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A study on the fabrication of polycrystalline Si wafer by vacuum casting method and the measurement of the efficiency of solar cell

Geun Hee Lee† and Zin Hyoung Lee*

Nuclear materials development team, KAERI, Taejon 305-600, Korea
**Department of Materials Science & Engineering, KAIST, Taejon 305-701, Korea*

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Abstract Si-wafers for solar cells were cast in a size of 50×46×0.5 mm^3 by vacuum casting method. The graphite mold coated by BN powder, which was to prevent the reaction of carbon with the molten silicon, was used. Without coating, the wetting and reaction of Si melt to graphite mold was very severe. In the case of BN coating, SiC was formed in the shape of tiny islands at the surface of Si wafer by the reaction between Si-melt and carbon of the graphite mold on the high temperature. The grain size was about 1 mm. The efficiency of Si solar cell was lower than that of Si solar cell fabricated on commercial single and poly crystalline Si wafer. The reason of low efficiency was discussed.

Key words Silicon wafer, Vacuum casting, BN coating, Si Solar cell

1. Introduction

The main motivation for developing devices of solar energy is laid on the desire to get away from fossil fuels with their adverse effect on the environment, and to replace the limited amount of them. The major reason for the low penetration of PV (Photovoltaic) today is the high cost, and its also the main reason why the solar energy has not yet been used widely in most countries.

Silicon is one of the most important fundamental materials in modern semiconductor industry. It is also very useful as the substrate material for solar cells. Conventional methods of the fabrication of Si wafer are either the slicing of Si crystals cast as bars [1-3] or the direct growing of Si sheet from the molten Si [4]. However these methods have some economical disadvantages resulting from slicing loss, limited wafer size, and difficulty of growing process. In this study, the new direct fabrication method of Si wafer for the solar cell substrate was proposed, which is the vacuum casting method [5]. Further, the reaction between molten silicon and mold (or mold coating materials) was exposed in the study as well. The casting parameters such as pressure, temperature and filling method were investigated to improve the cast wafer quality. The results from those investigations are also included in this study. The Si solar cell was fabricated by diffusion process. Its efficiency was measured under AM1.5 condition.

†Corresponding author
Tel: +82-42-868-8565
Fax: +82-42-868-8346, 8549
E-mail: wlghlee@hotmail.com

2. Experimental Background

The reaction between mold and molten silicon must be prevented by using proper mold or mold coating materials. Some researchers [6] used Si_3N_4 as coating material of graphite mold for ingot casting of poly-crystalline silicon. In this case Si_3N_4 was useful for protecting mold and easy to detach the silicon ingot from the mold. Ravishankar *et al.* [7] used $CaCl_2$ as the coating material of quartz crucible for Bridgman growth of silicon. $CaCl_2$ prevented the reaction of molten silicon with quartz mold. And the grown crystal had very large grain size over 5 cm. Celmer *et al.* [8] proposed $SrCl_2$ for the protective coating materials. Ciszek *et al.* [9] studied various die materials for silicon ribbon growth by EFG (Edge defined Film-fed Growth) method. Based on his work, the BN die was regarded as the most durable and non-wetting properties in molten silicon. In this study, BN was used as the mold coating materials for vacuum casting of silicon wafer.

3. Experimental Procedure

The experimental setup for the vacuum casting of silicon wafer is shown in Fig. 1. Silicon was melted in the graphite crucible by induction heating. Several mold and crucible forms were tested to obtain a proper filling of

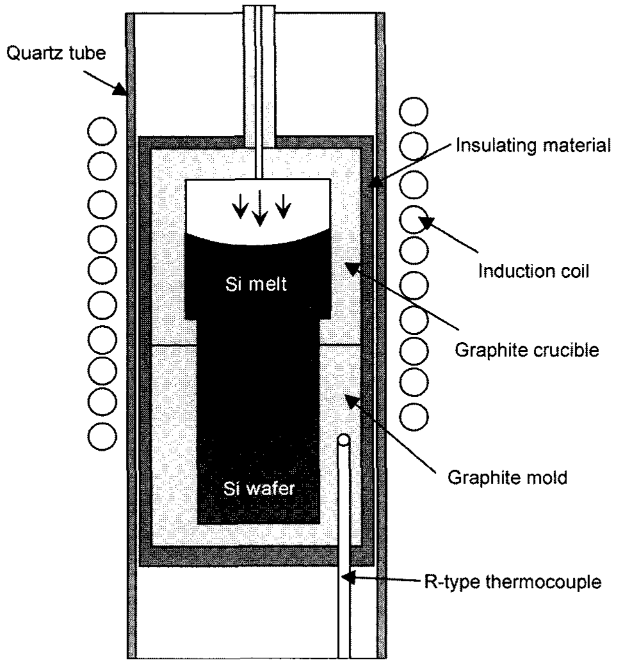

Fig. 1. Experimental setup. The Si melt was pushed into the mold cavity by Ar gas pressure.

molten silicon to the mold cavity by a pressure difference. The bottom pouring was tried first. The crucible placed under the graphite mold. However it was impossible to prevent the gas leakage through the parting line of the mold, because the mold is made of two parts. So the position and the design of crucible and mold were changed. In this work, the mold positioned under the crucible to apply proper over pressure only on top of the melt. Through the tube on the crucible cover (Fig. 1), Ar gas pressure can be applied above the silicon melt to push the molten silicon into the mold cavity. The target size of cast silicon wafer was 50×46×0.5 mm^3. The graphite mold wall was coated with BN powder. Mold temperature was measured at 40 mm from the bottom of 80 mm mold as shown in Fig. 1. Silicon of metallic or semiconductor grade was charged in the graphite crucible and heated up to 1450°C in 200 torr Ar atmosphere. After 30 min in 1450°C the molten silicon was pushed into the graphite mold and cooled in the furnace. The surface appearance and the microstructure of the cast silicon wafer was observed by optical microscopy and SEM (Scanning Electron Microscopy). The compositional analysis was conducted by using XRD (X-Ray Diffraction) and WDS (Wave-Dispersive X-ray Spectroscopy). The contamination from some impurities was analyzed by FTIR(Fourier Transform Infrared Spectroscopy). The resistivity was measured to determine the carrier concentration of Si wafer with four-point probe method.

After casting, Si wafer was polished by 0.1 μm Al_2O_3 slurry. The poly crystalline Si solar cell was fabricated on this Si wafer by diffusion process. The structure was n^+pp^+. After making solar cell, the photovoltaic efficiency(η) was measured under AM1.5 condition. The solar cell on polycrystalline Si wafer from Waker Corp. was also fabricated, and its efficiency was measured. The size of the area of solar cell was 10×10 mm^2.

4. Results and Discussion

4.1. Casting of Si-wafer by vacuum casting

The silicon wafer obtained by vacuum casting in a mold half coated with BN is shown in Fig. 2(a). The initial melt flow line from top to bottom is discernable on the left side of wafer surface. When molten Si entered the mold, the whole entrance was not uniformly filled. Because of its instability in the surface of the melt, only some parts of the melt surface broke first and flowed down the mold. The shape of this stream remained in the wafer after solidification. This line however could be removed after a mechanical grinding of approximately 100 μm depth.

For proper filling, the pressure difference and the mold temperature were very important. When the pressure was too high, the molten Si overflowed, and vice versa. In other word, when the pressure was insufficient, the melt didnt filled the mold cavity at all. So it

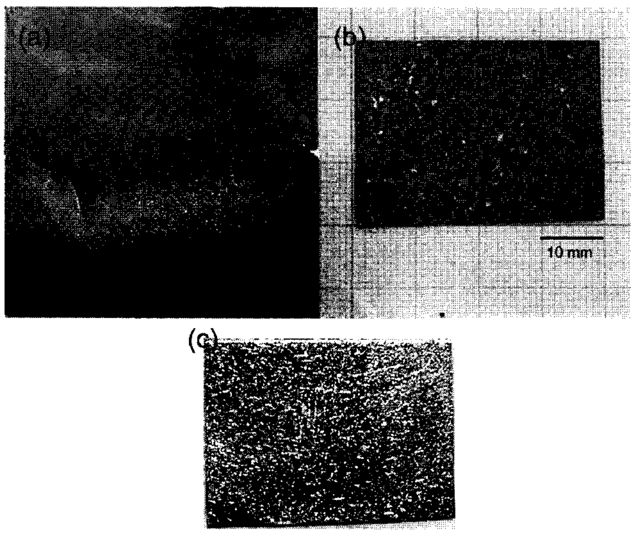

Fig. 2. Si wafer cast by vacuum casting method; (a) As cast Si wafer, (b) Si wafer after polishing and etching in 45% KOH solution for 50 sec and (c) poly crystalline Si solar cell.

was essential to achieve the proper pressure difference. The mold cavity with 0.5 mm thickness was filled with molten Si by 100~150 torr over pressure. The mold temperature is also important. In the case of a high temperature of the mold such as 1420°C, the molten Si reacted with the BN coated graphite mold and stuck together strongly. It was impossible to release the Si wafer. However at the mold temperature below 1280°C, the molten Si reacted little with the mold. It was easy to detach the Si wafer from the mold wall. There was a certain temperature gradient in the graphite mold. After several trials the measured mold temperature was controlled at below 1280°C for the prevention of the reaction with mold.

Figure 3 shows the surface morphology and the composition of the as cast Si wafer surface in BN-coated graphite mold at over 1350°C. There were tiny islands on the surface, which were identified as SiC by SEM and WDS analysis. Their diameter was about 20~30 μm. Although the graphite mold was coated with BN, the diffused carbon through the BN coating layer reacted with molten Si, and formed SiC particles on the surface. The BN powder from the coating also stuck to the surface. The XRD result shown in Fig. 4(a) confirms this result. After 1 hr ultra-sonic cleaning, the most of BN could be removed. Figure 4(b) shows this results, however the SiC was not removed. It was difficult to prevent the reaction between Si and carbon completely. The chemical etching (KOH : IPA (Iso-Propyl Alcohol) : distilled water = 1.4 : 7.7 : 90.0) was slightly helpful to remove SiC particle by etching the surface of Si wafer. It may weaken the bonding strength between the Si and the SiC particle. And the SiC particle could be removed completely by mechanical grinding with sand paper (500 mesh) for about 5min. As decreasing mold temperature to 1280°C, this SiC was not formed, so it was not detected by XRD analysis (Fig. 4(c)).

In the case of BN coating, the grain size of Si was about 1 mm (Fig. 2(b)). According to Ghosh *et al.* [10], the efficiency of solar cell would be increased with the grain size up to 100 mm, but reached saturation at about 1mm. Therefore Si wafer cast in the BN coated mold can be used well for the solar cell application depending on the grain size. The molten Si does not wet the BN substrate [11, 12].

The contamination of Si, by other impurity like carbon, is shown in Fig. 5 with FTIR analysis results. The relative peaks near wave number of 600 show the bonding of Si and C. Although these results were qualitative, it can be known that the pure Si with semiconductor grade (pure Si-S) had the highest purity by showing the lowest relative peak intensity. The Si wafer cast in the BN coated graphite mold at 1280°C (BN-1280°C-S) had more C contamination than that of pure Si. The case of BN coating at high temperature (1350°C) using metallic grade Si (BN-1350°C-M) was the worst.

From the resistivity measurement, the carrier concentration was about 10^{18} (cm^{-3}) and 10^{19} (cm^{-3}) when semiconductor grade Si and metallic grade Si were used, respectively.

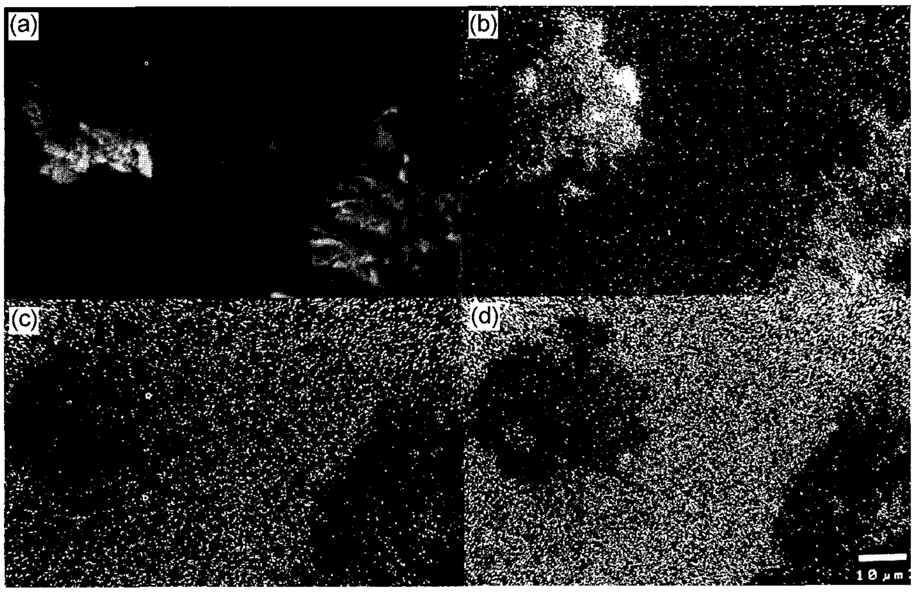

Fig. 3. SEM and WDS analysis of the Si-wafer surface cast in the BN coated graphite mold. (a) SEM image (b) C mapping (c) N mapping and (d) B mapping.

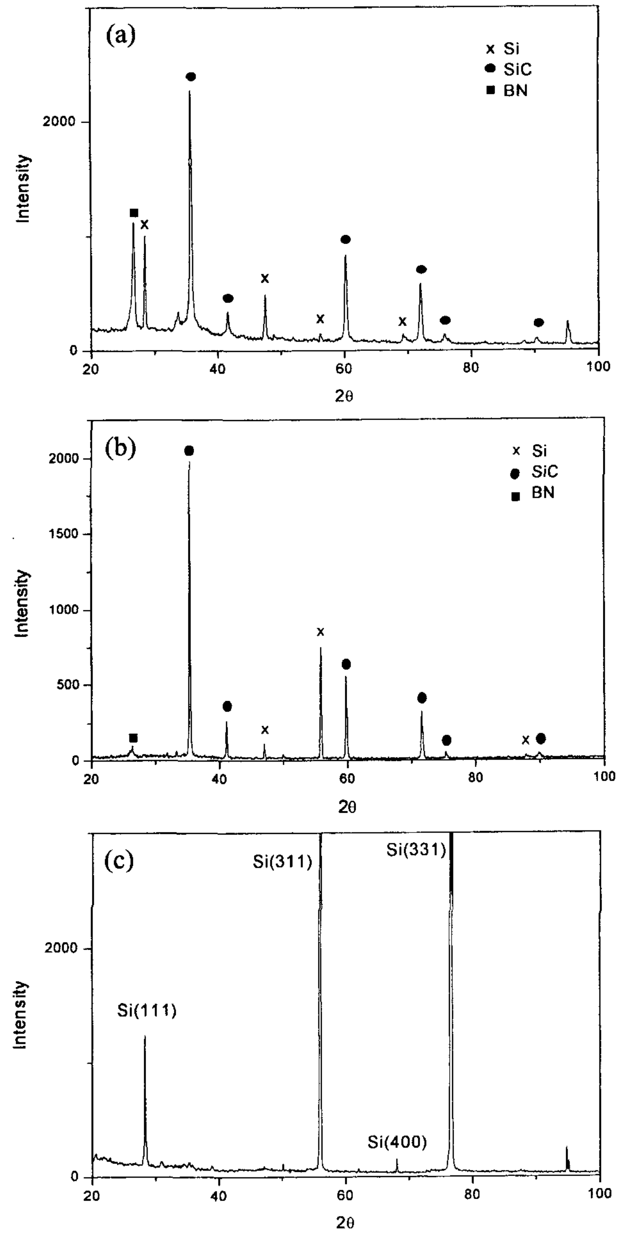

Fig. 4. XRD result of Si-wafer cast in the BN coated graphite mold. (a) As-cast Si-wafer in the graphite mold at 1350°C shows the peaks of SiC and BN (b) After ultra-sonic cleaning most of BN is removed but SiC still remains. (c) As-cast Si-wafer in the graphite mold at 1280°C.

The vacuum casting method can have the proper economical potential to reduce the fabrication cost of solar cell. The graphite mold was reused. No cutting process was involved during the entire process of a wafer fabrication. It could enable high material yield because there is no slicing loss. The automatic system for mold change, for example to rotate the molds in a multi-stage system, will make the production rate higher than that of this small scale experiment.

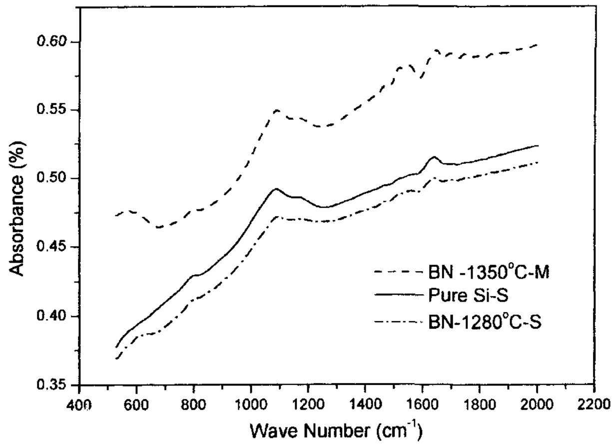

Fig. 5. Results of FTIR analysis of each Si-wafers. The C contaminations are shown in each sample near the wave number 600. There are also O contaminations in other peaks (wave number : 1100). S and M in the legend indicate the Semiconductor grade and Metallic grade of Si respectively.

4.2. Fabrication of poly-crystalline Si solar cell and Measurement of its efficiency

After casting poly crystalline Si solar cell was fabricated on this Si wafer. It was n^+pp^+ type solar cell. The

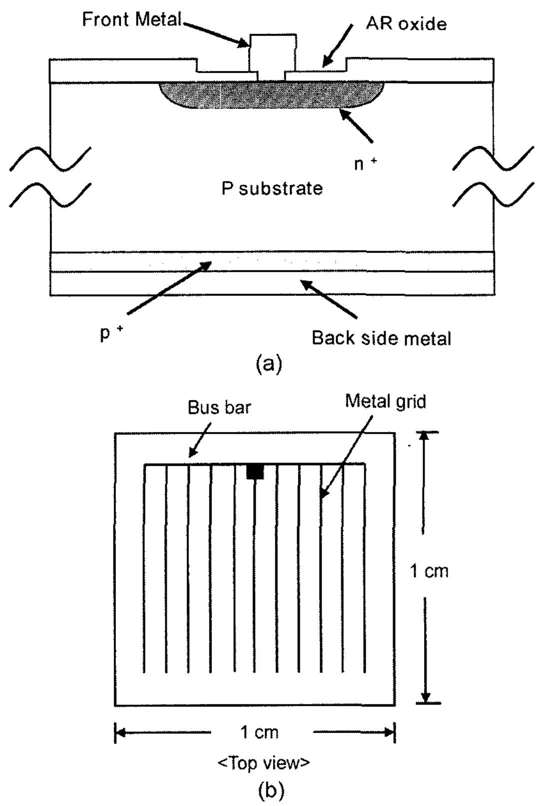

Fig. 6. Configuration of solar cell (a) solar cell structure of cross-sectional view and (b) of top view.

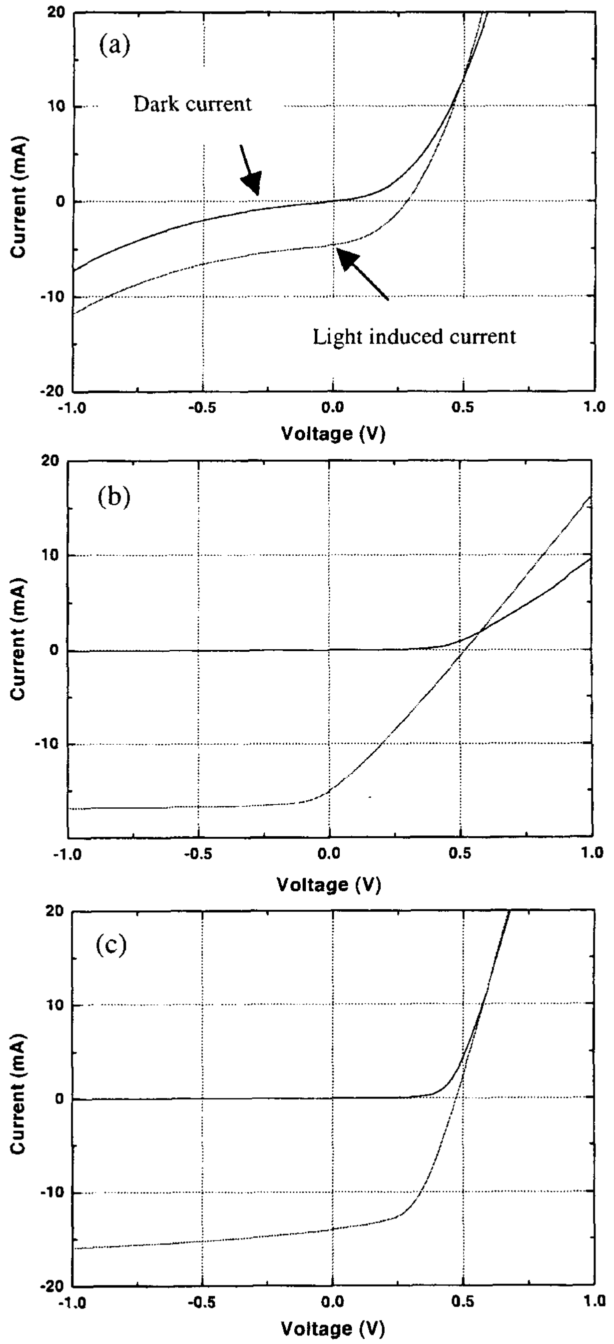

Fig. 7. I-V characteristics of Si solar cell (a) poly-crystalline Si cast by vacuum casting, (b) poly-crystalline Si from Waker Corp. and (c) single crystalline Si. The upper and lower lines in each curve indicate the dark and light induced current, respectively.

photovoltaic efficiency(η) was measured in AM1.5 condition under the solar simulator (WXS-105H). The solar cells using the commercial single and poly crystalline Si wafer with large grain size were fabricated. Its efficiency was measured to compare with that of the solar cell fabricated on the vacuum cast Si wafer. The size of the area of solar cell was 10×10 mm^2.

Figure 6 shows the configurations of tested solar cell. The cross sectional structure of solar cell was shown in Fig. 6(a). The SiO_2 layer as AR (Anti-Reflection) coating was deposited on the surface with 110 nm. The total thickness of solar cell was about 300 μm. The bus bar in Fig. 6(b) had 100 μm width and 9 mm length, and the metal grid had 50 μm width and 9 mm length. It covered the 5% of total area of solar cell.

Figure 7 shows the I-V characteristic curve of dark and photo conditions. Figure 7(a) is that of polycrystalline Si cast by vacuum casting method. It shows very low short-circuit current (I_{sc} = 4.625 mA), open circuit voltage (V_{oc} = 280 mV) and efficiency (η = 0.475%). Si solar cell fabricated on commercial polycrystalline (Fig. 7(b)) and single crystalline (Fig. 7(c)) also shows relatively lower conversion efficiency than other reported samples [13, 14]. Table 1 is the summarized data of these experiments. The one reason of inefficiency of Si wafer cast by vacuum casting will be the unskilled fabrication. Furthermore, the severe over-doping (> $10^{18}/cm^3$) of Si-wafer from BN-coating would be the other reason. The BN coating might act as the dopant of Si-wafer during casting. Although the wetting didn't occur between BN coating and Si melt, at the relatively high temperature BN can diffuse into the Si melt. The contamination over 10^{18} ($/cm^3$) was much higher concentration than that of usual solar grade Si wafer. The small grain size is another reason of poor efficiency. The grain size was about 1 mm. It was about 10 times smaller than that of commercial polycrystalline Si-wafer. This grain boundary provides the recombination center of electron-hole pair, and reduce the efficiency of Si solar cell. It will be necessary to test other coating materials in aspect of the contamination and the grain size.

Table 1
Comparison of the photovoltaic efficiency(η) of each Si solar cell

	Si-wafer cast by vacuum casting	Poly-crystalline Si-wafer (Waker)	Single crystalline Si-wafer
I_{sc} (mA)	4.625	15.23	14.07
V_{oc} (mV)	280	520	470
Fill factor	0.392	0.271	0.529
Efficiency (η : %)	0.457	0.939	3.155

5. Conclusion

A direct casting method of poly-silicon wafer was developed to reduce the cost of solar cell substrate. A mold cavity with 50×46×0.5 mm^3 in size was filled with molten Si by 100~150 torr over pressure of Ar-gas. It was important to apply proper over pressure and to control the mold temperature for a fabrication of Si wafer. With the BN coating, Si wafer had 1mm order grain size, and the contamination of carbon from the mold and coated BN was negligible at below 1280°C of the mold temperature. However the excess carrier (over doping) came from the BN coating. It made the efficiency of solar cell be much lower than that of commercial single and poly crystalline of Si solar cell. A non-contaminating, durable material to be used as mold cavity or coating are desired.

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