

# Novel Recycling Method for Boron Removal from Silicon by Thermal Plasma Treatment Coupled with Steam and Hydrogen Gases

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**Abstract:** Boron (B) separation from photovoltaic silicon (Si) remains a research challenge in the recycling field. In this study, a novel B-removal process was developed using thermal plasma treatment coupled with steam and hydrogen gases. Experiments were performed on artificially B-doped Si using various plasma conditions of mixed argon (Ar)/steam/hydrogen gases and varied refining time. The B concentration in all of the samples decreased with increasing refining time. The use of the plasma mixed with Ar/steam/hydrogen gases resulted in a significant improvement of the efficiency of B removal compared with the Ar/steam plasma refining. In addition, with increasing steam content in the plasma with mixed Ar/steam/hydrogen gases, the B-removal rates increased.

**Keywords:** silicon; recycling; refining; solar cell; plasma; boron

## 1. Introduction

Recently, sustainable energy has attracted considerable attention, and solar energy, one type of sustainable energy, has been widely studied and applied in various applications [1,2]. Photovoltaics (PVs) are generally used to convert solar energy into electricity. The PV industry started in the 1980s with the first use of multicrystalline silicon (Si) wafers [3,4], and Si-based solar cells still make up more than 90% of the PV market because of the conventional use of Si and its low cost [5,6]. As the lifetime of PV cell modules is generally ~20–30 years, the current amount of PV-module waste is increasing [1,7]. In fact, the amount of PV-module waste dramatically increased over the last decade [8,9].

Meanwhile, reducing the cost of producing high-purity Si for solar applications is an important issue in the manufacture of low-cost Si solar cells. Recycling of end-of-life PV modules could be a cost-effective method to economically fabricate Si. Moreover, it would help protect the environment by decreasing the amount of PV-module waste comprising heavy metals and polymers [10,11]. According to a recent study, the recycling of PV modules can have considerable economic and environmental benefits, with the implementation of appropriate policies [12].

The removal of impurities in Si is an essential step in recycling PV-module waste because the impurities disturb electricity generation and reduce the lifetime of minority carriers in Si [13]. To decrease environmental pollution and energy consumption, new refining techniques have been developed, including metallurgical purification processes such as directional solidification, secondary

refining, slag refining, hydrometallurgy, solvent refining, and plasma refining [14–18]. Boron (B), one of the major impurities in Si with a large segregation coefficient and low vapor pressure, is difficult to separate from Si using traditional metallurgical methods such as vacuum refining and directional solidification, as opposed to other impurities such as iron, tin, and aluminum [19,20]. Possible methods of refining Si include solvent refining and gas blowing; however, their use in industry is limited because of their high cost and associated processing difficulties [13,21–24]. Currently, the plasma refining method is considered by many researchers to be a convenient and easy method for practical continuous production.

In this study, Si was refined by plasma treatment coupled with steam and hydrogen gases, which is a modification of the conventional plasma method. B-doped Si was melted using an electromagnetic cold crucible (EMCC), a promising method for melting metals without contamination by the crucible, and the molten Si was treated by plasma with various steam and hydrogen contents. The refined Si was then characterized using inductively coupled plasma optical emission spectrometry (ICP-OES) with thermodynamic studies.

## 2. Materials and Methods

The starting materials were prepared by alloying Si chips from a treated poly-silicon-based solar cell (99.999%, Loser Chemie GmbH, Zwickau, Germany) and B granules (99.7%, Sigma-Aldrich, St. Louis, MO, USA). Then, 99.9 g of the prepared Si was melted using a plasma arc melting apparatus (Plasnix, Incheon, South Korea) with a power of 50 kW in an argon (Ar) atmosphere. Next, 0.1 g of B was added into the molten Si to produce B-doped Si. The concentration of B in the fabricated B-doped Si was approximately 1000 ppm, and the specimens used in the refining experiments had concentrations within 5% deviation from the targeted concentration.

The refining processes were performed using a vacuum chamber apparatus using an EMCC and a plasma torch, including a gas nozzle for injecting Ar, hydrogen, and steam, as schematized in Figure 1. The fabricated 100 g of B-doped Si was melted in the EMCC with a constant electric supply power of 10 kW in an Ar atmosphere (760 torr). After melting the B-doped Si, the plasma torch, positioned 5 cm above the cold crucible, was ignited using high-frequency oscillation. While operating the plasma arc, various flow rates of Ar (10.3–12 liters per minute (LPM)), steam (0.64–1.94 LPM), and hydrogen (0 and 0.44 LPM) gases were consistently supplied into the molten Si from the plasma torch to keep each of the concentrations constant. The composition of gas was computed for each gas flow rate. The molten Si temperature was calculated by pyrometer (ENDURANCE E1RH, Fluke, Eindhoven, The Netherlands) and maintained near 2100 °C by controlling the supply of power, and the specimens for each condition were sampled using a quartz tube every 2 min from 0 to 8 min. The experimental conditions are summarized in Table 1.

**Table 1.** Experimental conditions for B removal from Si by thermal plasma treatment coupled with steam and hydrogen gases.

Experimental Conditions	5.1H <sub>2</sub> O	5.1H <sub>2</sub> O/3.5H <sub>2</sub>	10.2H <sub>2</sub> O/3.5H <sub>2</sub>	15.3H <sub>2</sub> O/3.5H <sub>2</sub>
Ar (vol %)	94.9	91.4	86.3	81.2
H <sub>2</sub> O (vol %)	5.1	5.1	10.2	15.3
H <sub>2</sub> (vol %)	0	3.5	3.5	3.5
Plasma Power (kW)	10	10	11	11
Molten Si Temperature (°C)	2090	2121	2104	2113
Reaction Area of Molten Si, A (m <sup>2</sup> )			$3.85 \times 10^{-5}$	
Volume of Molten Si, V (m <sup>3</sup> )			$3.92 \times 10^{-5}$	
V/A (m)			1.02	

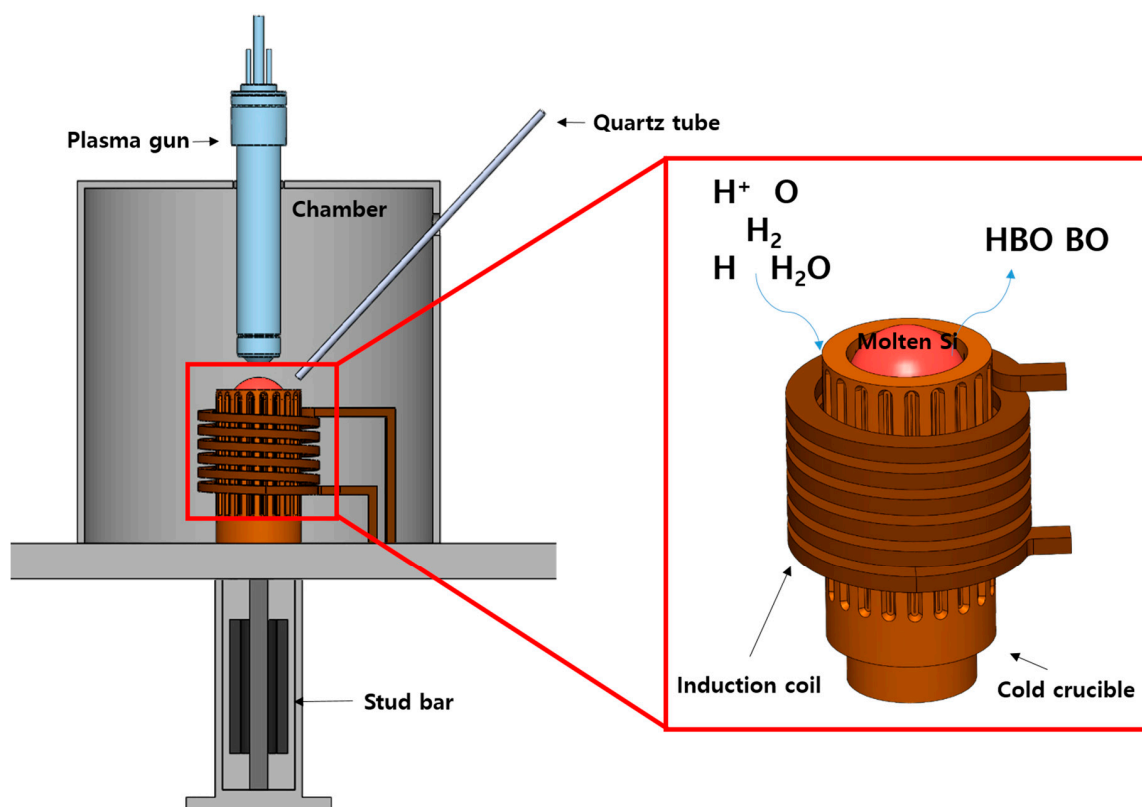


Figure 1. Schematic of the experimental apparatus for recycling Si.

The B contents in the refined Si under various conditions were determined using ICP-OES (iCAP 6300, Thermo Fisher Scientific, Waltham, MA, USA). The B contents were obtained on three samples ( $n = 3$ ) for each condition. A thermodynamic study of the B-based compounds was performed using HSC thermodynamic software.

### 3. Results and Discussion

#### 3.1. Thermodynamic Study

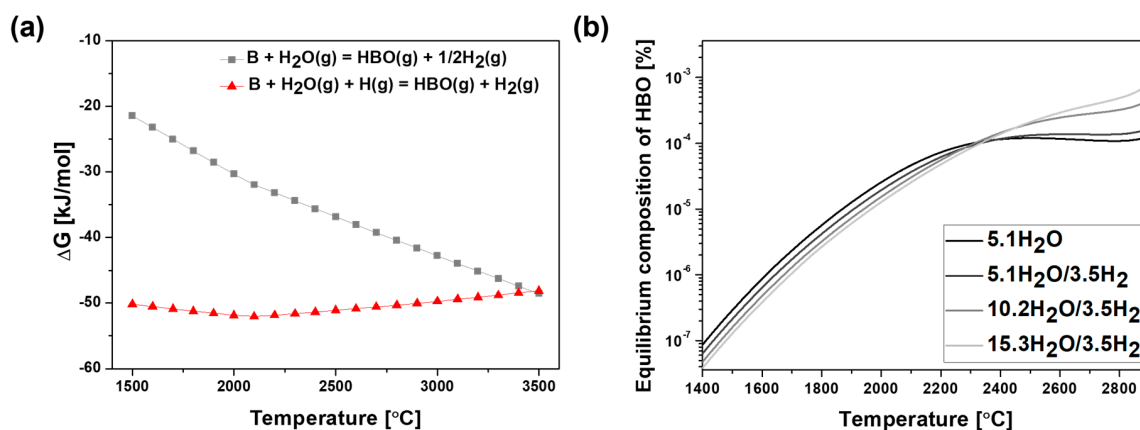
The thermodynamics of refining Si was studied to optimize the composition of the reacting gas and temperature of the refining reactions. Various attempts to eliminate B in Si with reactive gases such as  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{H}_2$ , and  $\text{CO}_2$  have previously been made using gas blowing or plasma treatment [24–26]. Among them,  $\text{H}_2\text{O}$  is one of the most-used gases in the plasma method for removing B.  $\text{H}_2\text{O}$  gas oxidizes Si to silicon oxides such as  $\text{SiO}$  or  $\text{SiO}_2$ , and they also react with the B dissolved in Si and form boron oxide ( $\text{B}_x\text{O}_y$ ), which has a high vapor pressure [27]. Recently,  $\text{H}_2$  gas has also been used to reduce B.  $\text{H}_2$  gas significantly increases the rate of B removal by prohibiting the formation of a silicon oxide film on the surface of the molten Si, thus allowing an increase in the real reaction area [24].

Recent studies have shown that gas mixtures with more than two components are more effective in removing B than a single gas [17]. Therefore, the synergy effect of  $\text{H}_2\text{O}$ – $\text{H}_2$  gas mixtures has been investigated. HBO gas, which can be formed when H and O sources exist, is considered the most volatile B compound according to many studies [17,20]. Safarian et al. proposed the following mechanism of B removal with hydrogen and steam:



They stated that B removal can be performed by the interaction of B and H, dissolved in molten Si, with steam at the liquid–gas interfacial area. The standard Gibbs free energy curves of HBO formation with  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}-\text{H}_2$  are presented in Figure 2a. Note that the reaction in Equation (1) occurs more easily than the reaction without  $\text{H}_2$ . Moreover, this reaction will be accelerated in plasma conditions.

The relation between the equilibrium compositions of HBO and the temperature in each Si–B–H– $\text{H}_2\text{O}$  system was determined, as shown in Figure 2b. The equilibrium compositions of all the systems increased with increasing working temperature, suggesting that the possibility of B removal increased with the increase in the volatilities of HBO. However, the system of  $5.1\text{H}_2\text{O}$  without  $\text{H}_2$  exhibited higher equilibrium compositions of HBO than any of the other systems below  $2300\text{ }^\circ\text{C}$ , and this result contradicts those reported in previous studies. In the general plasma process, the partial temperature of metals such as Si is above  $2300\text{ }^\circ\text{C}$ . At temperatures above  $2300\text{ }^\circ\text{C}$ , the ascending order of the equilibrium amounts of HBO for the four systems flipped, and the  $15.3\text{H}_2\text{O}-5.1\text{H}_2$  system contained the highest amount of HBO. Therefore, to remove B more effectively, the refining temperature should be high, but below a certain threshold to minimize Si loss, which increases rapidly with increasing temperature [28]. From this thermodynamic study, it was possible to infer the optimal working conditions.



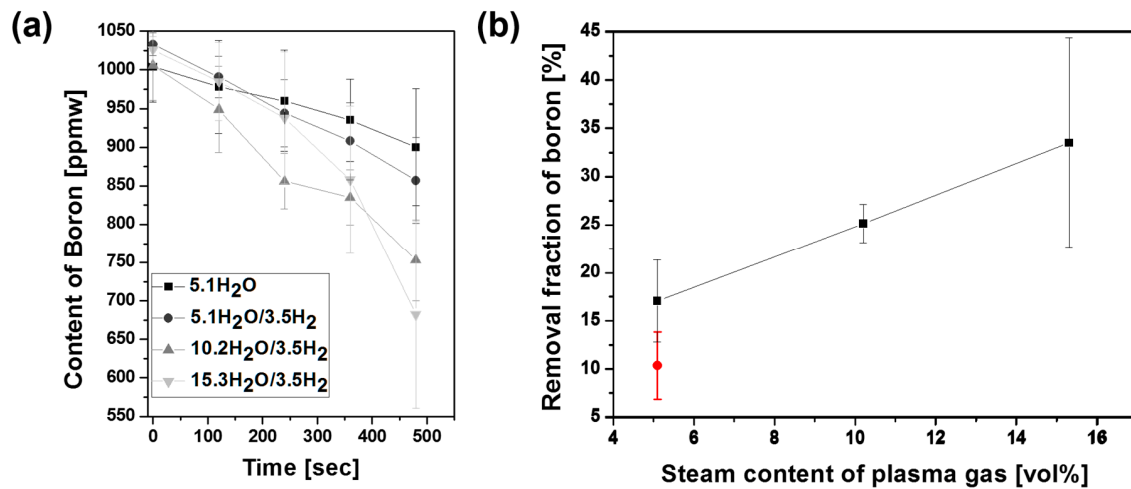
**Figure 2.** (a) Standard Gibbs free energy change of HBO as a function of temperature and (b) equilibrium composition of HBO as a function of temperature in various Si–B–H– $\text{H}_2\text{O}$  systems (B/Si ratio:  $10 \times 10^{-4}$ ).

### 3.2. Experimental Study

Based on the thermodynamic study of B removal, Si was refined by thermal plasma treatment coupled with steam and hydrogen gases. During plasma treatment, Si chips were melted in a cold crucible with an induction field (Figure 1). There were no defects in the Si ingot, and no Cu contamination was detected in any of the fabricated specimens based on ICP-OES analysis (data not shown), suggesting that the EMCC method is a powerful method for melting and refining Si compared with other commercial methods such as vacuum arc, plasma arc, and electron beam melting [2,25,28,29].

Figure 3a shows the B contents in the refined Si and the removal fraction of B evaluated by ICP-OES. The Si alloyed with B using the plasma arc melting method contained approximately 1000 ppmw of B. The contents of all the samples decreased with increasing refining time from 0 to 8 min, as shown in Figure 3a. For the refined Si with  $5.1\text{H}_2\text{O}$  and no  $\text{H}_2$  gas, the B contents of Si slightly decreased from 1004 to 900 ppmw, whereas the condition with an additional 3.5 vol %  $\text{H}_2$  gas showed a greater decrease in B content from 1033 to 857 ppmw. The addition of  $\text{H}_2$  gas may have assisted the removal of B, and these results are consistent with the thermodynamic study. With increasing refining time, the absolute value of the B contents in the refined Si ingot with  $10.2\text{H}_2\text{O}/3.5\text{H}_2$  and  $15.3\text{H}_2\text{O}/3.5\text{H}_2$  plasma treatment significantly decreased and the final contents after 8 min of refinement were 753 and 682 ppmw, respectively. However, these data exhibited a fluctuating trend

and not a linear graph, compared with the refining conditions of 5.1H<sub>2</sub>O and 10.2H<sub>2</sub>O/3.5H<sub>2</sub>, due to the larger Si loss with larger steam contents [26,28,30].



**Figure 3.** (a) B contents in refined Si as a function of plasma refining time with various refining conditions and (b) removal fraction of B as a function of steam content of plasma gas with 3.5 vol % hydrogen after 8 min of melting (the red dot represents the removal fraction of B without hydrogen gas).

The quantified reduction rates of B are also shown in Figure 3b. The removal fraction of B after 8 min of plasma treatment was defined as follows:

$$\text{Removal fraction of B (\%)} = 100 \times \frac{B_i - B_f}{B_i} \quad (2)$$

where  $B_i$  represents the concentration of B in the Si chips and  $B_f$  is the B content in the Si ingot after 8 min of plasma treatment. The removal fraction of B with 5.1H<sub>2</sub>O was 10.4%, as observed in Figure 3b. With an increase in the amount of added steam from 5.1 to 15.3 vol % with 3.5 vol % H<sub>2</sub>, the removal fraction of B increased linearly and the elimination rate values of the samples produced by 5.1H<sub>2</sub>O/3.5H<sub>2</sub>, 10.2H<sub>2</sub>O/3.5H<sub>2</sub>, and 15.3H<sub>2</sub>O/3.5H<sub>2</sub> conditions were 17.0%, 25.1%, and 33.5%, respectively. Many previous studies on refining Si using plasma treatment or gas blowing showed similar trends, and the authors explained that this phenomenon is related to a half-order relation of steam to the elimination rate of B [24,31]. Generally, the required purity of Si for solar application is approximately 6N–7N with a B content of under 1.0 ppmw [32]. Our results did not meet the requirements, since we added excessive amount of B to our starting Si material. However, these results indicate that our designed conditions have great potential to remove B in short amount of time.

Generally, the removal fraction of B from Si can be expressed by the pseudo-first-order equation when the concentration of steam and hydrogen is kept constant, suggested by Suzuki [25]. The rate of reaction ( $r$ ) is defined as:

$$r = -\frac{d[B]}{dt} = k_{app} \cdot [B] \quad (3)$$

where  $k$  represents the apparent rate constant ( $s^{-1}$ ),  $[B]$  is the concentration of B (ppmw), and  $t$  is time (s). The reaction rate equation can be integrated as follows:

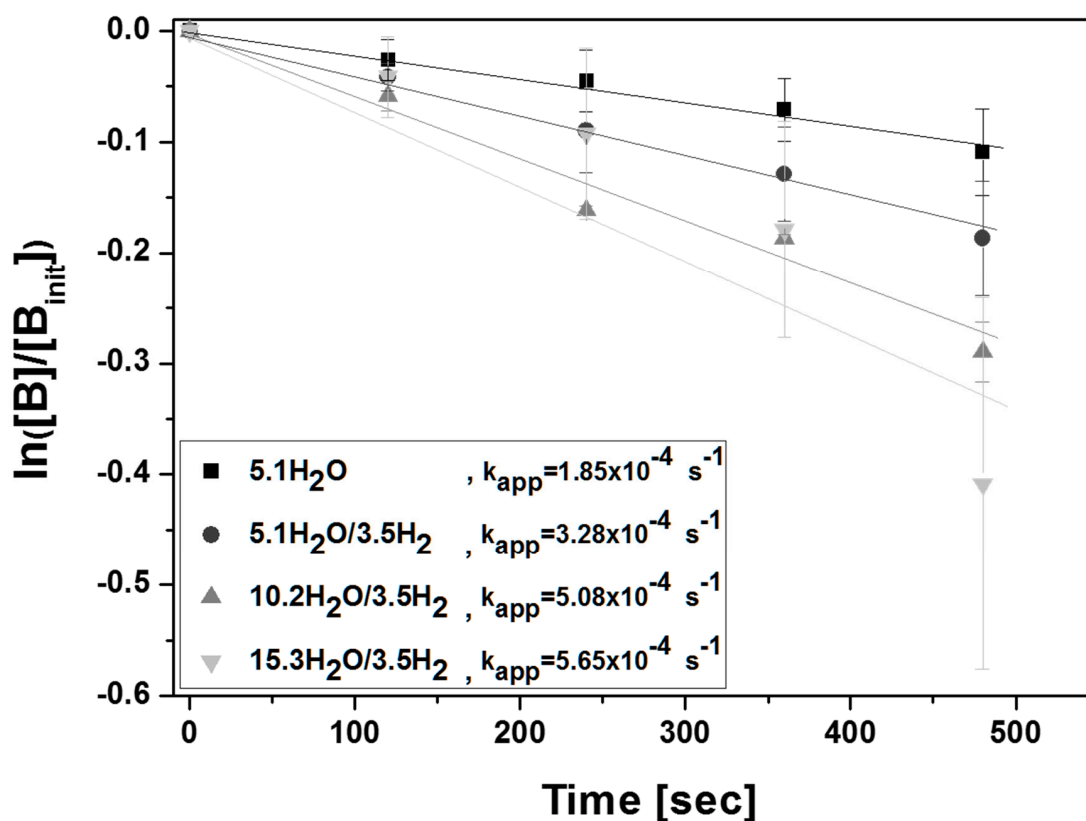
$$\ln\left(\frac{[B]}{[B]_{init}}\right) = -k_{app} \cdot t \quad (4)$$

where  $[B]_{init}$  is the initial content of B in Si.

Figure 4 presents a logarithmic plot of  $[B]/[B]_{int}$  as a function of plasma refining time for various refining conditions. The graphs correspond to the first-order rate constant. However, as mentioned

above, result of  $15.3\text{H}_2\text{O}/3.5\text{H}_2$  still exhibited a fluctuating trend and not a linear graph, due to the unstable gas flow as a result of the increase in steam and hydrogen gas and the larger Si loss with larger steam content. The calculated apparent rate constants for  $5.1\text{H}_2\text{O}$ ,  $5.1\text{H}_2\text{O}/3.5\text{H}_2$ ,  $10.2\text{H}_2\text{O}/3.5\text{H}_2$ , and  $15.3\text{H}_2\text{O}/3.5\text{H}_2$  conditions were  $1.85 \times 10^{-4}$ ,  $3.28 \times 10^{-4}$ ,  $5.08 \times 10^{-4}$ , and  $5.65 \times 10^{-4} \text{ s}^{-1}$ , respectively. To calculate the mass transfer coefficient,  $k_m$ , we obtained the reaction area (A) and volume (V) of molten Si using the diameter of the plasma torch nozzle (0.7 cm) and the density of B-doped Si, respectively (Table 1) assuming that the B reaction occurs at the area the plasma gas is impinging. The mass transfer coefficient is described as follows [24,25]:

$$k_m = k_{app} \cdot \frac{V}{A} \quad (5)$$



**Figure 4.** Logarithmic plot of  $[B]/[B_{int}]$  as a function of plasma refining time for various refining conditions.

From Equation (5), the computed values of the mass transfer coefficient for each plasma condition were  $1.89 \times 10^{-4}$ ,  $3.34 \times 10^{-4}$ ,  $5.18 \times 10^{-4}$ , and  $5.76 \times 10^{-4} \text{ m}\cdot\text{s}^{-1}$ . The trend of the mass transfer coefficient value is consistent with the rate of B elimination, and the absolute values of these data are larger than those of the Suzuki group, who investigated Si refining using plasma or other methods such as gas blowing [23–25]. These results demonstrate that plasma coupled with steam and hydrogen gases effectively removed B from Si by forming HBO from the reaction with B and active  $\text{H}_2\text{O}$  and  $\text{H}_2$ .

#### 4. Conclusions

B-doped Si from a PV solar cell module was successfully refined by thermal plasma treatment with steam and hydrogen gases. The B content in Si decreased with the use of plasma combined with steam and hydrogen gas. The rate of B elimination of  $5.1\text{H}_2\text{O}$  was 10.4 vol %; the addition of 3.5 vol %



H<sub>2</sub> gas resulted in an increase in the B elimination rate. As the steam flow rate increased from 5.1 to 15.3 vol % with constant 3.5 vol % H<sub>2</sub> gas, the rate of B elimination significantly increased, and the value of 15.3H<sub>2</sub>O/3.5H<sub>2</sub> was 33.5%. The mass transfer coefficients of each plasma condition were  $1.89 \times 10^{-4}$ ,  $3.34 \times 10^{-4}$ ,  $5.18 \times 10^{-4}$ , and  $5.76 \times 10^{-4}$  m·s<sup>−1</sup>, respectively, and these values exceeded the values reported by other groups. Therefore, this novel plasma process with steam and hydrogen gases shows potential as a method for recycling Si from PV modules by B removal.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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