-doped a-Si:H at 80K is shown in Fig. 5.

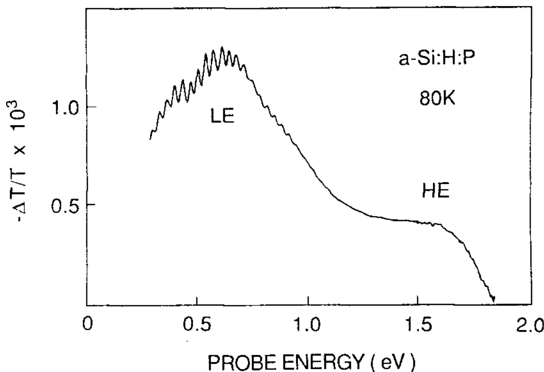

Fig. 5 PM spectrum of 10^{-3} P-doped a-Si:H at 80K.

In contrast to a-Si:H (Figs. 1 and 2), we found that the PM shape does not change much with temperature or with excitation intensity; all spectral features have the same dependence on temperature and pump intensity. Two well defined bands are observed in Fig. 5. The first band LE peaks at 0.6 eV whereas the second band HE has a broad maximum between 1.2 and 1.6 eV. Our picosecond PM results [9] have shown that photocarriers in 10^{-3} a-Si:H:P are quickly (< 10 nsec.) trapped in charged states introduced by doping. Electrons are trapped in shallow impurity states P_4^+ ($e+P_4^+ \rightarrow P_4^o$) whereas holes are trapped in deep DB states D^- ($h+D^- \rightarrow D^o$). Therefore, we attribute the first PA band in Fig 5 to electron transitions from P_4^o into the CB. From the spectrum we determine that this state is centered at 0.3 eV below the CB. The second PA which is centered at 1.25±0.1eV is ascribed to transitions from D^o into the CB. The PB contributions in Fig. 5 which are centered at 0.85±0.1eV and at 1.7±0.1eV are due to photo-bleaching of electron transition from D^- into the CB and from the VB into P_4^+ respectively.

Our analysis shows that compared to undoped a-Si:H the D^- level in a-Si:H:P is pushed toward midgap by about 0.25 eV consistent with the DLTS results and with recent excitation spectra of photoconductivity [8]. Since D^o and D^- transitions involve the same band (CB) it is possible to calculate U_{eff}=1.25–0.85=0.4±0.2eV. This is close to U_{eff} of DB defects in undoped a-Si:H (U_{eff}=0.6±0.2eV) , indicating that the DB defects in these two materials are not very different.

CONCLUSIONS

By measuring the PM spectrum in doped and undoped a-Si:H we have shown that the DB energy levels are different in the two materials consistent with D. Adler's predicition [11]. $D^-(D^+)$ is centered at 0.6±01eV below (above) the CB (VB) in undoped a-Si:H, whereas in heavily doped a-Si:H:P D^- is centered at 0.85 eV from the CB. This implies that it is not possible to extract U_{eff} of DB by comparing the absorption spectra of doped and undoped a-Si:H as has been previously proposed [12], but measurements of D^- and D^o have to be made on the same material. This is a strong advantage of the PM technique [3,5] in which the various charged states are derived from the PA and PB contributions on the same material. From our data we obtained the value of U_{eff} for the DB which is 0.6±0.2eV in undoped a-Si:H and 0.4±0.2eV in a-Si:H:P.

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