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Detection of deep-lying defects in a-SiH:C alloy films

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Deep-lying defect levels in a-SiH:C films are detected by means of a light-activated charge-storage experiment. The level energies and widths are determined for a series of films, a-$Si_{1-x}H{:}C_x$, in the compositional range $0 < x < 0.35$. The defect is identified as the negatively charged Si dangling bond.

INTRODUCTION

Amorphous silicon- (a-SiH) based alloy materials have attracted wide research interest in recent years because of the prospect of tailoring optical, electronic, and structural properties for specific semiconductor applications. It is well documented that alloying with substances like C, Ge, Sn, N, and O shifts the optical gap continuously[1,2] between 1 and 3 eV and this has already been employed in a number of devices.[3] However, it has also been found that only small alloying ratios yield acceptable electronic transport properties. This is attributed to an increased density of localized states which act as deep traps or recombination centers, and inhibit the transport process by reducing the mobility lifetime product of the charge carriers.[4] Although the distribution of localized states covers all of the mobility gap, it is likely to show some structure due to (broadened) levels which correspond to particular topological features in the amorphous network. This is well documented for the case of unalloyed a-SiH where the undercoordinated Si atom, Si(3), is known to give rise to localized states in the gap. Depending on the electronic occupation of the dangling bond the Si(3) defect comprises three energetic levels, $Si(3)^+$, $Si(3)^0$, and $Si(3)^-$. These have been identified in various experiments over the last years, but despite the effort devoted to this problem, the results have remained controversial.[5,6] The published data seem to indicate a compositional dependence of the defect energy.[7] Most recently Pantelides pointed out the possibility that the overcoordinated Si atom may also act as an electronically active center.[8] In his view, the customary identification of the defect as Si(3) is inconclusive, the center should instead be associated with a fivefold coordinated Si atom.

This study is aimed at the exploration of deep states in a-SiH:C alloys. It involves a charge-storage experiment on a set of a-SiH:C films in the compositional range between 0 and ~ 35 at.% C. The experimental method allows for the probing of trap states at a depth 0.5 eV $< \varepsilon <$ 1.5 eV below the conduction-band mobility edge.[9]

The results show that deep-level carrier trapping occurs at a well-defined level throughout the compositional range. The energy of the level is found to be nearly constant with respect to the vacuum level, which indicates that it originates from a common defect in all the films. A detailed comparison with electron-spin-resonance (ESR) data further suggests that the detected level is identical to the one customarily identified as $Si(3)^-$. It will be shown that the results are of importance not only for the understanding of the system of a-SiH-based alloys but also in the ongoing discussion of defect energies in unalloyed a-SiH.

EXPERIMENTAL DETAILS

The a-SiH:C films were deposited on the grounded anode in a dc glow discharge reactor[10] using pure silane and methane as reactive gases. The total gas pressure was in the range of 0.4–0.5 mbar and the total gas flow rate was 20 sccm (cm^3/min at standard temperature and pressure) across the 4×4-in. anode. The substrate temperature was 250 °C and the cathode current density was usually adjusted to 0.5 mA/cm^2. The neutral gas composition, p_{CH_4}/p_{total}, for deposition covered a range from 10% to 80%, corresponding to $0.05 < x < 0.35$ in the a-$Si_{1-x}H{:}C_x$ films. The unalloyed a-Si:H sample was prepared in a 13.56-MHz rf-glow discharge system using a pure silane flow of 50 sccm, gas pressure 0.8 mbar, and a substrate temperature of 270 °C. For the charge-storage experiments 3-μm-thick films on 2-mm Al platelets were used. Semitransparent top contacts of 0.05 cm^2 were provided by vacuum evaporation of Al or Pd. For the ESR measurements samples from the same substrate as in the charge-storage experiment were mounted in a 9-GHz Varian ESR spectrometer in a fashion that the microwave magnetic field was aligned in plane with the metal substrate. This provided for minimum loss in quality factor ($Q \simeq 7000$) and allowed for a detection sensitivity of 10^{12} spins $mW^{-1/2}$. A detailed description of the ESR apparatus is given elsewhere.[11]

The charge-storage experiment is schematically shown in Fig. 1(a). A Hewlett-Packard voltage pulse generator (8012 B) was used to apply a bias voltage to the sample and a JK pulsed laser (model 2000) (wavelength 355 nm, pulse duration 100 ps) was used to illuminate the films through the front contact. The wavelength of the laser was chosen to ensure surface near absorption and the pulse intensity was sufficient to allow for space-charge-limited injection conditions. Photocurrents were recorded with $\sim$5-ns time resolution using a Tektronix 7812 D digitizer and integrated to determine the total amount of charge under the current transients. Figure 1(b) shows

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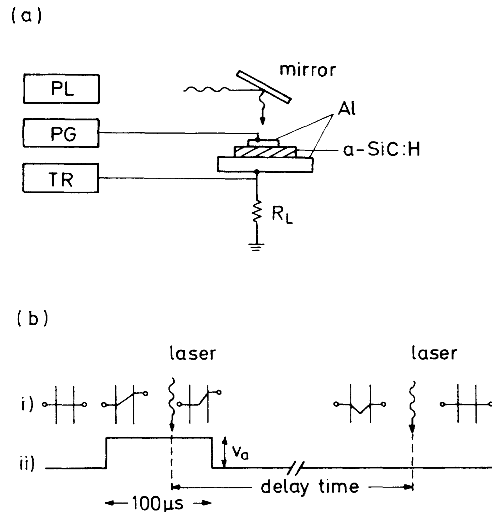

FIG. 1. (a) Schematic diagram of the experimental setup. PL: pulsed laser; PG: voltage pulse generator; TR: Transient recorder; R_L: load resistor. (b) Experimental time sequence: (i) potential distribution across the film; (ii) bias voltage and laser pulse sequence.

the experimental time sequence which involves as a first step the photogeneration of carriers in a region close to the transparent top contact and their separation in the applied electric field. Under space-charge-limited conditions[12] this process gives rise to a photocurrent transient whose amplitude is independent of the laser pulse intensity. The applied electric field is then completely collapsed in the absorption region, as illustrated in part (i) of Fig. 1(b). Some 10 μs after the laser pulse the applied potential is reduced to zero, which results in an internal potential profile which can entirely be attributed to the remaining trapped space charge. Because of the presence of deep traps in the material the modified potential distribution is sustained over considerable time periods. We have previously reported[9] retention times up to 10^4 s in a-SiH:C; here we have observed nearly no detrapping up to 10^5 s. Thermal detrapping of the carriers and subsequent drift in the space-charge field leads to a slow reduction of the space charge with time. In the second step of the experiment, occurring at a delay time t, the remainder of the trapped charge, $Q(t)$, is probed by applying another laser flash identical to the initial one. The effect of this second flash is to collapse the internal potential profile, i.e., a redistribution of the net space charge takes place which results in zero potential throughout the sample. This is just the situation prior to the experiment. The corresponding displacement current transient is of opposite polarity as initially and the integrated charge gives a direct measure of the residual trapped space charge at the delay time. Since the drift mobility of holes in the undoped a-SiH alloys is considerably smaller than that of electrons, the transients can be associated with electron drift. The dependence of $Q(t)$ on temperature and time can be modeled in terms of a trap emission process using the trap depth and distribution as fitting parameters. To obtain reproducible photocurrent transients it was necessary to neutralize any preexisting trapped space charge. This was usually achieved by illuminating the films under short-circuit conditions prior to the initial laser pulse exposure.

RESULTS AND DISCUSSION

In Fig. 2, the dependence of the stored charge Q on delay time and temperature is shown. The data have been normalized with respect to Q_0, the integrated current response to the initial laser pulse. The decay curves are not of simple exponential form but exhibit dispersion suggestive of a range of carrier-release time constants, similar as recently observed by Hepburn *et al.*[13] in a-SiH:N gated field effect transistors. The decay of $Q(t)$ can be expressed in the form

$$Q(t)=Q_0\int\frac{N(\varepsilon)}{N_t}\exp\left[\frac{-t}{\tau}\right]d\varepsilon\ , \tag{1}$$

where N_t is the total trap density, $N(\varepsilon)$ the trap density at energy ε, τ is the characteristic time constant for the emission process from energy ε in the gap to the conduction-band mobility edge, given by the activated form

$$\tau=\nu^{-1}\exp\left[\frac{\varepsilon}{k_BT}\right]\ , \tag{2}$$

with ν an attempt to escape frequency. For $N(\varepsilon)$ a Gaussian distribution was used, centered at energy ε_0 with characteristic energy $\Delta\varepsilon$,

$$N(\varepsilon)=\frac{N_t}{\sqrt{\pi}}\exp\left[-\left[\frac{\varepsilon-\varepsilon_0}{\Delta\varepsilon}\right]^2\right]\ . \tag{3}$$

The solid lines in Fig. 2 are fitted curves for the model parameters $\varepsilon_0=1.15$ eV, $\Delta\varepsilon=0.18$ eV, taking $\nu=10^{12}$ s^{-1}. The fit is sensitive to approximately 10% in the two energetic parameters.

For the purpose of comparison a fit based on $\varepsilon_0=1.18$ eV, $\Delta\varepsilon=0.18$ eV, and $\nu=10^{12}$ s^{-1} is drawn in broken lines. These parameters are seen to give a clear deviation from the experimental data, thus demonstrating the good sensitivity of the fit.

The fitting procedure was applied to the whole set of

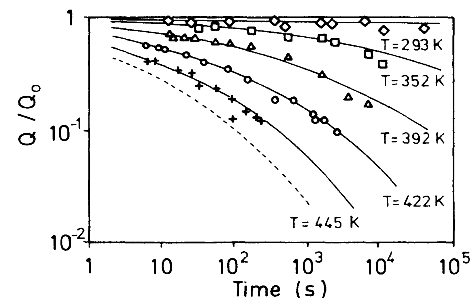

FIG. 2. Temporal decay of trapped charge $Q(t)$ at various temperatures for sample 6 of Table I. Solid lines represent the fit to the trap distribution discussed with $\varepsilon_0=1.15$ eV, $\Delta\varepsilon=0.18$ eV, $\nu=10^{12}$ s^{-1}. Dotted lines illustrate the sensitivity of the fit to a change of ε_0 to $\varepsilon_0=1.13$ eV.

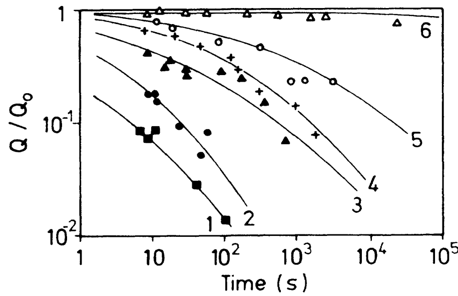

FIG. 3. Temporal decay of trapped charge $Q(t)$ for the six films of Table I. Filled symbols were used for measurements taken at $T=293$ K, open symbols correspond to $T=240$ K. Measurements at other temperatures are omitted for clarity.

samples, as indicated in Fig. 3. It is evident that the retention times decrease significantly with lowered band gap. For gas ratios $p_{CH_4}/p_{tot} < 50\%$ it was necessary to take all of the data at lower temperature for experimental convenience, since detrapping occurs within a few seconds at room temperature. This may also explain that charge-storage processes have not yet been reported in unalloyed a-SiH films. The results of the fit are summarized in Table I along with data from a standard characterization of the films. We note a continuous shift of the trap level toward energies deeper in the gap when the mobility gap E_g widens. The level is observed to broaden with increasing carbon content. The width of the level, here ranging from 0.08 to 0.12 eV, is consistent with values of 0.12 eV deduced for a-SiH by Johnson and Biegelson,[14] and the value of 0.08 ± 0.02 eV from results on a-SiH:N reported by Hepburn *et al.*[13]

In the past there have been a number of investigations concerned with the energetic shift of the mobility edges in a-SiH based alloys. Generally it is found that the widening of the gap is predominantly due to a shift of the conduction band toward higher energy. Evangilisti *et al.*[15] as well as Abeles *et al.*[16] find no discontinuity at the valence band within ~0.15-eV experimental accuracy using a-SiH/a-SiH:C heterostructures.

More recently Okayasu, Fukui, and Matsumura[17] concluded from current-voltage measurements, that the discontinuity is just about 0.1 eV at an energy gap of 2.1 eV. The results of these investigations are reproduced in Fig. 4. This allows us to put the present results for ε_0 on

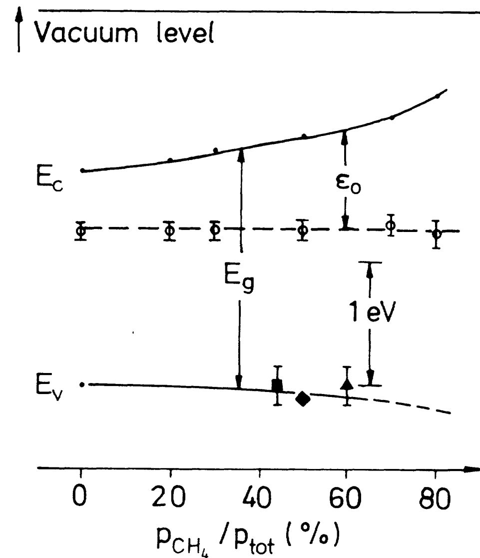

FIG. 4. Plot of mobility edges and trap-level energies with respect to the vacuum level using the data of Table I, data from Evangelisti *et al.* (■), Ref. 15; Abeles *et al.* (▲), Ref. 16; and Okayasu *et al.* (◆), Ref. 17.

an absolute energy scale with the vacuum level as a reference energy. Evidently, throughout the compositional range, ε_0 lies at the same energy with respect to the vacuum level, suggesting that the trap is associated with a single type of defect. (Beyond $E_g \simeq 2.2$ eV, there exist no reported data on the energies of the valence or conduction band, which makes a conclusive remark for sample No. 6 difficult.)

We now turn to an interpretation of this finding. Toward low carbon content ε_0 tends to a value of 0.52 eV, which coincides with the position of $Si(3)^-$ measured for unalloyed a-SiH films. As mentioned above, this value is at present subject to some controversy. To resolve this controversy Le Comber and Spear[5] have recently stressed the importance of including nonexponential relaxation behavior due to level broadening in the analysis of experimental data. If we hypothesize that the trap level is identical to the $Si(3)^-$ site, this idea is clearly confirmed in the present work, where $\Delta\varepsilon/\varepsilon_0$ is found to be in the range of 0.2 and the decay $Q(t)$ is nonexponential. The present data also support a suggestion by Kocka[7] that ε_0 is com-

TABLE I. Neutral gas ratios, p_{CH_4}/p_{tot}; optical band gap, E_g; conductivity activation energy, E_A; trap-level energy, ε_0 with respect to conduction-band mobility edge, E_c; trap-level width, $\Delta\varepsilon$; spin density, N_S; and g value for the set of samples.

Sample No.	p_{CH_4}/p_{tot}	E_g (eV)	E_A (eV)	ε_0 (eV)	$\Delta\varepsilon$ (eV)	N_s (10^{18} cm^{-3})	g value
1	0	1.72	0.76	0.52	0.09	0.1	2.0060 ± 0.0015
2	0.1	1.78	0.85	0.58	0.07	0.86	2.0058 ± 0.0015
3	0.3	1.90	0.95	0.62	0.10	2.7	2.0060 ± 0.0015
4	0.5	2.05	1.1	0.8	0.10	6.4	2.0055 ± 0.0015
5	0.7	2.31	1.3	0.85	0.12	16	2.0060 ± 0.0015
6	0.8	2.48	1.4	1.15	0.18	13	2.004 ± 0.0015

position dependent and support his conclusion that in undoped a-SiH ε_0 is found to be close to 0.5 eV. This hypothesis is further consistent with the results of Ref. 13, where the charge-storage center in a-SiH:N is identified as the $Si(3)^-$ dangling bond with an energy of 0.8 eV below the conduction-band mobility edge. It should be noted, however, that the present work, since it indicates a continuous shift in ε_0 with alloy content, suggests that the value of ε_0 in alloyed films is not identical with the dangling-bond energy in unalloyed films, at variance with Ref. 13.

The hypothesis that the trap emission process originates from the $Si(3)^-$ site implies that trapping occurs at the neutral dangling bond, $Si(3)^0$, which can independently be probed by ESR experiments. We have therefore measured the signal strength and g factor for the set of films. As shown in the table, the g value remains approximately constant around 2.0055 ± 0.0015, the value known to be characteristic for $Si(3)^0$ in a-SiH. Only in the most heavily carbonated film it decreases to 2.004 ± 0.0015, indicating an admixture of C dangling bonds with $g = 2.003$.[18] The resonance due to undercoordinated C is usually not resolved in ESR measurements, due to the small difference in g value and the comparatively large width of the resonance line.[18] The observed constancy in g value indicates that $Si(3)^0$ formation dominates over the formation of C dangling bonds in this compositional range. This behavior is explained by the fact that the C–H bond is stronger than Si—H bond, which leads to the preferential attachment[19] of H to C in these alloys. Thus, with increasing carbon content and limited H concentration more Si dangling bonds are expected to remain unterminated and this in turn gives rise to the increased spin density which reaches 10^{19} cm^{-3} in the C-rich specimens. Unfortunately, the charge-storage experiment does not lend itself toward a direct comparison with the ESR data. This is due to the fact that the ESR measurement probes the neutral $Si(3)^0$ site while the emission observed in charge storage originates from the charged $Si(3)^-$ defect, which is likely to have a different energy. Further, since the charging process occurs under space charge limited conditions, $Q(t)$ contains no quantitative information on the trap density, other than that N_t is sufficient to collapse all of the applied field. Nevertheless, it is believed that the presented evidence strongly suggests the correctness of this hypothesis.

In conclusion, I have reported the detection of a well-defined deep trap level throughout a wide compositional range of a-SiH:C alloy films. The trap acts as a charge-storage center for electrons and can be probed using a light-activated charging experiment. The width of the level was found to increase with carbon content while its energy remains constant with respect to the vacuum level. A comparison with the $Si(3)^-$ defect energy in unalloyed undoped a-SiH and independent ESR experiments are in agreement with the idea that the detected level is the $Si(3)^-$ dangling bond.

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