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Steady-state photomodulation spectroscopy of a-Si:H/a-SiN$_x$:H multilayer structures

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The steady-state photomodulation (PM) spectrum and its temperature dependence were studied in a-Si:H/a-SiN$_x$:H multilayer structures (MLS). We found that the photocarrier properties in MLS with Si sublayer thickness $d_S < 20$ Å are dominated by band-tail broadening resulting from increase in disorder. The PM spectrum for MLS with $d_S > 20$ Å is mainly due to interface-related defects; because of its similarity with the PM spectrum of P-doped a-Si:H we identify the defects as charged dangling bonds.

INTRODUCTION

Photomodulation spectroscopy (PM) is a powerful method for studying the band-tail and defect states in amorphous materials by optically altering and probing the occupancies of these states.[1] The transient PM measurements can provide information about the relaxation and recombination processes of photogenerated carriers.[2] Both steady state and transient PM have been extensively applied to amorphous semiconductors, in particular to doped and undoped a-Si:H.[1-3] The PM spectra of undoped a-Si:H have been interpreted in terms of carrier trapping in band-tail states and in deep-level defects;[1] for doped a-Si:H one has to take into account the impurity states as well.[4] In this Rapid Communication we report the first PM studies on a-Si:H/a-SiN$_x$:H multilayer structures (MLS) from which information about disorder in the a-Si:H layers and the influence of the defect states at the interfaces has been obtained.

From x-ray diffraction measurements[5] the a-Si:H/a-SiN$_x$:H MLS are known to have well-defined sublayers and relatively abrupt interfaces. The optical gap as well as the width of the Urbach edge increase with decreasing Si sublayer thickness as has been observed[5] by optical absorption measurements and by photoluminescence (PL). The studies of electrical transport and photoconductivity[6] show that the MLS have low sheet resistivity compared with unlayered a-Si:H and the density of defect states is lower than in P-doped a-Si:H with comparable dark resistivity. This has been attributed to charge-transfer doping from the nitride to the silicon sublayers which raises the Fermi level significantly without introducing a large number of bulk defects. In addition, electroabsorption measurements[7] point out that strong internal electric fields (up to 10^5 V/cm) exist in the Si sublayers. In this paper we show that all of these MLS properties have a profound influence on the photocarrier recombination kinetics and consequently on the PM spectrum.

EXPERIMENT

Two light sources are needed for the PM spectroscopy:[1] a pump beam for photogeneration of carriers and a probe beam for measuring the photoinduced changes in transmission. For steady-state PM measurements the pump was a chopped ($f = 75$ Hz) Ar^+ laser beam with an adjustable intensity from 1 to 100 mW/cm^2, while 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, and Si detectors and lock-in amplifiers. The photoluminescence was recorded under the same condition and subtracted out from the measured ΔT. Since the contribution of photoinduced reflectivity is negligibly small in a-Si:H for probe energies below 1.7 eV,[8] the photoinduced absorption (PA) is proportional to $\Delta T/T$. The samples were held in a cryostat and measurements were done at temperatures ranging from 10 to 300 K.

The a-Si:H/a-SiN$_x$ multilayer structures were prepared[5-7] using the plasma-assisted chemical vapor deposition technique on polished c-Si or quartz substrates held at 240 °C. Pure Si:H$_4$ was used for the a-Si:H sublayers and a 5:1 mixture of NH$_3$ and Si:H$_4$ for the a-SiN$_x$:H sublayers. The Si sublayer thickness d_S was varied from 7 to 204 Å while the ratio d_S/d_N was kept constant at 0.85. The number of sublayers was adjusted so as to keep the film thickness approximately at 1 μm.

MULTILAYER STRUCTURES WITH $d_S < 20$ Å

Steady-state PM spectra for the MLS with $d_S = 7$ and 10 Å measured at 80 K are shown in Fig. 1; a typical PM spectrum for an unlayered a-Si:H on sapphire substrate at 10 K is also shown for comparison. The interference fringes which usually dominate the PM spectra for MLS (especially for the films deposited on quartz substrates) have been averaged out. The optical gap in the nitride layers is about 3.8 eV (Ref. 5) and therefore these layers do not absorb the pump beam. It is apparent that the peak of the PA band shifts to higher energies for smaller d_S and this is in agreement with similar upward shifts in the PL band and in the energy gap for MLS with small d_S.[5] It is also apparent in Fig. 1 that the onset of PA in these MLS is more gradual and occurs at higher energies compared with the PA onset of the unlayered a-Si:H. The PA observed in unlayered a-Si:H at low temperatures has

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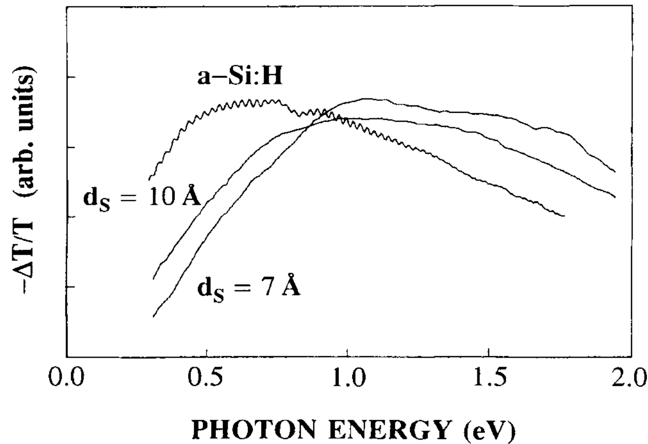

FIG. 1. PM spectra for MLS with $d_S = 7$ and 10 Å at 80 K compared with an unlayered a-Si:H at 10 K. The data on a-Si:H at 80 K are similar to those at 10 K but less accurate because of stronger photoluminescence.

been associated with photocarriers trapped in the band tails.[1–3] From studies of PL in unlayered a-Si:H it was concluded[9] that the photocarriers are trapped in deeper states in samples with broader band tails and their energy distribution is wider. Since the PA is due to optical transitions of trapped photocarriers, it follows that the onset of the PA is expected to be higher and more gradual for samples with broader band tail. We thus interpret the PM features observed for MLS with $d_S < 20$ Å shown in Fig. 1 as due to a broadening of the band tail in a-Si:H with decreasing d_S. Band-tail broadening has been observed also in other measurements of MLS with small d_S such as optical absorption[5] (the Urbach tail broadens) and PL[5] (bandwidth broadens), and it has been attributed to an increase in disorder as verified by Raman scattering[10] (phonon linewidth increases). A possibility for explaining the increase of disorder for very small d_S may be alloying of a-Si:H with N.

The PA strength at 0.33 eV for $d_S = 7$ and 10 Å as a function of temperature is shown in Fig. 2 and is compared to that for the unlayered a-Si:H. Since the PA strength is proportional to the steady-state density of photogenerated carriers which depends on the recombination rate,[3] the relatively weak temperature dependence of the PA indicates that the photocarrier recombination in MLS is not governed by a thermally activated process as in unlayered a-Si:H.[3] A plausible explanation for this is that the carriers thermalize among the band-tail states by directly hopping down to lower energies;[11] this process is only weakly temperature dependent. The alternative process of thermal release into the delocalized states at higher energies and consequent retrapping at deeper levels depends strongly on temperature,[12,13] and this is not consistent with the MLS data. This suggests that the increased disorder and the resultant band-tail broadening in MLS with small d_S strongly influence the recombination kinetics of the photocarriers in the Si sublayers. We plan to study the recombination kinetics by time-resolved measurements.

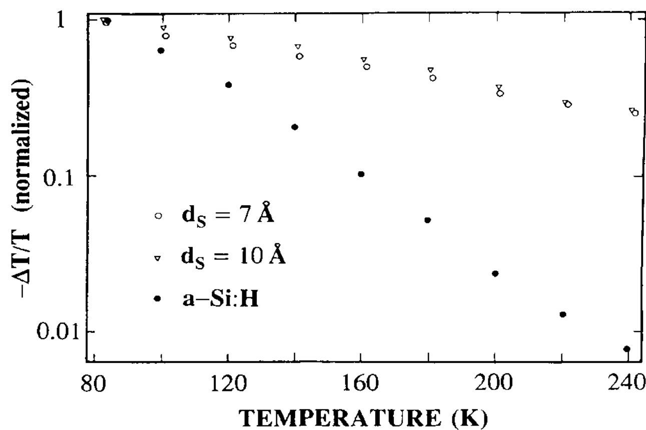

FIG. 2. Temperature dependence of the PA strength of MLS with $d_S = 7$ and 10 Å compared with that of unlayered a-Si:H.

MULTILAYER STRUCTURES WITH $d_S > 20$ Å

In Fig. 3 the PM spectra for MLS with $d_S = 39$ and 126 Å are shown with an arbitrary vertical displacement. It is apparent that the two spectra are different from those for the thinner Si sublayer samples (Fig. 1): The onset and the maximum of the PA band shift to lower energies and a second PA onset is seen near 1.2 eV. The PM spectra shown in Fig. 3 for the two MLS are very similar. In fact, it is observed that the spectrum remains almost unchanged for d_S varying from 25 to 204 Å, rather than gradually changing toward the PA spectrum of unlayered a-Si:H. We have also examined the PA strength as a function of Si sublayer thickness and found that at 80 K

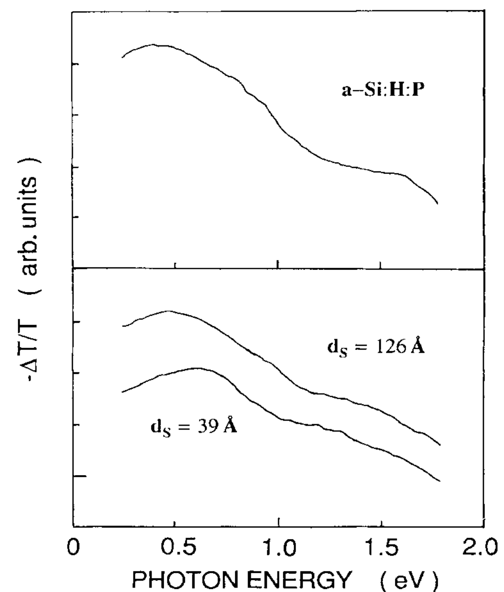

FIG. 3. PM spectra of MLS with $d_S = 39$ and 126 Å at 80 K compared with the PM spectrum of a 10^{-3} P-doped a-Si:H at 80 K.

the PA at 1.3 eV increases linearly with $1/d_S$ (for $d_S < 200$ Å) as shown in Fig. 4. This strongly indicates that the PA band is associated with the sublayer interfaces rather than with the bulk, since the number of interfaces in our samples (which have an approximately constant thickness) increases with $1/d_S$. We interpret this observation as due to the separation of carriers by the strong internal electric field in the Si sublayers[7] and their fast trapping at the interfaces. The picosecond measurements in the MLS with d_S varying from 25 to 204 Å indeed show[14] that photocarriers arrive at the interfaces in less than 10 nsec at 80 K. We therefore associate the PM spectra for MLS with $d_S > 20$ Å with interface-related states in the gap.

Figure 3 also shows the PM spectrum of an unlayered P-doped *a*-Si:H (prepared at 10^{-3} PH_3/SiH_4 gas ratio) and its resemblance to the two MLS spectra is apparent. The PM spectrum of P-doped *a*-Si:H has been associated[4,15] with charged impurities (P_4^+) near the conduction band producing a PA band near 0.3 eV, and charged dangling bond states (D^-) which introduce a second PA onset at around 1.2 eV. We note that the temperature dependence of the PA for MLS with $d_S > 20$ Å and for the P-doped *a*-Si:H are also very similar.

In light of the similarities between the PM properties of P-doped *a*-Si:H and MLS with $d_S > 20$ Å we propose that the second PA band in the MLS is due to photogenerated holes trapped at negatively charged defects. Based on the nearly linear relation between the PA strength and the number of interfaces, we identify these charged defects as doubly occupied dangling bonds (D^-) associated with the interfaces. Our interpretation is not in contradiction with the results obtained from other experiments[6] which suggest that the density of defects in *a*-Si:H/*a*-SiN_x:H MLS is one order of magnitude lower than in unlayered singly doped *a*-Si:H with comparable dark resistivity. The reason for this is that our steady state PM measurements are more sensitive to the interface defects than to the bulk since the photocarriers are driven by the internal electric fields and arrive at the interfaces shortly after photoexcitation. The different PM spectra observed for $d_S < 10$ Å (Fig. 1) indicate that different traps are involved whose origin has not been identified.

The lower-energy PA band (Fig. 3) is not as strongly dependent on $1/d_S$ as the higher-energy PA band although the trend remains. We attribute it to transitions of electrons trapped above the Fermi level into the conduction band (CB). Since the Fermi level is close to the CB throughout the Si sublayer,[6] the low-energy PA band in MLS shifts to lower energies compared to the PA in unlayered undoped *a*-Si:H.

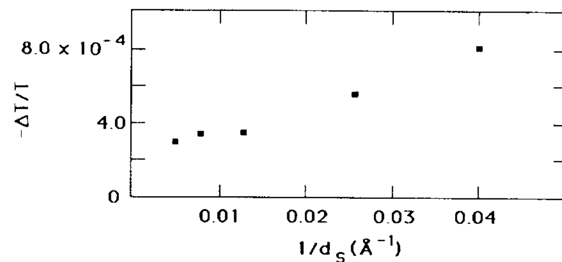

FIG. 4. PA strength at 1.3 eV for MLS with $d_S > 20$ Å as a function of $1/d_S$ at 80 K.

In conclusion, we find that the photocarrier properties in MLS are qualitatively different when the Si sublayers are thinner or thicker than 20 Å. When the Si sublayer d_S is thinner than 20 Å, they are dominated by strong disorder which results in substantial band-tail broadening. This produces a shift of the band-tail-related photoinduced absorption toward higher energies and a weaker temperature dependence compared to unlayered *a*-Si:H. For the MLS with $d_S > 20$ Å the shape of the PM spectrum changes very little with d_S while the strength of the PA above 1 eV increases with $1/d_S$, showing that it is due to interface-related defects. The PM spectrum and its weak temperature dependence for MLS with $d_S > 20$ Å are very similar to those observed in singly doped *a*-Si:H where the PM has been associated with carriers trapped at charged dangling bonds and impurities. From this comparison we identify the interface-related deep defects as charged dangling bonds.

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