Low Temperature Boron Doping into Crystalline Silicon by Boron-Containing Species Generated in Cat-CVD Apparatus

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Abstract

We have discovered that phosphorus (P) atoms can be doped into crystalline silicon (c-Si) at temperatures below 350°C or even at 80°C by using species generated by catalytic cracking reaction of phosphine (PH₃) molecules with heated tungsten (W) catalyzer in Cat-CVD apparatus. As further investigation, here, we study the feasibility of low temperature doping of boron (B) atoms into c-Si by using decomposed species generated similarly from diborane (B₂H₆) molecules. Dependency of properties of doped layers on catalyzer temperature (T_{cat}) and substrate temperature (T_s) is studied by both the Van der Pauw method based on the Hall-effect measurements and secondary ion mass spectroscopy (SIMS) for B doping in addition to P doping. It is found that, similarly to P doping, the surface of n-type c-Si is converted to p-type even at T_s=80°C for T_{cat} over 800°C when c-Si is exposed to B₂H₆ cracked species for a few minutes, and that the heat of substrate over 300°C is likely to help for B doping contrary to P doping.

KeyWords

Cat-CVD, Cat-doping, Radical doping, Low temperature doping.

1. Introduction

Lowering process temperatures is a key issue for improvement in the performance of crystalline silicon (c-Si) solar cells. Low process temperatures below 350 °C lead to the suppression of oxygen-related defect creation in Czochralski- (CZ-) grown c-Si, resulting the improvement in the conversion efficiency of c-Si solar cells [1]. In addition, due to the requirement for reduction of Si usage, the use of c-Si substrates thinner than about 100 μm is strongly desired. However, the conventional high temperature processes in impurity doping and metallization do not appear acceptable because of wafer bowing or breaking. The formation of amorphous Si (a-Si)/c-Si hetero-junction in c-Si solar cells is one of the solutions to avoid high temperature processes. However, the low-temperature doping of phosphorus (P) or boron (B) atoms into c-Si can be also an alternative way of fabricating c-Si solar cells at low temperatures and such low temperature doping may improve even the performance of hetero-junction cells due to the desirable modification of surface potential in c-Si.

Recently, low-temperature and/or shallow doping techniques, such as plasma doping [2-8], atomic layer deposition (ALD) of dopants [9-11] and the formation of doping layers by molecular beam epitaxy (MBE) [12-18], have been developed. However, we have also discovered that an n-type layer can be formed at temperatures as low as 80 °C to 350 °C on the surface of a p-type c-Si substrate by exposing it in species generated by the catalytic cracking reaction of phosphine (PH_3) molecules with heated tungsten (W) catalyzer in a catalytic chemical vapor deposition (Cat-CVD) apparatus [19, 20]. This novel impurity doping technique appears another alternative technique, since the technique can avoid the creation of plasma damage at c-Si surface due to energetic ions.

Here, we study on the doping by catalytically cracked species (Cat-doping) for doping of B atoms into c-Si substrates and feasibility of low temperature formation of p-type layer there. It is found that B atoms can be doped at temperatures as low as 80°C, similarly to P doping, when c-Si substrates are exposed in catalytically generated species from B₂H₆, and also that the substrate temperatures help to B-doping when it exceeds over 350°C contrary to P doping.

2. Experimental Procedure

The Cat-doping of impurities into c-Si wafers was performed by using the conventional Cat-CVD apparatus. A single spiraled W wire with a diameter of 0.5 mm and a length of 210 cm was installed at a distance of 12 cm from the substrate. A B₂H₆ gas is simply introduced into a Cat-CVD chamber in which W catalyzer was set. In the present experiment, the B₂H₆ gas diluted to 2.25% with helium (He) gas was used as a doping source. The flow rate of doping gas is expressed by the total gas flow including He gas, and the pressure during process is by total gas pressure. Si wafers were chemically treated in deionized water, Semico-clean 23 (Furuuchi Chemical) and hydrofluoric acid. Then, it was set on the substrate holder in the Cat-CVD apparatus. Experimental conditions for Cat-doping are summarized in Table 1.

The majority sheet carrier concentration was evaluated by using the Van der Pauw method based on the Hall-effect measurements with a Bio-Rad HL5500PC measuring system. The magnetic field for the measurements of the Hall voltage was kept at 0.32 T. The n-type c-Si wafers with a resistivity higher than 1000 Ωcm were used as substrates for such Hall-effect measurements.

Figure 1 shows the cross-sectional schematic view of a sample for the Hall-effect measurement. The sample is coated with a thin non-doped a-Si layer deposited in a different chamber continuously after doping, to avoid the effect of Fermi level pinning due to the defects in the bare c-Si surface. It has been known that the coating of c-Si surface with a thin non-doped a-Si layer helps to make low defect c-Si surface [21]. Desirable thickness of such a cap layer is investigated and usually kept as thin as 10 nm, to avoid influence of measurement on carrier concentration in c-Si [19]. Four aluminum (Al) electrodes were evaporated to form the Van der Pauw configuration. Finally, the samples are annealed for 60 s at 350°C to form an ohmic contact. As shown later, this short time annealing does not appear to affect the data taken at temperatures lower than 350°C.

The impurity profiles after B or P doping were measured by the secondary ion mass spectroscopy (SIMS). In SIMS analysis, cesium ions with acceleration voltage as low as

1 kV were used as probe ions to realize high depth resolution (high resolution mode).

3. Results and discussion

Figure 2(a) shows the Hall-effect voltages of both original p-type c-Si substrate and P-doped layer on the p-type c-Si as a function of applied currents under the magnetic field of 0.32 T as described already. On the other hand, Figure 2(b) shows the similar Hall-effect voltages of both P-doped layer (same to Figure 2(a)) and B-doped layer in n-type c-Si. T_s during the Cat-doping was fixed at 350°C and T_{cat} was at 1,300°C. The process time of Cat-doping was 10 min. as described in Table 1. When the time of Cat-doping increases, initially, the sheet carrier concentration increases. However, it is likely to saturate after about 10 min or so, and the profiles of Cat-doped atoms measured by SIMS also tend to saturate after almost same times. The situation and the SIMS profiles appear same for B and P Cat-doping. At the moment, we do not know the exact mechanism of the Cat-doping. Before saturation, the peak concentration of profile of Cat-doped atoms appears to increase exponentially with the time by following the simple thermal diffusion equation, but after the peak concentration reaches to a certain value, maybe, the solid solubility limit, the profiles are likely to stop the change and saturate there. The mechanism is still under the investigation.

It is clearly shown that the surface of p-type c-Si is converted to n-type by P doping, and that the surface of n-type c-Si is also converted to p-type by B doping. Similar results are also found even at $T_s=80^\circ\text{C}$, although the samples are annealed at 350°C for 60 s for ensuring the ohmic contact of Al electrodes. The Hall voltage of B Cat-doped layer appears larger than that of P Cat-doped one. The Hall voltage is inversely

proportional to the carrier concentration in the doped layer. Since the carrier concentration of B Cat-doped layer at $T_{\text{cat}}=1,300^{\circ}\text{C}$ is 1/4 to 1/5 smaller than that of P Cat-doped one as shown in Fig. 4 later, the Hall voltage for B Cat-doped sample may become larger than that of P Cat-doped sample.

Figure 3 shows the SIMS profile of B atoms in c-Si after Cat-doping treatment for 600 s at $T_s=350^{\circ}\text{C}$ for the sample coated with 10nm a-Si layer. It is confirmed that B atoms are incorporated in the vicinity of c-Si surface even at T_s of 350°C . If we define the doping depth of B atoms as a depth at which the concentration of the B atoms decreases to 1/10 of the maximum, it is as shallow as 4 nm. Since the profile appears to follow on the exponential form, we can also define the doping depth by the depth at which the value becomes to 1/e of the maximum. However, we simply adapted the 1/10 value of the maximum, because it also means a decade-decrease. The result implies that B atoms are doped only at the surface of c-Si and the surface concentration is as high as the order of 10^{22} cm^{-3} , although the absolute value of concentration by SIMS with high depth resolution mode includes sometimes a few order of magnitude errors.

Figure 4 shows the sheet carrier concentration of c-Si surface after P- and B-related Cat-doping treatment at $T_s=350^{\circ}\text{C}$ as a function of T_{cat} under the conditions summarized in Table I. It is known that the P doping is possible at T_{cat} over 1000°C , while P atoms are not effectively doped at T_{cat} lower than 800°C . This suggests that the existence of species decomposed by catalytic reaction is essentially important for the Cat-doping, since usually the density of decomposed species depends on T_{cat} and it is likely to increase as T_{cat} increases. On the other hand, there is no significant T_{cat} dependence of the sheet carrier concentration for B doping. The B doping can be observed even when the catalyzer is not heated for $T_s=350^{\circ}\text{C}$.

Figure 5 shows the sheet carrier concentration of c-Si substrates after the exposure to flow of B_2H_6 as a function of T_s when the catalyzer is not heated. For $T_s=300^\circ\text{C}$ or less, the sheet carrier concentration is quite low, implying that the effective B doping does not occur. On the other hand, the sheet carrier concentration increases to $3\times 10^{12}/\text{cm}^2$ at $T_s=350^\circ\text{C}$, as already shown in Fig. 4. The results are understandable because the thermal decomposition of B_2H_6 molecules is likely to begin for the temperature over 300°C [22, 23].

In order to know whether the Cat-doping can be really possible even for B doping, we attempted the similar Cat-doping treatment for sufficiently low T_s . Figure 6 shows the sheet carrier concentration of c-Si substrates after the Cat-doping treatment at $T_s=80^\circ\text{C}$ as a function of T_{cat} . It is shown that the B doping can be realized when T_{cat} exceeds over 500°C . These experimental results appear to simply suggest that the thermal decomposition of B_2H_6 on heated substrates plays a certain role when T_s is over 350°C , although catalytic decomposition of B_2H_6 becomes effective when T_s is not high enough to decompose it thermally. And also, the results suggest that the influence of annealing of electrodes for 60 s does not appear to affect seriously on obtained data, since the results for 80°C are different from those of 350°C .

The sheet carrier concentration takes maximum at T_{cat} of 800°C , and decreases at higher temperatures. This is probably due to the facts that the surface of a W wire is

converted to tungsten boride [24] and the efficiency of decomposition itself may be suppressed.

If we compare the results of Figs. 4 and 6, the sheet carrier concentrations of the B Cat-doped samples of $T_s=80^\circ\text{C}$ are larger than those of $T_s=350^\circ\text{C}$ for $T_{\text{cat}}=800$ and $1,000^\circ\text{C}$, although the influence of heat of substrate should be added in the B-doped samples of $T_s=350^\circ\text{C}$. When the substrate temperature is high, many amounts of B_2H_6 molecules might be decomposed thermally at the surface of a substrate and the B_2H_6 molecules remained in the gas phase inside a chamber might be much reduced, because the surface area of the substrate is much larger than that of a catalyzing wire. The B_2H_6 molecules for the decomposition at the heated catalyzing wire might be smaller than that of the case of $T_s=80^\circ\text{C}$, although the doping efficiency of cracked species may be larger than that of thermally decomposed ones. This is a simple speculation for explanation of the phenomena.

The Cat-doping is a newly discovered phenomenon, and there are many things not explained clearly. However, the fact that we can dope impurities in the shallow region of c-Si wafers at low temperatures will lead this promising technology to new feasibilities.

4. Conclusion

Shallow B doping layers can be formed on c-Si by using the species catalytically generated from B_2H_6 at temperatures as low as 80°C . The B-doped layer on n-type c-Si is converted to p-type even if T_s is only 80°C . When the substrate temperature is about 350°C , the doping appears to be affected by the thermal decomposition of B_2H_6 . This Cat-doping will be utilized to control of potential at the surface of c-Si, not only for p- or n- formation, and various application will be considered.

Acknowledgements

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References

1. F. Shimura, "Oxygen in Silicon", *Semiconductors and Semimetals*, vol. **42**, (Academic Press, 1994), p.251 and Chapter VII.
2. B. Mizuno, L. Nakayama, N. Ao, M. Kubota, T. Komeda, *Appl. Phys. Lett.*, **53**, (1988), 2059.
3. Y. Sasaki, C. Jin, K. Okashita, H. Tamura, H. Ito, B. Mizuno, H. Sauddin, R. Higaki, T. Satoh, K. Majima, Y. Fukagawa, K. Takagi, I. Aiba, S. Ohmi, K. Tsutsui, H. Iwai. *Nucl. Instrum. Methods, Phys. Res., Sect. B* **237**, (2005), 41.
4. Y. Sasaki, H. Ito, K. Okashita, H. Tamura, C. G. Jina, B. Mizuno, T. Okumura, I. Aiba, Y. Fukagawa, H. Sauddin, K. Tsutsui, H. Iwai, *Proc. 16th Int. Conf. Ion Implantation Technology*, 2006, p.524.
5. B.-W. Koo, Z. Fang, L. Godet, S. B. Radovanov, C. Cardinaud, G. Cartry, A. Grouillet, D. Lenoble, *IEEE Trans. Plasma Sci.*, **32**, (2004), 456.
6. G. H. Yon, G. H. Buh, T. Park, S. J. Hong, Y. G. Shin, U. I. Chung, J. T. Moon, *Jpn. J. Appl. Phys.*, **45**, (2006), 2961.
7. Y. Sasaki, K. Okashita, S. Hayashi, K. Nakamoto, T. Kitaoka, B. Mizuno, M. Kubota, M. Ogura, O. Nishijima, *Proc. of 2010 Int. Dry Process Symposium*, 2010, p.103.

8. Y. Sasaki, K. Okashita, K. Nakamoto, T. Kitaoka, B. Mizuno, M. Ogura, *IEDM Tech. Dig.*, 2008, p.917.
9. W. Clarke, X. Zhou, A. Fuhrer, T. Reusch, M. Simmons, *Physica*, **E40**, (2008), 1566.
10. J. L. O'Brien, S. R. Schofield, M. Y. Simmons, R. G. Clark, A. S. Dzurak, N. J. Curson, B. E. Kane, N. S. McAlpine, M. E. Hawley, G. W. Brown, *Phys. Rev.*, **B64**, (2001), 161401.
11. F. J. Ruess, L. Oberbeck, M. Y. Simmons, K. E. J. Goh, A. R. Hamilton, T. Hallam, S. R. Schofield, N. J. Curson, R. G. Clark, *Nano Lett.*, **4**, (2004), 1969.
12. H. J. Gossmann F. C. Unterwald, *Phys. Rev.*, **B47**, (1993), 12618.
13. H. P. Zeindl, T. Wegehaupt, I. Eisele, H. Oppolzer, H. Reisinger, G. Tempel, F. Koch, *Appl. Phys. Lett.*, **50**, (1987), 1164.
14. M. W. Denhoff, T. E. Jackman, J. P. McCaffrey, J. A. Jackman, W. N. Lennard, G. Massoumi, *Appl. Phys. Lett.*, **54**, (1989), 1332.
15. N. L. Matthey, M. G. Dowsett, E. H. C. Parker, T. E. Whall, S. Taylor, J. F. Zhang, *Appl. Phys. Lett.*, **57**, (1990), 1648.
16. H. P. Zeindl, T. Wegehaupt, I. Eisele, *Thin Solid Films*, **184**, (1990), 21.

17. E. F. Schubert, “Delta-Doping of Semiconductors”, (Cambridge University Press, Cambridge, U.K., 1996), p. 69.
18. A. C. Gossard, “Epitaxial Microstructures”, *Semiconductors and Semimetals*, (Academic Press, 1994), **vol.40**, p.2.
19. T. Hayakawa, Y. Nakajima, K. Koyama, K. Ohdaira, H. Matsumura, *Jpn. J. Appl. Phys.*, **51**, (2012), 061301.
20. T. Hayakawa, Y. Nakashima, M. Miyamoto, K. Koyama, K. Ohdaira, H. Matsumura, *Jpn. J. Appl. Phys.*, **50**, (2011), 121301.
21. K. Koyama, K. Ohdaira, and H. Matsumura, *Thin Solid Films*, **519**, (2011), 4473.
22. P. Roca i Cabarrocas, S. Kumar, B. Drevillon, *J. Appl. Phys.*, **66**, (1989), 3286.
23. H. Habuka, S. Akiyama, T. Otsuka, Wei-Feng Qu, *J. Crystal Growth*, **209**, (2000), 807.
24. H. Itoh, T. Matsudaira, S. Naka, H. Hamamoto M. Obayashi, *J. Mat, Sci.* **vol.22**, (1987), 2811.

Table caption

Table 1. The conditions of Cat-doping treatments.

Figure captions

Fig. 1. Cross-sectional schematic of a Hall element.

Fig. 2. Hall voltage of Cat-doped c-Si wafers as a function of applied current for P-doping and B-doping samples.

Fig. 3. SIMS profile of boron atoms in a c-Si wafer after radical treatment.

Fig. 4. Sheet carrier concentration on radical-treated c-Si wafers at a substrate temperature of 350 °C during the radical treatment as a function of catalyzer temperature for P-doping and B-doping samples.

Fig. 5. Sheet carrier concentration on c-Si wafers after exposure to B₂H₆ flow under an unheated catalyzer as a function of substrate temperature during the radical treatment.

Fig. 6. Sheet carrier concentration on c-Si wafers after radical treatment at a substrate temperature of 80 °C during the radical treatment as a function of catalyzer temperature.

Table 1. by T. Ohta *et al.*,

Table 1. The conditions of Cat-doping treatments.

Cat-doping treatment at a substrate temperature of 350 °C.	
Source gas	B_2H_6
Flow late of B_2H_6	140 sccm
Pressure	1 Pa
Substrate temperature	350 °C
Catalyzer temperature	Room Temperature - 1300 °C
Exposure time	600 s
SIMS sample	
Source gas	B_2H_6
Flow late of B_2H_6	140 sccm
Pressure	1 Pa
Substrate temperature	350 °C
Catalyzer temperature	800-1300 °C
Exposure time	600 s
Exposure to B_2H_6 flow under an unheated catalyzer.	
Source gas	B_2H_6
Flow late of B_2H_6	140 sccm
Pressure	1 Pa
Substrate temperature	Room Temperature - 350 °C
Catalyzer temperature	Room Temperature
Exposure time	600 s
Cat-doping treatment at a substrate temperature of 80 °C.	
Source gas	B_2H_6
Flow late of B_2H_6	140 sccm
Pressure	1 Pa
Substrate temperature	80 °C
Catalyzer temperature	Room Temperature - 1800 °C
Exposure time	600 s

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