Mid-gap states measurements of low-level boron-doped a-Si:H films

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Abstract

Previous measurements of the effects of low-level boron-doping on a-Si:H thin films indicated that the conductivity decreased as a function of boron concentration. This effect was reinvestigated in this work by measuring the leakage current of stacked p–i–n diodes as a function of boron concentration. The supporting measurements employed films deposited onto insulating substrates. The diodes were also examined by a charge recovery measurement to measure the dangling-bond density of states (DOS) near between 0.7 and 1.0 eV from the conduction band edge. The spectrum shows a broad band with a peak at 0.88 eV, which increases as a function of the boron concentration, but does not shift with respect to energy. The dangling-bond density increase is proportional to the B_2H_6/SiH_4 gas flow ratio, but not linear with respect to boron concentration in the film. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

It is well known that the electrical properties of a-Si:H change upon additions of boron [1–3]. Spear and Le Comber [1] showed that concentrations as low as 10 ppm can decrease the room temperature conductivity by as much as 3 orders of magnitude, while Yang et al. [2] showed that the ambipolar diffusion length can increase by 10 times in the 0.1 ppm range. Addition of dopant has been shown to increase the total density of defect states as measured by various methods [4]. The primary point of this paper is to determine the energy at which these new defects appear as boron is introduced into a-Si:H and show how these defects affect the leakage current. The method of mapping the defects within the gap was made by a technique called transient depletion current (TDC).

2. Experimental

The samples grown for this experiment were p–i–n stacks with conductive contacts grown by PECVD and in situ doping of the n and p layers. The i-layer was 900 nm a-Si:H doped using 100 ppm B_2H_6 in H_2. In this paper the flow rate ratio of B_2H_6 to SiH_4 is used to specify the doping level. The total area of the stack was about 4.1×10^{-2} cm^2. SIMS measurements of the incorporated boron concentration were made with a 9×10^{15} cm^{-3} detection limit.

Density of states (DOS) measurements were made using the TDC technique. Briefly, the technique uses a charge recovery technique to separate steady-state generated charge from transient charge. When applying a reverse bias to the diode stack the measured charge comes from the equation,

$$Q(t) = Q_D + Q_L + C_g V, \qquad (1)$$

where, $Q(t)$ is the total charge after a certain hold time under reversed bias, Q_D the space-charge

within the depletion region, Q_L the steady-state leakage through the diode and C_gV is the charge from the geometric capacitance. Charge associated with the Q_D space-charge region is from active electrical defects within the band gap and is assumed to exhibit a thermal emission rate:

$$R_e = v_e \exp\left(\frac{-(E_c - E)}{kT}\right), \qquad (2)$$

where v_e is the electron attempt frequency.

Fig. 1 shows a schematic diagram of biasing scans made for different bias hold times and illustrates how to interpret the data to extract Q_D. For a given scan, the diode is initially short-circuited, until delay time is equal to zero, whereupon it is changed to the reverse bias voltage. The initial linear increase in charge is related to the geometric capacitance of the diode based on the thickness of the space-charge region and the dielectric constant of the diode material. After a given delay, the bias is reset to zero. The geometric capacitance can either be estimated from the dimensions of the diode, or by measuring the slope of the linear portion of the curve at the application of the reverse bias and Q_L is the amount of unrecovered charge when resetting the bias to zero.

Increasing the length of time in which the film is held under reverse bias, allows charge collection from energetically deeper states from the band edge. Assuming a fixed jump frequency, it is possible to relate bias time to energy depth as a
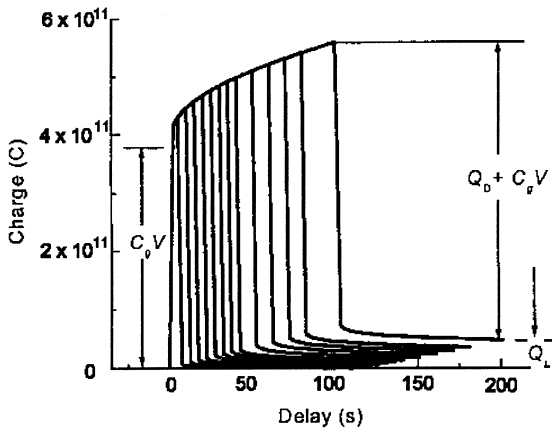

Fig. 1. Schematic diagram of data collection [3].

function of thermal emission. By numerically differentiating the transient charge as a function of elapsed time, it is then possible to estimate the DOS using the following approximation:

$$g(E_c - E) \approx \frac{j_D(t)\,t}{(kT)\,qL}, \qquad (3)$$

where $E_c - E$ is the depth from the conduction band edge, j_D the current density collected from the depletion region, t the hold time at reverse bias and L is the mean distance of deep levels within the depleted layer to the collection layer.

The TDC and reverse bias leakage current experiments used a electrometer (Keithley 6517A) with timing and data collection supplied by a PC (HPIB-equipped), connected to the sample via a probe station. TDC data was collected at 2.5 V reverse bias.

3. Results

Fig. 2 shows the DOS energy spectrum from the conduction band edge derived from TDC measurements. The intrinsic material has an asymmetric band that appears to be two peaks, a larger one at 0.88 ± 0.02 eV and one at 0.83 ± 0.02 (?) eV. As boron is added to the film, the 0.88 eV peak appears to increase, while the 0.83 eV peak appears to blend into the side of the 0.88 eV peak. The measurements show that the DOS spectrum increases as a function of boron-doping, however there appears to be no shift in the position or shape of the DOS.

Fig. 3 is a plot of the total number of states over the energy range measured as a function of the gas flow concentration of B_2H_6 and is either sublinear or bimodal. It has a bimodal linear relation, with a slope of 5×10^{-3} below 5×10^{18} boron cm^{-3} and the intercept at the integrated DOS for undoped a-Si:H. Above 5×10^{18} boron cm^{-3}, the slope is less than 3×10^{-4}. Fig. 4 shows the integrated DOS over the same energy range but as a function of the B_2H_6/SiH_4 ratio. One immediate observation of the integrated DOS Figs. 3 and 4 is that they differ between gas phase and solid phase boron concentration. Such a difference occurs with
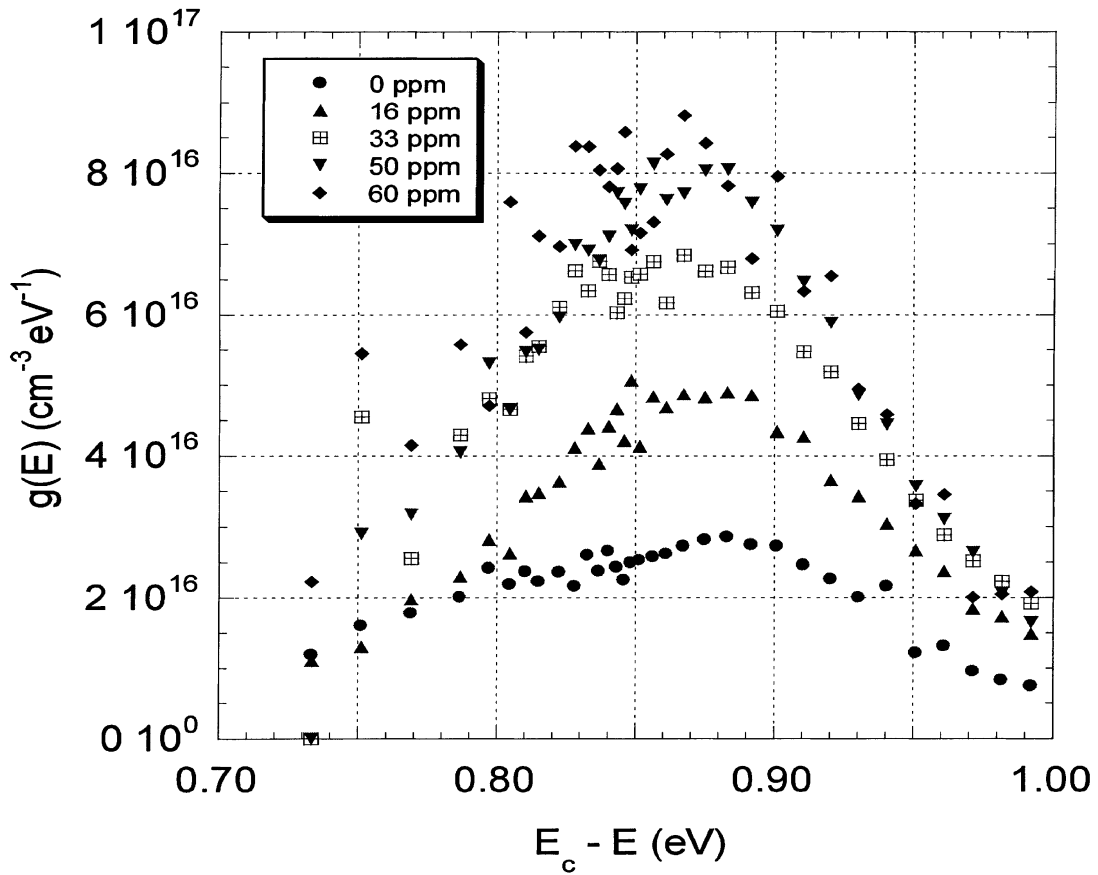
Fig. 2. The DOS energy spectrum with respect to the B_2H_6/SiH_4 gas flow ratio, as derived from the TDC technique.
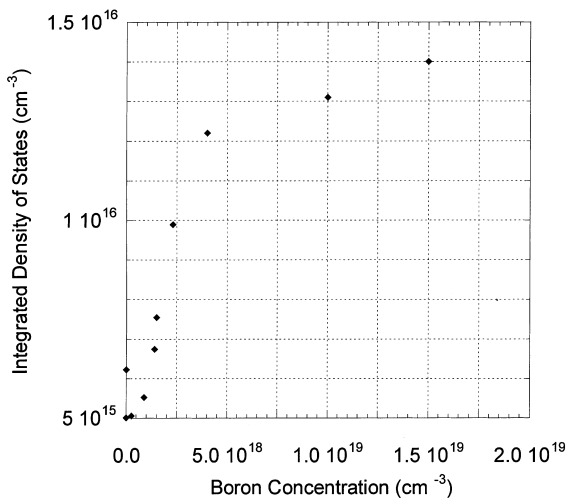

Fig. 3. The integrated DOS near the mid-gap as a function of the boron concentration in a-Si:H.

changes in doping efficiency too, but the functionality is different [5].

Fig. 5 shows the incorporated boron concentration as a function of the B_2H_6 gas stream concentration and that it is sublinear with an exponent about 0.8, over more than four orders of magnitude. Correlating the data in Figs. 3 and 5 shows that the ratio of introduced defects as a function of incorporated boron is about 5×10^{-3}.

4. Discussion

The DOS spectrum shown in Fig. 2 has a shape that we expect and is of a similar shape to n-type material measured by DLTS, though the energies for the films shown here are about 0.1 eV further from the conduction band [6,7]. Based on the fact
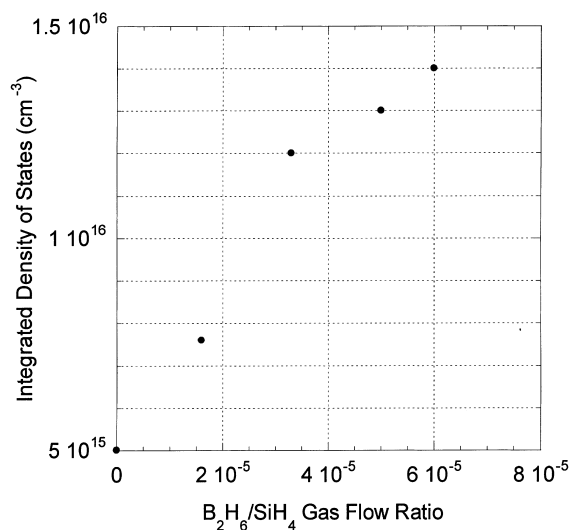
Fig. 4. The integrated DOS as a function of B_2H_6:SiH_4 ratio of the incoming gas stream.
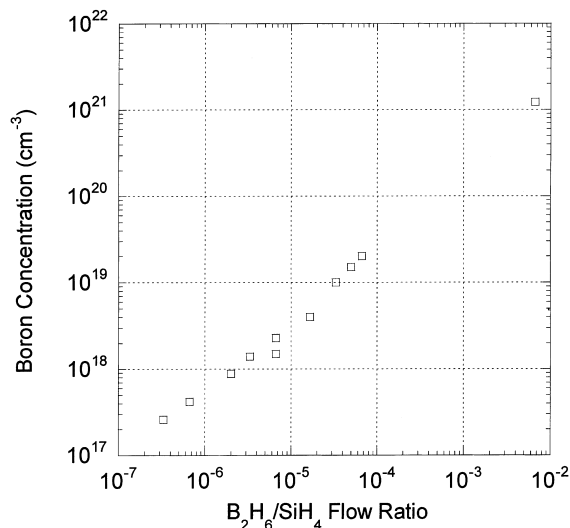

Fig. 5. Incorporated boron in a-Si:H as a function of B_2H_6 in the gas stream.

that there is neither a change in shape nor position of the peak we suggest that the addition of boron does not affect the electrical properties of the dangling bonds.

The bimodal effect of the dangling-bond density with respect to solid phase boron concentration may be evidence of a saturation in the production of dangling bonds due to the presence of boron. In other words, 5×10^{18} cm^{-3} boron is a critical concentration above which the mean distance of boron atoms (<3.6 nm) is such that the a-Si:H network is underconstrained. This condition would allow for additional disorder without producing as many dangling bonds.

The integrated number of deep-level defects is about 10 times less than the number of defects found in a-Si:H with similar concentrations of phosphorus [4]. One explanation is that boron has a greater likelihood of being incorporated into the a-Si network without creating coordination defects than does phosphorus or other column V dopants.

Another possible explanation for the different relation of deep-level state creation and boron content is that the boron incorporation process and dangling-bond creation process are simply two outcomes for the addition of B_2H_6 to the gas stream, but that they are independent of one another. The linear relation of Fig. 4 implies that defect density is limited by B_2H_6 concentration in the gas stream. This hypothesis is further supported by the observation that B_2H_6 in the gas phase affects a-Si:H growth kinetics.

5. Summary

The TDC technique has been demonstrated to detect deep-level defects and that as boron is added to a-Si:H, the concentration of the deep-level states increase, but the shape and energy of the defects within the gap remains constant. Furthermore, the increase in the deep-level DOS is proportional to the B_2H_6/SiH_4 ratio in the gas stream implying that it is the presence of B_2H_6 and not necessarily the presence of boron in a-Si:H that controls dangling-bond defect creation.

Acknowledgements

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