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The effect of passivation of boron dopants by hydrogen in nano-crystalline and micro-crystalline silicon films

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Abstract. It is well known that the value of room-temperature conductivity σ_{RT} of boron-doped silicon films is one order lower than that of phosphorus-doped silicon films, when they are deposited in an identical plasma-enhanced chemical vapour deposition system. We use surface acoustic wave and secondary-ion mass spectrometry techniques to measure the concentration of total and electrically active boron atoms. It is shown that only 0.7% of the total amount of incorporated boron is electrically active. This is evidence that hydrogen atoms can passivate substitutional B–Si bonds by forming the neutral B–H–Si complex. By irradiating the boron-doped samples with a low-energy electron beam, the neutral B–H–Si complex converts into electrically active B–Si bonds and the conductivity can be increased by about one order of magnitude, up to the same level as that of phosphorus-doped samples.

1. Introduction

In the last decade, Sah *et al* [1] and Pankove [2] have suggested that dangling bonds in boron-doped crystalline silicon (c-Si) samples annealed in an atomic hydrogen atmosphere may be passivated by hydrogen atoms. In this case, the substitutional boron atoms will be neutralized and the resistance of the samples will be increased. Usually, the acceptors in silicon are trivalent atoms at substitutional sites and thus three electrons of an acceptor can bond only three of the four surrounding Si atoms, as shown in figure 1(*a*). Therefore, one of the surrounding Si atoms might form a dangling bond, which produces a hole by capturing a valence band electron. If a hydrogen atom moves towards this dangling bond, it may produce a B–H complex and compensate the dangling bond; thus the B–H complex would be neutralized. As a result, it would not obtain an electron from the valence band, as shown in figure 1(*b*). Another model of H-passivated boron dopants is shown in figure 1(*c*), in which the H is situated at the bond-centre site along an axis between an acceptor atom and an adjacent Si atom. Direct evidence for these models is the resistance increase of boron-doped samples.

Highly hydrogen-diluted silane has been employed as a reactant gas in a conventional plasma-enhanced chemical vapour deposition reactant system (PECVD) for depositing undoped, boron-doped and phosphorus-doped hydrogenated microcrystalline silicon films (μc-Si:H). The substrate temperature T_s is in the range 280–300 °C. Experimental results have shown that the maximum room-temperature conductivity of phosphorus-doped μc-Si:H

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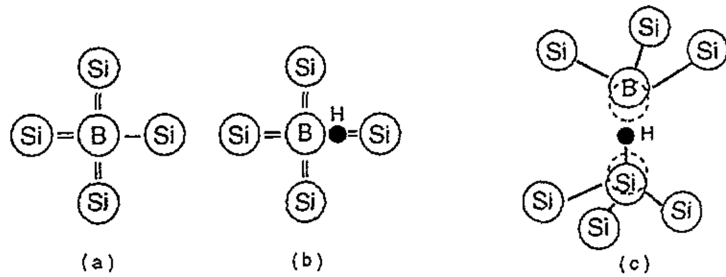

Figure 1. A substitutional boron atom in a silicon film: (*a*) a dangling bond; (*b*) after neutralization by a hydrogen atom; (*c*) a model of the hydrogen–boron complex in μc-Si:H films.

samples can reach 10 Ω^{-1} cm^{-1}. On the other hand, the conductivity value for boron-doped μc-Si:H samples deposited in an identical deposition system can only reach 1 Ω^{-1} cm^{-1} [3, 4], which is one order lower than that of phosphorus-doped samples.

For polycrystalline silicon films deposited in a low-pressure chemical vapour deposition system (LPCVD) at T_s of 600–800 °C, the highest room-temperature conductivity of both boron-doped and phosphorus-doped silicon films can reach the level of 10^2 Ω^{-1} cm^{-1}, simultaneously [5]. As verified by hydrogen release experiments, the hydrogen content in the silicon films disappears on annealing at temperatures $T_s > 600$ °C. A comparison between boron-doped μc-Si:H films and LPCVD polycrystalline silicon films leads us to believe that the passivation effect of hydrogen atoms could play an important role in the lowered conductivity of boron-doped μc-Si:H films deposited by PECVD. In this work, an electron beam irradiation treatment has been applied to boron-doped and phosphorus-doped μc-Si:H films. Interestingly, depassivation behaviour has been observed for boron-doped μc-Si:H films. The result of this treatment raises the conductivity of boron-doped samples by about one order magnitude. This is direct evidence for the model in figure 1.

2. Sample preparation

We use highly hydrogen-diluted silane as a reactant gas. The SiH_4-to-SiH_4+H_2 ratio C is selected to be in the range of 0.5–10%. The substrate temperature T_s is 280–300 °C, the RF power (13.65 MHz) is 50–115 W, the separation distance between two parallel electrodes in the deposition chamber is 1.5–2.0 cm and the pre-vacuum of the chamber is about 10^{-3} Torr.

For undoped samples prepared at a T_s of 280 °C and a RF power of 85 W, because of the etching effect of the [H] radicals in the plasma, the deposition process can remove the weak Si–Si and Si–H bonds at the surface of growing films and promote crystallization of the film. The degree of crystallization of growing films can be controlled by selecting the ratio of C, from which the etching ability of the [H] radicals in the plasma is dominant. Thus, the room-temperature conductivity of the growing films changes from 10^{-8} Ω^{-1} cm^{-1} (hydrogenated amorphous silicon (a-Si:H)) to 10^{-2} Ω^{-1} cm^{-1} (hydrogenated nanocrystalline silicon (nc-Si:H)), when the deposition rate drops from 12 to 15 Å s^{-1}. The average crystallite size d of μc-Si:H films has been evaluated as 5–6 nm from the Scherrer formula using the FWHM of the (111) peak of x-ray diffraction patterns. Some of these films consist of nc-Si:H [6, 7].

On the other hand, for the doped samples prepared with a PH_3-to-SiH_4 ratio of 1.2%, a B_2H_6-to-SiH_4 ratio of 2.0% and a SiH_4-to-SiH_4+H_2 ratio C of 0.5% with an applied

RF power of 110 W, the maximum room-temperature conductivity is 14 Ω^{-1} cm^{-1} for N^+-type samples (phosphorus doped), 1.5 Ω^{-1} cm^{-1} for P^+-type samples (boron doped), and 1.0×10^{-2} Ω^{-1} cm^{-1} for undoped samples. Highly conductive N^+ and P^+ layers have been fabricated for the emitter regions of bipolar transistors; the value of the common emitter direct current gain h_{fE} is 20 for N^+–P–N devices and 5 for P^+–P–N devices [5]. The temperature coefficient of h_{fE} for these transistors is less than that of conventional transistors and, therefore, the thermal stability of these transistors is better.

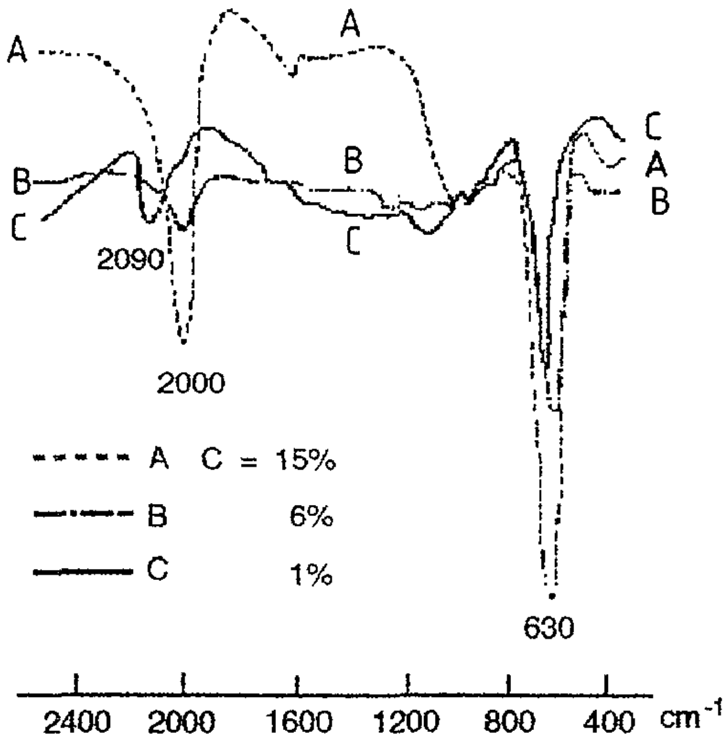

Figure 2. The IR spectrum of undoped silicon films.

3. The analysis of infrared spectrum of hydrogenated silicon films

Figure 2 gives the infrared (IR) spectrum for the deposited samples. Curves A, B and C in figure 2 represent the various samples deposited at different ratios of diluted silane, namely $C = 15\%$, 6% and 1%, respectively. The TEM diffraction patterns reveal that curve A is an a-Si:H film, curve C is a nc-Si:H film and curve B is at an intermediate stage, namely a μc-Si:H film. For the a-Si:H film, strong absorption appears owing to Si:H bond stretching at 2000 cm^{-1}. For the μc-Si:H film the absorption peak is still at 2000 cm^{-1}, but the intensity of the peak is weaker and the width of the peak wider. For the nc-Si:H film, with nanophase morphology, the absorption peak on curve C has apparently shifted from 2000 to 2090 cm^{-1}. The IR absorption peak at 2090 cm^{-1} is attributed mainly to Si–H_2 bondings [5].

Figure 3 shows the IR spectra of three nc-Si:H samples, where curves A, B and C denote undoped, phosphorus-doped and boron-doped samples, respectively. It shows that there is only a 2090 cm^{-1} $Si–H_2$ absorption peak for undoped and phosphorus-doped samples, similar to curve C in figure 2. It is interesting to note that not only is there a peak at 2090 cm^{-1} but also a Si–H bond stretching absorption peak appears at 1995 cm^{-1} for the boron-doped sample. We believe that this is important evidence of the existence of neutral B–H–Si complexes in boron-doped μc-Si:H and nc-Si:H films as shown in figure 1. This explains why the conductivity of hydrogenated boron-doped silicon films is one order less than that of hydrogenated phosphorus-doped silicon films.

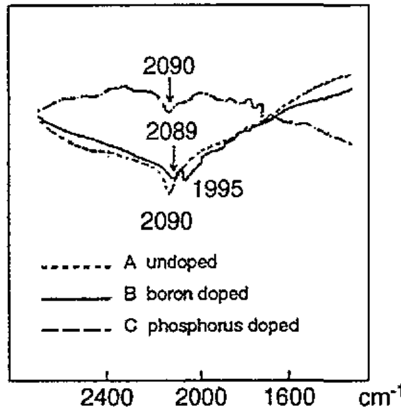

Figure 3. The IR spectrum of doped μc-Si:H films.

4. The ratio of electrically active to non-active boron in μc-Si:H films

The travelling-wave method offers an alternative to the time-of-flight technique for measuring drift mobilities. The measured drift mobilities are then sensitive to the material properties at the surface, the so-called surface acoustic wave (SAW) method [8]. Alder *et al* [9] have suggested that the open-circuit voltage V across the sample to be measured can be written as

$$V = RI = \mu E_{ac}^2 L/v$$

where E_{ac} is the RMS electric field, L is the interaction length and v the phase velocity. So, we may obtain the mobility μ for the sample.

We measured the conductivity $\sigma_{RT} = 1.8 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ of a B-doped sample using the SAW technique in the dark at room temperature; we then obtained the drift hole mobility of the sample as $\mu_h = 7.63 \times 10^{-3}\ cm^2\ V^{-1}\ s^{-1}$. Therefore, we can calculate the carrier concentration, e.g. the electrically active boron atoms, from the formula $\sigma = N_A e \mu_h$, using $N_A = 1.4 \times 10^{19}\ cm^{-3}$. On the other hand, the total boron concentration in the boron-doped samples is measured as $N_B = 2.0 \times 10^{21}\ cm^{-3}$ by secondary-ion mass spectrometry (SIMS) using a Rigaku IMA-2A spectrometer. This indicates that the ratio of electrically active boron atoms to the total amount of boron is $N_A/N_B = 0.7\%$. This result suggests that most of the substitutional boron atoms in boron-doped samples are neutralized by hydrogen.

It is believed that the low-energy electron beam irradiation treatment with appropriate irradiation conditions can cause the B–H–Si complex to become dehydrogenated, after which the substitutional boron atoms revert to their acceptor behaviour.

5. Electron beam irradiation experiment on hydrogenated silicon films

In order to find further evidence for the existence of non-electrically active boron atoms in the network, we subjected the hydrogenated boron-doped and phosphorus-doped silicon films to electron beam irradiation.

The electron beam irradiation system has a high-vacuum reaction chamber, in which there are two plates made of aluminium with a diameter of 40 mm. The upper plate is an electron gun and the lower plate is a sample holder. The electrodes are connected with a high-voltage DC source. Helium gas is introduced into the chamber and a glow discharge of helium gas fills the chamber. The cathode is bombarded by positive ions from the plasma and the secondary electrons emitted are attributed to the target. Thus, a continuously regulated electron beam was obtained over the energy range 0–8 keV with an electron beam current of up to 1 A. The electron beam irradiation is uniform over an area of diameter 40 mm.

There are three major parameters of the electron beam irradiation: the current density of the beam, the beam voltage (i.e. the electron energy) and the irradiation time. These parameters have been measured and the results are shown in figures 4, 5 and 6, respectively. We choose the values of the irradiation parameters as 21 mA cm^{-2}, 3 keV and 10 s, respectively, in the present work.

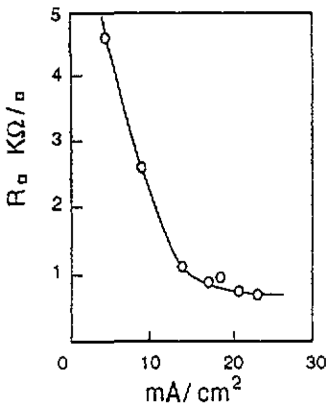

Figure 4. The variation in the $R_\square$-values of the film with the current density of electron beam irradiation.

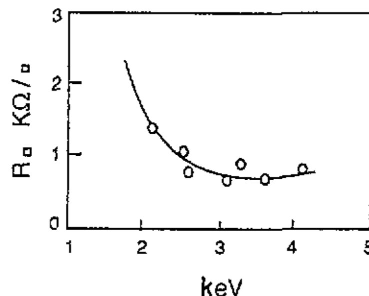

Figure 5. The variation in the $R_\square$-values of the film with the electron energy of electron beam irradiation.

The conductivities of various silicon films after the electron beam irradiation treatment are as follows: phosphorus doped films, $\sigma_{RT}^{N^+} = 14 \rightarrow 17\ \Omega^{-1}\ \text{cm}^{-1}$; boron-doped films, $\sigma_{RT}^{P^+} = 1.5 \rightarrow 20\ \Omega^{-1}\ \text{cm}^{-1}$. This shows that when the phosphorus-doped samples are subjected to the irradiation treatment, the room-temperature conductivity does not increase much. However, the room-temperature conductivity of boron-doped samples after irradiation treatment varies from 1.5 to 20 Ω^{-1} cm^{-1}, over one order of magnitude. It is believed that electron beam irradiation causes the dehydrogenation of boron atoms from the non-electrically active states into the electrically active acceptor states.

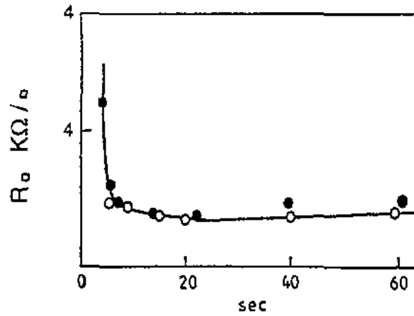

Figure 6. The variation in the $R_\square$-values of the film with the annealing time of electron beam irradiation.

6. Conclusions

In this paper, the acceptor behaviour of boron atoms in μc-Si:H films was measured by IR spectroscopy, SIMS and the SAW method. The experimental results show that most of the substitutional boron atoms should be compensated by hydrogen atoms in the films and are converted into neutral B–H–Si complexes. This is the main reason why the room-temperature conductivities of boron-doped silicon films are lower than those of phosphorus-doped silicon films. Low-energy electron beam irradiation technology has been used to treat the boron- and phosphorus-doped silicon samples. Electron beam irradiation can convert the neutral B–H–Si complexes in boron-doped silicon films into electrically active B–Si bonds and the conductivities of boron-doped samples can then be increased to the same magnitude as the conductivities of phosphorus-doped samples. We consider that the dehydrogenation caused by electron beam irradiation in boron-doped samples is not a thermal process, because the irradiation duration is very short.

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