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Catalytic Doping of Phosphorus and Boron Atoms onto Hydrogenated Amorphous Silicon films

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Abstract

We investigate the low temperature doping of phosphorus (P) and boron (B) atoms onto hydrogenated amorphous silicon (a-Si:H) films by catalytic doping (Cat-doping). The conductivity of a-Si:H films increases as catalyzer temperature increases, and the increase in the conductivity is accompanied by significant reduction in the activation energy obtained from the Arrhenius plot of the conductivity. We also confirm no additional film deposition during Cat-doping. These results suggest that decomposed species are effectively doped onto a-Si:H films similar to the case of Cat-doping onto crystalline Si (c-Si).

1. Introduction

Catalytic doping (Cat-doping) is a doping method by exposing samples to radical species generated by the catalytic cracking of phosphine (PH_3) or diborane (B_2H_6) gas molecules on a heated tungsten catalyzer. It has been demonstrated that P and B Cat-doping is possible for c-Si at substrate temperatures of 80-350 °C [1]. By introducing a P Cat-doped layer on a c-Si surface, the performance of Si heterojunction (SHJ) solar cells can be effectively improved [2].

In this paper, we attempt to perform Cat-doping for a-Si:H. If Cat-doping onto a-Si:H is realized, the fabrication processes of SHJ solar cells can be dramatically simplified. Furthermore, Cat-doping through a hard mask may enable us to realize areal selective doping to a-Si:H films, which is useful particularly for the fabrication of heterojunction back-contact (HBC) solar cells.

2. Experimental procedures

19.8×19.8×0.4 mm^3-sized Corning Eagle glass was used as substrates. Intrinsic a-Si:H films with a thickness of ~20 nm were deposited on the glass substrates by catalytic chemical vapor deposition (Cat-CVD) under the conditions summarized in Table 1. P or B Cat-doping was then performed to the intrinsic a-Si:H films, whose conditions are also summarized in Table 1. Substrate temperature (T_{sub}) and catalyzer temperature (T_{cat}) during Cat-doping were systematically changed.

Al coplanar electrodes were evaporated through a hard mask on the P or B Cat-doped a-Si:H films to evaluate their conductivity from I-V curves. Since the depth of Cat-doped layers was unknown, the conductivities were calculated by assuming that P and B atoms were uniformly doped in depth and the thickness of doped layers was 20 nm. I-V characteristics were measured on a semiconductor parameter analyzer. The activation energy (E_a) of the conductivity of Cat-doped a-Si:H films was obtained by changing the temperature of the samples from 50 to 150 °C during I-V measurement and by using Arrhenius equation.

In order to check the deposition of a-Si:H films during Cat-doping due to the generation of Si-related radicals from a-Si on chamber walls, we also performed Cat-doping onto glass substrates and measured their optical transmittance.

3. Results and discussion

Fig. 1 shows the conductivity of P Cat-doped a-Si:H films at T_{sub} = 350 °C as a function of T_{cat}. The conductivity of an intrinsic a-Si:H film was 6.8×10^{-11} S/cm, which is a typical conductivity of intrinsic a-Si:H. The a-Si:H films Cat-doped at T_{cat} of less than 1100 °C have conductivities similar to that of intrinsic a-Si:H. On the other hand, the conductivities of Cat-doped a-Si:H films increase at T_{cat} of more than 1100 °C. Umemoto *et al*. have reported that PH_3 molecules are decomposed to P and H radicals by catalytic cracking on a W catalyzer heated at more than 1000 °C, and the amount of such radicals increases exponentially as T_{cat} increases [3]. The conductivities of a-Si:H films Cat-doped at other T_{sub} also show similar dependence on

Table. 1 Conditions of intrinsic a-Si film deposition and P or B Cat-doping.

	T_{sub} (°C)	T_{cat} (°C)	Duration (s)	Pressure (Pa)	Gas	Flow rate (sccm)
intrinsic a-Si	160	1800	90	1	SiH_4	10
P doping	50-350	R.T.-1700	300	2	2.25% PH_3 (He-diluted)	20
B doping	50-350	R.T.-1800	300	2	2.25% B_2H_6 (He-diluted)	20

T_{cat}. The catalytic cracking of PH_3 molecules is promoted by increase in T_{cat} increase, which probably leads to more effective doping of P atoms. In contrast, the influence of T_{sub} on the conductivities is not clear. B Cat-doping onto a-Si:H films also show a tendency similar to the case of P Cat-doping.

Fig. 2 shows the E_a of the conductivity of P Cat-doped a-Si;H films as a function of T_{cat} at a T_{sub} of 350 °C. The E_a of the conductivity of intrinsic a-Si:H was 0.85 eV, which is almost half of the band gap of intrinsic a-Si:H used in this study. As shown in Fig. 2, E_a decreases with increase in T_{cat}. This is also a clear experimental evidence of the formation of doped layers by Cat-doping.

Fig. 3 shows the optical transmittance spectra of glass substrates after P Cat-doping at various T_{cat}. If doped a-Si:H is deposited during Cat-doping, optical transmittance must decrease in short wavelength region due to absorption in a-Si:H. The transmittance of glass substrates after Cat-doping at all the T_{cat}, however, does not decrease. This result indicates that n- and p-a-Si:H films are not deposited during Cat-doping, and increasing in the conductivities of a-Si:H films and decrease in E_a are due to the doping of P and B atoms onto intrinsic a-Si:H films by Cat-doping.

4. Conclusions

We have confirmed the effectiveness of P and B Cat-doping onto a-Si:H films. Cat-doping onto a-Si:H films leads to increase in their conductivities accompanied by decreases in E_a. Increase in the conductivity of a-Si:H films is enhanced at higher T_{cat}, which is because of more efficient decomposition of dopant gas molecules and resulting formation of more radicals. The Cat-doping of P and B atoms onto a-Si:H films will be utilized for the fabrication of SHJ and HBC solar cells.

Acknowledgements

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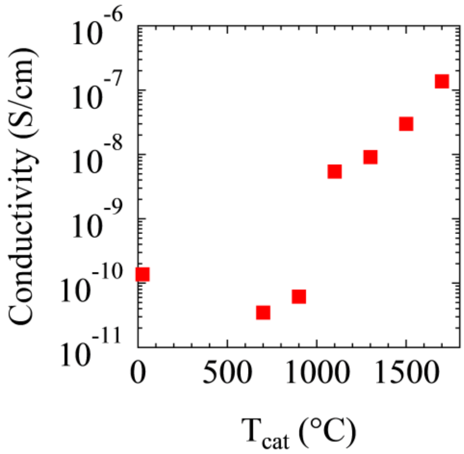

Fig. 1 Conductivity of P Cat-doped a-Si:H films as a function of T_{cat} at a T_{sub} of 350 °C.

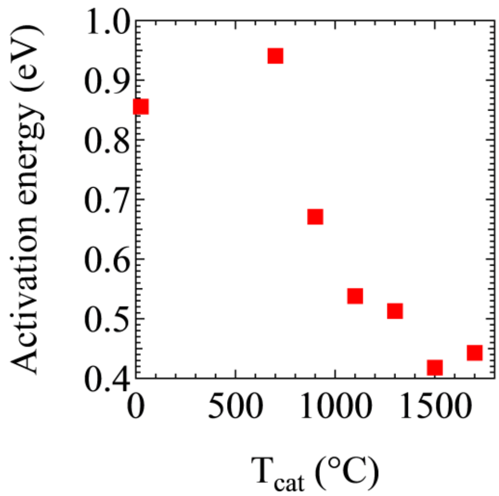

Fig. 2 $E9_a$ of the conductivity of P Cat-doped a-Si;H films as a function of T_{cat} at a T_{sub} of 350 °C.

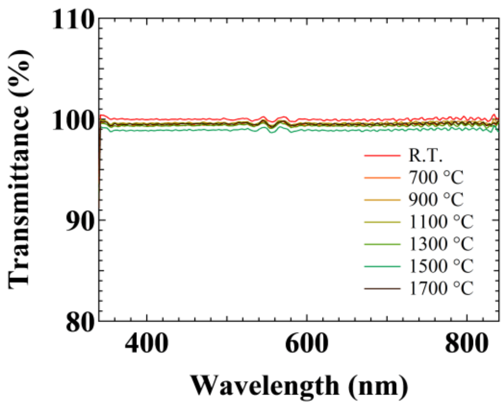

Fig. 3 Optical transmittance spectra of glass substrates after P Cat-doping at various T_{cat}.