Removal of Boron from Metallurgical-grade Silicon by Applying the Plasma Treatment

Kichiya SUZUKI, Tomonori KUMAGAI¹⁾ and Nobuo SANO

Department of Metallurgy, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113 Japan.

1) Formerly Faculty of Engineering, The University of Tokyo. Now at Recruit Co., Ltd., Chuuo-ku, Tokyo, Japan.

(Received on November 7, 1991; accepted in final form on January 24, 1992)

The removal of boron from metallurgical-grade silicon was investigated by applying an Ar/H₂O plasma treatment to develop a new production technique for low cost solar-grade silicon (SOG-Si).

The concentration of boron in MG-Si decreased from 35.7 to 0.4 ppmw, satisfying the requirement for SOG-Si, using Ar+1.24vol%H₂O plasma gas for 25 min of melting time. It has been demonstrated that the overall rate of elimination of boron is controlled by the diffusion of boron in silicon melts. The removal of boron is affected by the kind of plasma operating gas with the highest elimination rate of boron by Ar/H₂O plasma. The experimental findings support that boron in silicon reacts with oxygen in gas only at the plasma-impinging area.

It may be said that only this technique has the possibility to lower boron content of silicon down to the required 0.1 ppm for SOG.

KEY WORDS: silicon; solar cell; refining; thermal plasma; boron.

1. Introduction

The crystalline silicon solar cell has drawn strong attention as a candidate for supplementary power generation in the near future and its importance is rapidly growing for conservation of earthly environment at the moment.

A solar cell for power generation has been produced using expensive off-grade electronic silicon (SEG-Si). Therefore, the cost of electricity by the present solar cell is very high and it cannot compete with existing large scale commercial power. One of the prerequisites for large-scale photovoltaic energy conversion using silicon solar cell is a substantial reduction in its manufacturing cost.

The ultimate purpose of this study is to develop a process that enables us to produce inexpensive solar grade silicon (SOG-Si). Many different approaches¹⁾ have been proposed in the area of low-cost silicon feedstock processing. Among them, a processing route *via* refining of metallurgical grade silicon (MG-Si) seems to offer the best chance of producing SOG-Si at low cost. A technical problem in this processing is to effectively remove boron and phosphorus from MG-Si, contents of which are in the range from 20 to 40 ppmw. These impurities are doping elements for SOG-Si, so that their concentrations are required to be controlled below 1 ppmw. However, both elements are very difficult to be removed by using a directional solidification or zone melting technique because their segregation coefficients are close to unity. The authors have carried out a series of experiments for

removing boron and phosphorus by applying vacuum, flux, and plasma treatments.^{2,3)} The behavior of boron during Ar/H₂O plasma treatment is reported in the present study.

2. Experimental Principle

The affinity of boron toward oxygen is as high as that of silicon. Two practical methods are considered for removing boron from MG-Si, one is a flux treatment and the other is an oxidizing plasma treatment. In the flux treatment, boron is oxidized to form boron oxide, B₂O₃, which is stable in basic fluxes such as silicates of alkaline earth metals. Thus the boron in MG-Si is expected to be oxidized and transferred into basic fluxes. Experimental results in connection with the flux treatment have been reported elsewhere by the authors.³⁾ As described there, boron content of MG-Si after this treatment will not be low enough, unless a very large amount of flux is used.

In the plasma treatment, gaseous boron oxides such as BO, B₂O, B₂O₃, etc. are expected to form at temperatures higher than 2300 K. Of these boron oxides, BO has a relatively high vapor pressure. For example, the vapor pressure of BO is estimated to be 74 Pa for an activity of boron in silicon of 10⁻⁴ under the oxygen partial pressure controlled by Si(l)+O₂(g)=SiO₂(l) at 2273 K, while those of BO₂ and B₂O₃ are 0.15 and 0.056 Pa, respectively. Therefore, boron may be removed as BO from silicon melts under oxidizing plasma conditions.

As described earlier, the authors have investigated the removal of boron using an Ar/O₂ or Ar/CO₂ plasma²⁾ and have found that the oxidizing plasma treatment is more effective than the flux treatment for removing boron. In the present study, the behavior of boron in an Ar/H₂O plasma has been investigated and compared with previous results by an Ar/O₂ or Ar/CO₂ plasma. The removal of boron in silicon by use of an Ar-H₂-H₂O gas mixture has been reported by Theuerer⁴⁾ for zone melting. Amouroux *et al.*⁵⁾ used an Ar-H₂-O₂ gas mixture for high-frequency induction plasma and Baba *et al.*⁶⁾ used an Ar-H₂O or Ar-He-H₂O for a non-transfer type plasma with 600 g of silicon in a quartz crucible.

3. Experimental

3.1. Equipments

As shown in Fig. 1, the plasma furnace was equipped with a transfer type torch with 10 kW of maximum output. A weakly oxidizing plasma was prepared by the addition of wetted Ar to a main Ar carrier. The total flow rate was controlled to be $1.16 \times 10^{-4} \text{ m}^3/\text{s}$ throughout the present experiments.

The wetted Ar was prepared by passing Ar through a

Fig. 1. Schematic representation of the plasma melting furnace.

Table 1. Manufacturer's analysis of MG-Si used in the present study.

Impurities	Content (ppmw)
C	60
B	30-40
Al	500-900
Fe	260-400
Ti	10
Cu	2
Ca	60

stainless steel water bath, 70 mm i.d. and 280 mm in height. The percentage of H₂O in the plasma gas was controlled by changing the flow rate of argon. The tubing between the bath and the torch was wound with a ribbon heater to prevent condensation of water vapor.

3.2. Procedures

A flaky MG-Si containing 35.7 ppmw of boron was mainly used and in some cases other samples having 5 and 15 ppmw of boron were used. Table 1 shows the manufacturer's analysis of the sample.

Approximately 5.5 g of silicon were melted on a water-cooled copper disk with 28 mm in diameter. The boron elimination and silicon loss were investigated as a function of melting time under various conditions. After the sample was treated, it was turned over to repeat the same treatment to make sure of its homogeneity. Therefore, melting time is defined as the total time for treating the top and bottom parts of the sample. With this technique, the reproducibility of boron analysis was controlled to within $\pm 10\%$. As shown in Table 2, the operating parameters are H₂O concentration of the plasma gas, kind of oxidant, initial concentration of boron in silicon, and flux addition.

Analysis of boron was performed by inductively coupled plasma emission spectroscopy (ICP-ES).

4. Results and Discussion

4.1. Effects of H₂O Concentration of the Plasma Operating Gas on the Rate of Boron Elimination and Silicon Loss

The results of boron elimination and silicon loss after 10 min are presented as a function of H₂O vol% of the operating gas in Fig. 2. As is seen in the figure, the rate

Table 2. Experimental parameters and their ranges of variation.

Parameter	
Boron content of silicon	5, 15, 35.7 ppmw
Experimental time	4-25 min
Plasma gas composition	Ar + H ₂ O (H ₂ O: 0-14.6 vol%) Ar + 0.44 vol% H ₂ O + 0.44 vol% CO ₂
Addition of flux	CaF ₂ (10-30 mass%)

Fig. 2. Dependence of the rate of boron elimination and silicon loss on the H₂O content of plasma gas in 10 min of melting time.

Fig. 3. Dependence of the rate of boron elimination and silicon loss on O_2 and CO_2 content of plasma gas in 10 min of melting time.

Fig. 4. Rate of boron elimination and silicon loss with $Ar + 1.24\text{vol}\%H_2O$ plasma gas as a function of time.

of boron elimination (η_B) and silicon loss (δ_{Si}) increased linearly with increasing the concentration of H_2O . Figure 3 shows the previous results with an Ar/O_2 or Ar/CO_2 plasma for comparison. In both cases of Ar/O_2 and Ar/CO_2 , η_B also increased with increasing the concentration of O_2 or CO_2 at the beginning of melting, but it levels off beyond about 0.2 vol% of oxidizing gas concentration. These differences in the trend of η_B between Ar/H_2O and Ar/O_2 or Ar/CO_2 plasmas are caused by whether or not an SiO_2 film is formed on the surface of silicon melts during melting. The formation of SiO_2 film was observed on the surface in both cases of Ar/O_2 and Ar/CO_2 plasmas, but not in the case of Ar/H_2O plasma. Thus, water vapor in the plasma gas suppresses the formation of solid oxide of silicon by forming only gaseous SiO , resulting in enhancement of the gaseous removal of boron.

4.2. Kinetics of the Removal of Boron

Figure 4 shows the change in boron concentration with time using an $Ar + 1.24\text{vol}\%H_2O$ plasma. It can be seen that η_B rapidly increases at the beginning of melting until about 15 min and then it levels off. The maximum elimination was 98.9% around at 25 min melting time, the final concentration of boron in silicon being 0.4 ppmw. This boron level is lower than that required for SOG-Si.

In the previous study,²⁾ which was carried out with

Fig. 5. Relation between $\ln\{[B]/[B]_0\}$ and melting time for boron elimination with $Ar + 1.24\text{vol}\%H_2O$ plasma gas.

MG-Si containing 28.5 ppmw of boron by using an $Ar + 0.7\text{vol}\%CO_2$ plasma, the maximum elimination was about 90% at 30 min melting time and the final concentration of boron was about 4 ppmw. On the other hand, the rate of silicon loss was about 1.6%/min in the previous study in contrast with 0.4%/min in this case at the fixed oxygen content of the plasma gas. Obviously from this comparison, the Ar/H_2O plasma has certain advantages over the Ar/CO_2 or Ar/O_2 for removal of boron from silicon.

The rate equation for removing boron is expressed by Eq. (1) or (2), assuming the rate is controlled by the diffusion of boron from the bulk to the surface of the silicon melt.

$$-\frac{d[B]}{dt} = k\{[B] - [B]_i\} \quad \text{.....(1)}$$

$$\ln \frac{[B] - [B]_i}{[B]_0 - [B]_i} = -kt \quad \text{.....(2)}$$

where, k : apparent rate constant (sec^{-1})

$[B]$: concentration of boron at time, t (ppmw)

$[B]_0$: initial concentration of boron (ppmw)

$[B]_i$: concentration of boron at surface of the melt (ppmw)

t : time (sec).

Assuming that the concentration of boron at surface of the melt is nearly zero, Eq. (2) is rewritten by Eq. (3);

$$\ln\{[B]/[B]_0\} = -kt \quad \text{.....(3)}$$

Figure 5 shows the plot of $\ln\{[B]/[B]_0\}$ vs. t on the basis of the data in Fig. 4. As is seen in this figure, a nearly linear relation between $\ln\{[B]/[B]_0\}$ and t was obtained. From this result, the assumption made above seems to be valid in this case. The value of k can be obtained from the slope in Fig. 5 and was calculated as $3 \times 10^{-3} \text{ sec}^{-1}$.

The apparent rate constant is expressed as follows;

$$k = k_m(A/V) \quad \text{.....(4)}$$

where, k_m : mass transfer coefficient (m/s)

A : reaction area of silicon melt (m^2)

V : volume of silicon melt (m^3).

Accordingly, if the value of A/V is known, the value of k_m can be calculated from Eq. (4). The shape of the

silicon melt was like a button, 2 cm in diameter and 1.5 cm in thickness at center. From the shape and size of the melt, the reaction area, A , can be calculated 5.5 cm² by rotating ellipsoid approximation. The volume of the silicon melt may be estimated as 2.4 cm³ from 5.5 g of the sample weight and 2.33 g/cm³ of the density of silicon. The value of A/V , therefore, is 2.3 cm⁻¹ in this experiment, so that k_m is 1.3×10^{-5} m/s. This seems to be rather small as a value of k_m in spite of strong agitation of the melts by impinging plasma jet, leading to the following discussion.

In the above calculation, the boron reaction was assumed to occur over the whole silicon area. However, this reaction may be limited to only at the area where plasma gas is impinging. In other words, only the activated oxygen may react with boron in silicon. The plasma-impinging area is estimated to be 0.50 cm² assuming that the diameter is equal to that of the nozzle of the plasma torch, 0.8 cm.

Then the above k_m value would be modified to be 1.4×10^{-4} m/s, which is reasonable for the order of mass transfer coefficient under the present experimental conditions. Aratani, who is one of coauthors of Ref. 6), observed that k_m defined by Eq. (4) is inversely proportional to the square of crucible diameter under the same conditions and obtained 1.3×10^{-4} m/s, if the plasma-impinging area was used for estimation, which is in excellent agreement with our modified value. These findings strongly indicate that boron in silicon reacts with gas only at the plasma-impinging area.

4.3. Effect of the Initial Concentration of Boron on Its Removal

Figure 6 shows the effect of initial concentration of boron on its behavior as $\ln\{[B]/[B]_0\}$ vs. t together with the plots in Fig. 5. Linear relationships are seen between $\ln\{[B]/[B]_0\}$ and t for all different initial concentrations of boron, but the slopes of straight lines, i.e. apparent rate constants, depend on the initial concentration of boron. The values of apparent rate constants decrease with decreasing initial concentration of boron. Using the value of the slopes in Fig. 6, 1.0×10^{-4} and 7.4×10^{-5} m/s of k_m were obtained for 15 and 5 ppmw of initial boron concentrations, respectively, considering only the plas-

Fig. 6. Relation between $\ln([B]/[B]_0)$ and melting time for boron elimination with Ar+1.24vol% H₂O plasma gas with boron content ranging from 5 to 35.7 ppmw.

ma-impinging area. Moreover, the lowest boron level after 20 min of melting time was 0.5 to 0.9 ppmw independent of the initial concentration of boron. Accordingly, it was found that lowering initial concentration of boron gave no favorable effects on the removing behavior of boron. The reason for these experimental findings is not clear at the moment and should be studied further. There could be the possibility that boron reacts partially with gas even outside the plasma-impinging area when the boron level is relatively high.

Figure 7 shows the relationship between rate of silicon loss and melting time. The loss of silicon increased in proportion to melting time independent of the initial concentration of boron. Namely, it is controlled only by oxygen content of plasma gas. About 0.4 %/(min·vol% H₂O) was obtained as the rate of silicon loss per unit time and per unit percentage of H₂O from the slope in Fig. 7.

4.4. Effect of Kind of Oxidizing Gas for Plasma

It has been described earlier that an Ar/H₂O mixture is more effective than an Ar/O₂ or Ar/CO₂ for the removal of boron. An experiment using Ar+0.44vol% H₂O+0.44vol% CO₂ plasma was carried out to investigate the effect of coexistence of H₂O and CO₂ on boron

Fig. 7. Relation between the rate of silicon loss and melting time with Ar+1.24vol% H₂O plasma gas with boron content ranging from 5 to 35.7 ppmw.

Fig. 8. Comparison of Ar+1.24vol% H₂O plasma with Ar+0.44vol% H₂+0.44vol% CO₂ plasma with regard to the rate of boron elimination in 10 and 20 min of melting time.

Fig. 9. Dependence of the rate of boron elimination with Ar+1.24vol%H₂O plasma gas on relative flux addition to MG-Si.

elimination, keeping the same oxygen content of plasma gas as Ar+1.24vol%H₂O. For comparison, the melting time was fixed at 10 and 20 min. As is seen in Fig. 8, the rate of boron elimination with Ar+1.24vol%H₂O plasma is 10 to 15 % larger than that with Ar+0.44vol% H₂O+0.44vol%CO₂ plasma for both melting times.

The reason for this difference may be discussed in terms of the formation of SiO₂ film, as stated earlier in Sec. 4.1. When H₂O is mixed in a plasma working gas, H₂O will be dissociated at least to H and O, while CO₂ is to CO and O. This unstable H or CO may react with possibly formed SiO₂ to form gaseous SiO before recombination, cleaning the plasma impinging area of molten silicon.

The SiO vapor pressure for Eq. (5) at 2273 K, which is the observed highest temperature, with 1.24 vol% of water vapor content is estimated to be 1.63×10^4 Pa.

$$\Delta G^\circ = -70.6 \text{ kJ/mol} \quad \text{at } 2273 \text{ K} \quad \dots\dots(5)$$

assuming $P_{\text{H}_2\text{O}} = P_{\text{SiO}}$ and $P_{\text{H}} = 2P_{\text{H}_2} = 2 \times 1.24 \times 10^{-2} \times 1.013 \times 10^5 = 2.51 \times 10^3$ Pa.

Similarly, P_{SiO} for the same CO₂ content of the Ar/CO₂ mixture is 2.63×10^2 Pa, which is lower than the value for Ar/H₂O, 1.63×10^4 Pa, by a factor of approximately 62. In other words, it is presumed that with Ar/H₂O the plasma-impinging area, where gaseous boron oxide is likely to form, would be less contaminated by SiO₂ than in the case of Ar/CO₂ mixture, giving a more favorable condition for boron removal although it is not clear which is more important, excited oxygen species or enhanced mass transfer. This is consistent with the present observations described in the foregoing. Consequently, it is clear that Ar/H₂O mixture is more effective than Ar+H₂O+CO₂ mixture for the removal of boron.

4.5. Effect of Addition of Flux on the Removal of Boron

Figure 9 shows the relationship between boron elimination and percentage of CaF₂ in weight added to silicon melt during the first 10 min using Ar+1.1vol% H₂O plasma. It was found that the percentage of

elimination of boron increased by about 20% by the addition of CaF₂ up to 10%, while an amount of silicon loss did not change.

This improvement may be due to the formation of gaseous BF₃ following the reaction; $3/2(\text{CaF}_2) + 1/2(\text{B}_2\text{O}_3) = 3/2(\text{CaO}) + \text{BF}_3(\text{g})$, as indicated by Fedko *et al.*⁷⁾ or BOF by Humbert *et al.*⁸⁾ but it must be proved in the future.

5. Conclusions

The removal of boron from MG-Si has been investigated by using Ar/H₂O plasma to develop a low-cost SOG-Si. From a series of the experiments the following information was obtained:

(1) Boron in the MG-Si was reduced from 35.7 to 0.4ppmw, which is low enough for SOG-Si, using Ar+1.24vol%H₂O plasma.

(2) Kinetic analyses have been carried out using the data with Ar+1.24vol%H₂O plasma. It was found that the rate of removal of boron is controlled by the diffusion of boron in the silicon melt. The mass transfer coefficient was evaluated to be 1.4×10^{-4} m/s, considering the plasma-impinging area. In addition, it was found that the rate of silicon loss increased in proportion to melting time. The value of 0.4 %/(min·vol% H₂O) was obtained as the rate of silicon loss per unit melting time and per unit percentage of H₂O.

(3) Among weakly oxidizing plasma treatments for the removal of boron, the largest removal was obtained when using an Ar/H₂O operating gas, which is also effective to keep silicon loss at a low level, probably because the plasma-impinging area is kept clean.

(4) About 20% of enhancement of boron elimination was observed by adding CaF₂ up to 10%.

Acknowledgment

The authors thank Professor C. Finn, Northeastern University, for his help in preparing the manuscript.

REFERENCES

- 1) J. Dietl: Proc. 8th E.C. Photovoltaic Solar Energy Conf., Vol. 1, Kluwer Academic Publishers, Dordrecht, The Netherlands, (1988), 599.
- 2) K. Suzuki, K. Sakaguchi, T. Nakagiri and N. Sano: *J. Jpn. Inst. Met.*, **54** (1990), 161.
- 3) K. Suzuki, T. Sugiyama, K. Takano and N. Sano: *J. Jpn. Inst. Met.*, **54** (1990), 168.
- 4) H. C. Theuerer: *J. Met.*, **6** (1956), 1316.
- 5) J. Amouroux, F. Sliotman, N. Madigou, T. Rogen and D. Morvan: Proc. 8th Int. Symp. Plasma Chemistry, Vol. 3, Tokyo, (1987), 1868.
- 6) H. Baba, N. Yuge, Y. Sakaguchi, F. Aratani and Y. Habu: Proc. 10th E.C. Photovoltaic Solar Energy Conf., Kluwer Academic Publishers, Dordrecht, The Netherlands, (1991), 286.
- 7) J. Fedko and M. Krucinski: *Ironmaking Steelmaking*, **16** (1989), 116.
- 8) P. Humbert, R. Combes, J. Erin, D. Morvan and J. Amouroux: Proc. 10th E.C. Photovoltaic Solar Energy Conf., Kluwer Academic Publishers, Dordrecht, The Netherlands, (1991), 261.