

ESR IN HEAVILY DOPED CVD AMORPHOUS SILICON FILMS

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The dependences of ESR signals on measurement temperature and doping ratio are investigated for CVD a-Si. A signal with $g=2.0055$ disappears with P or B doping, and a signal with $g=2.0043$ and one with $g\sim 2.011$ appear in heavily P and B doped samples, respectively. These signals are proposed to arise from negative and positive charge states of weak bonds in a-Si, respectively. The dependences of the spin densities of them on doping and measurement temperature have been explained by this model.

I. Introduction

In chemically vapor-deposited amorphous Si films (CVD a-Si), a higher density of defects has been found than in glow discharge amorphous Si films (GD a-Si), and the density of these defects decreases with P [1,2] or B [3] doping. The ESR signal with $g=2.0055$ observed for samples deposited at low doping ratio disappears with the shift of the Fermi level E_F from near the middle of the gap to 0.15 eV below the conduction band edge E_C by P doping [1] or to 0.27 eV above the valence band edge E_V by B doping [4]. New signals with $g=2.0043$ for the P doped sample and with $g\sim 2.011$ for the B doped sample then appear. These signals for heavily P and B doped samples have first been observed by the present authors [2,5] and Voget-Grote [6], respectively. Similar signals to these two signals are observed by a photo-induced ESR in GD a-Si [7-9]. In the present paper, the measurement temperature dependences of the new ESR signals and the thermoelectric power S are measured, and the doping effects on the ESR and a possible model for paramagnetic centers in heavily doped samples are discussed.

II. Experimental

CVD a-Si samples were grown on quartz substrates by the thermal decomposition of $\text{SiH}_4\text{-PH}_3$ or $\text{SiH}_4\text{-B}_2\text{H}_6$ mixtures at a deposition temperature T_d of 500, 550 or 650 °C. The ESR apparatus is an X-band spectrometer with magnetic field modulation frequency 100 kHz, and the signal was observed between room and liquid nitrogen temperatures. In case of P doped a-Si, it has been found that the spin density of the signal due to conduction electrons observed for a sample crystallized by annealing at 1050 °C agrees with the density of P atoms estimated from the gas ratio $N_{\text{PH}_3}/N_{\text{SiH}_4}$ using the atomic density of crystalline Si [10,11]. For measurements of S , samples with Au electrodes separated by 1 mm were used.

III. Results

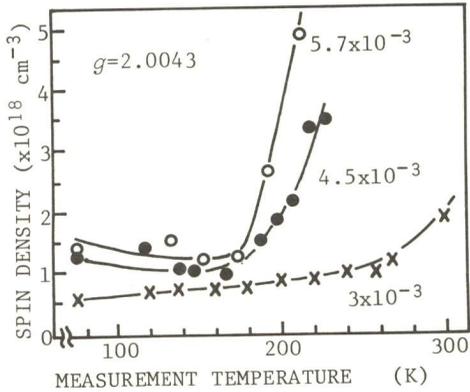


Fig.(1) Dependence of the spin density for the signal with $g=2.0043$ on measurement temperature observed for P doped CVD a-Si deposited with the doping ratios of 3×10^{-3} , 4.5×10^{-3} and 5.7×10^{-3} at $T_d=650^\circ\text{C}$

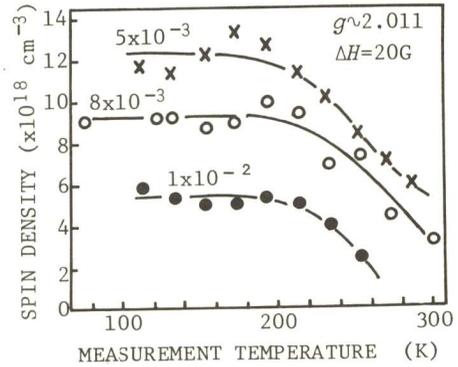


Fig.(2) Dependence of the spin density for the signal with $\Delta H \sim 20\text{G}$ at $g \sim 2.011$ on measurement temperature observed for B doped CVD a-Si deposited with the doping ratios of 5×10^{-3} , 8×10^{-3} and 1×10^{-2} at 550, 500 and 550°C , respectively

The ESR signal with $g=2.0055$ disappears at doping ratio above 3×10^{-3} for the P doped sample and above 5×10^{-3} for the B doped sample, and an ESR signal with a symmetric Lorentzian shape at $g=2.0043$ for the former and one at $g \sim 2.011$ for the latter appear. Figure (1) shows the dependence of the spin density N_S on measurement temperature for the P doped samples deposited with doping ratios of 3×10^{-3} , 4.5×10^{-3} and 5.7×10^{-3} . N_S is found to increase with increasing temperature above 180 K, and an increase of N_S can also be seen by increasing doping ratio. The linewidth ΔH increases with increasing of N_S [5]. The g -value is independent of measurement temperature and doping ratio. Figure (2) shows the dependence of N_S on measurement temperature for the B doped samples deposited at doping ratios of 5×10^{-3} , 8×10^{-3} and 1×10^{-2} . N_S rapidly decreases with increasing temperature above 220 K or doping ratio from 5×10^{-3} to 1×10^{-2} , showing the dependence reverse to that for the P doped sample shown in Fig.(1). The g -value and $\Delta H (\sim 20\text{G})$ are independent of measurement temperature and doping ratio. The value of N_S for the B doped sample also depends on annealing temperature [5]. N_S increases with annealing up to 700°C and then decreases at above that temperature.

IV. Discussion

Similar signals to the two signals observed for heavily doped samples have been observed by a photo-induced ESR in GD a-Si [7-9]. Street and Biegelsen [9], recently, have carried out the photo-induced ESR measurement at 30 K for undoped GD a-Si, and observed two signals similar to the present ESR signals; a narrow signal with $\Delta H \sim 6\text{G}$ at $g \sim 2.004$ and a broad signal with $\Delta H \sim 20\text{G}$ at $g \sim 2.013$. These signals are suggested to be due to conduction band tail electrons and valence band tail holes, respectively.

As a possible model for these paramagnetic centers, positive and negative charge states of a weak bond suggested by Kaplan [8] should be worth deliberation. The energy levels for these states are shown in Fig.(3). He has assumed the narrow and broad signals observed by a

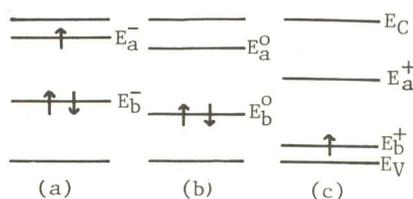


Fig.(3) Different charge states of a weak bond. Figures (a), (b) and (c) show the negative, neutral and positive charge states, respectively. E_a and E_b are the antibonding and bonding levels, respectively

signals are due to the negative and positive charge states, respectively. The identification in the present suggestion is reverse to that by Kaplan, and the question arises why these g -values are different from those for the divacancy in crystalline Si. However the question could be explained as follows by assuming that two dangling bonds forming a weak bond in a-Si are more strongly coupled than in the divacancy. The sign of the g -shift is determined by whether the level with an unpaired spin acts as electron or hole excitation level (the g -shift for the former is negative and that for the latter is positive) [13]. If $E_a - E_b$ shown in Fig.(3) is sufficiently large for a weak bond in a-Si, E_a^- and E_b^+ are expected to act as electron excitation level to E_C and hole excitation level to E_V , respectively. The cases (a) and (c) shown in Fig.(3) are realized when E_F shifts across E_a^- toward E_C and across E_b^+ toward E_V , respectively, and then ESR signals due to unpaired electrons in these levels appear. When E_F further shifts upward or downward, doubly negative or doubly positive charge state will result and these signals will disappear. Accordingly the values of N_S for signals from E_a^- and E_b^+ are expected to have a maximum at a certain position of E_F above E_a^- and below E_b^+ , respectively.

If the positions of E_F in P and B doped samples shift upward and downward with increasing temperature, respectively, the increase of N_S with increasing temperature or doping ratio for the signals with $g=2.0043$ could be explained by the increase of the density of unpaired electrons in E_a^- due to an upward shift of E_F across E_a^- toward the position resulting in the maximum N_S . On the other hand, the decrease of N_S with increasing temperature or doping ratio for the signal with $g \sim 2.011$ could be explained by the decrease of the density of unpaired electrons in E_b^+ due to a downward shift of E_F across the position resulting in the maximum N_S .

The temperature dependences of $E_C - E_F$ and $E_F - E_V$ in a linear approximation for n and p-type samples, respectively, are defined by

$$(E_C - E_F)_T = (E_C - E_F)_0 - \delta_C T, \quad (1)$$

$$\text{and } (E_F - E_V)_T = (E_F - E_V)_0 - \delta_V T. \quad (2)$$

The information for the coefficient δ_C or δ_V can be obtained from thermoelectric power S given by

$$S_C = -\frac{k}{e} \frac{(E_C - E_F)_0}{kT} + S_{0C}, \quad S_{0C} = -\frac{k}{e} \left(A_C - \frac{\delta_C}{k} \right) \text{ for n-type}, \quad (3)$$

$$\text{and } S_V = \frac{k}{e} \frac{(E_F - E_V)_0}{kT} + S_{0V}, \quad S_{0V} = \frac{k}{e} \left(A_V - \frac{\delta_V}{k} \right) \text{ for p-type}. \quad (4)$$

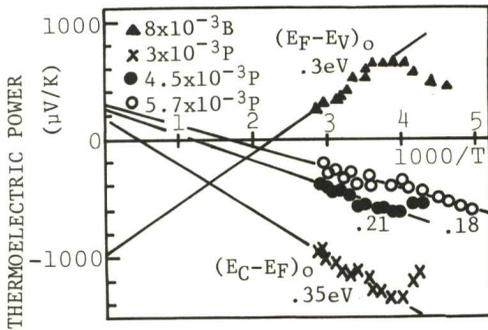


Fig.(4) Dependence of thermoelectric power S on measurement temperature for B doped sample deposited with the doping ratio of 8×10^{-3} and P doped samples deposited with the doping ratios of 3×10^{-3} , 4.5×10^{-3} and 5.7×10^{-3}

Here, A_C and A_V are determined by the energy dependence of the conductivity above E_C and below E_V , respectively. For heavily P doped GD a-Si, A_C is estimated to lie between 3 and 4 [14]. The temperature dependence of S for heavily P and B doped CVD a-Si films is shown in Fig.(4). From this result, the sign of δ_C and δ_V would have to be positive which is reverse to that for P doped GD a-Si [14], because the signs of S_{OC} and S_{OV} are positive and negative, respectively. Accordingly, the upward and downward shifts of E_F with increasing temperature for P and B doped samples, respectively, assumed for explaining the temperature dependence of N_S should be justified. From these results, the positions of E_a^- and E_b^+ are

considered to be centered at around 0.2 eV below E_C and 0.3 eV above E_V , respectively.

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