Journal of Korean Association of Crystal Growth
Vol. 4, No. 2 (1994) 119-130

Polycrystalline silicon films for solar cell application by solution growth

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태양전지용 다결정 실리콘 박막의 용액 성장법에 관한 연구

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Abstract To deposit silicon on borosilicate glass substrates, 18 different substrate combinations were investigated because of the difficulty of direct deposition of silicon. Successful results were obtained from Al-and Mg-treated glass and furnace annealed sputtered silicon deposited glass substrates. A continuous silicon thin film on a large area substrate was obtained in the temperature ranges from 420℃ to 520℃. These thin films might be applied to lower the cost of solar cells and solar cell modules.

요 약 저팽창 보로실리케이트 유리기판상에 직접 결정질실리콘 박막을 성장시켜 주는 것이 고순도 금속을 사용한 용액성장법으로는 어려운 관계로 18가지 다른 코팅을 유리기판상에 입혀 실험한 결과 알루미늄과 마그네슘 처리한 기판과 스퍼터링 방법으로 유리기판상에 실리콘 박막을 열처리해준 후 용액성장시켜준 기판의 경우에 양호한 결과가 나왔다. 성장온도 420℃ ~ 520℃ 범위에서 성장시킨 이 박막은 태양전지와 태양전지의 모듈가격을 낮추는데 응용될 것으로 사료된다.

1. Introduction

Many experimental work has been made to prepare silicon thin film on foreign substrates in order to inexpensive thin film solar cells [1 - 6]. The optimal solution to the problem of developing a low cost photovoltaic option appears to be to find a way of depositng a high performance photovoltaic material directly onto a supporting glass superstrate of material could be deposited directly onto glass to form a silicon thin film module as in Fig. 1, this would ultimately result in very little additional module cost above the cost of the glass. The main difficulties are the generally large thermal expansion mismatch between glass and silicon and the unsuitability of glass for high temperature deposition processes. However, these problems may be solved by lowering the silicon deposition temperature and by selecting an appropriate glass substrate.

Solution growth of silicon has become our preferred option for depositing silicon film. To be compatible with direct deposition onto glass substrate, deposition temperatures below 600℃ are required. In fact, the lower the deposition temperature, the better. Lower temperatures will enhance the refining action of deposition from solution as well as decreasing stress arising in the final film from thermal expansion mismatch effects. Hence, the lower the temperature, the less attention which has to be paid to contamination effects and the larger the choice of substrate material onto which the film can be deposited.

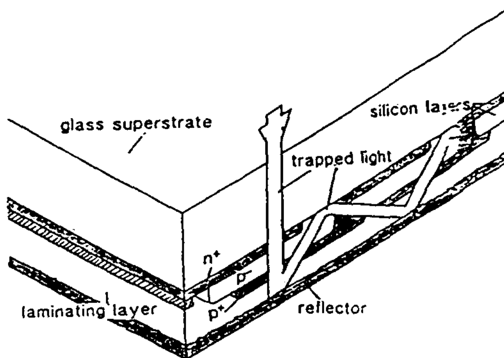

Fig. 1. Thin film polycrystalline silicon solar cell deposited directly onto glass substrate.

In the present work, solution growth of silicon on borosilicate glass substrate is described.

2. Substrate selection

Today, most windows, light bulbs and fluorescent light tubes are made of soda-lime glass. This usually contains between 8 and 12 weight percent calcium oxide (CaO) and from 12 to 17 % alkali oxide (mainly sodium oxide). These glasses have coefficients of expansion from 8 to 9×10^{-6} per℃, as do many of the lead alkali silicates [7]. B_2O_3 in quantities up to 10 ~ 15 at.% reduces the thermal expansion coefficient. Consequently, low expansion glasses have high silica content and low alkali content, with boric oxide usually present.

In the current experiment, low expansion borosilicate glass (Corning Code 7740) was selected as the substrate for solution growth of silicon. The reasons are (1) these glasses are available commercially at relatively low cost ; (2) the thermal expansion coefficient of borosilicate glass is relatively well matched with silicon (Fig. 2) [8]. This particular borosilicate

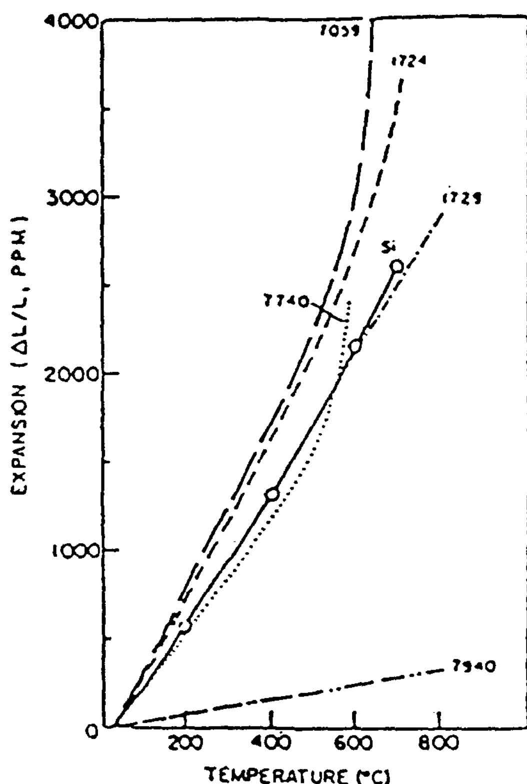

Fig. 2. Linear expansion coefficients as a function of temperature for several commercial glass substrates and silicon (Numbers : Corning code).

glass used for current work is rather simple in composition, being approximately 80.5 % SiO_2, 12.9 % B_2O_3, 3.8 % Na_2O, 2.2 % Al_2O_3, 0.4 % K_2O, but it is widely used for Pyrex brand scientific apparatus because of good durability, low coefficient of thermal expansion, good formability, and high deformation temperature [9].

3. Cleaning procedure

The cleanliness of the substrate surface exerts a decisive influence of film growth and adhesion. The choice of cleaning thchniques depends on the nature of the substrate the type of contaminants, and the degree of cleanliness required. To clean borosilicate glasses, a prepolish with precipitated calcium carbonate and a subsequent two-step etch in dilute sodium hydroxide and hydrochloric acid was recommended [9]. Other authors [10] cleaned a variety of glass, ceramic and single crystal substrates by first washing them in concentrated nitric acid, then in concentrated sodium hydroxide. The substrates were subsequently rinsed in water and alcohol and stored in vacuum desiccators. Acid cleaning cannot be used for all types of glass. This is especially true for glasses having a high barium, lead oxide content such as some optical glasses.

According to a report [11], a cold diluted mixture 5 % HF, 33 % HNO_3, 2 % Teepol and 60 % H_2O should be an excellent universal fluid for cleaning glass and silica. Various cleaning methods for glass can be found in [12].

4. Experiments and results

The aim was to deposit silicon thin film on borosilicate glass substrates by using a standard siliding boat system with gold-60 wt. % bismuth solvent. Eighteen different substrate combinations (Table 1) were employed. Because of the difficulty of direct deposition of silicon, various intermediate layers or surface texturings were introduced on the glass sub-

Table 1
Silicon on glass

Silicon deposition on:	Result
1. smooth surface glass substrate	×
2. surface roughened glass (by HF + HNO_3)	×
3. surface sand blasted glass	×
4. sand blasted + scribed glass	×
5. textured (inverted pyramid) SiO_2 +Si wafer	×
6. Al layer + textured SiO_2	×
7. CeO (1800 Å) + sand blasted glass	×
8. MgF (6100 Å) + sand blasted glass	×
9. ZnS (2200 Å) + sand blasted glass	□
10. ZnS (1450 Å) + textured SiO_2 + Si wafer	×
11. MgF (3000 Å) + ZnS (1850 Å) + sand blasted glass	×
12. Al layer (7900 Å) + sand blasted glass	△
13. sputtered silicon (5000 Å) + sand blasted glass	×
14. sputtered silicon (5000 Å) + sand blasted glass	×
15. Al (3000 Å) + sputtered Si + sand blasted glass annealed at 400℃ for 30 mins.	×
16. Mg (3000 Å) + sand blasted	△
17. Mg (3000 Å) + sand blasted glass-sinter (550℃, 2 hrs.)-etch in diluted acid-LPE	○
18. sputtered silicon (7000 Å) + sand blasted glass-sinter-LPE	○

× : No silicon deposition at all.
△ : Some possibility for application.
○ : Big possibility for application.
□ : No obvious way for application currently.

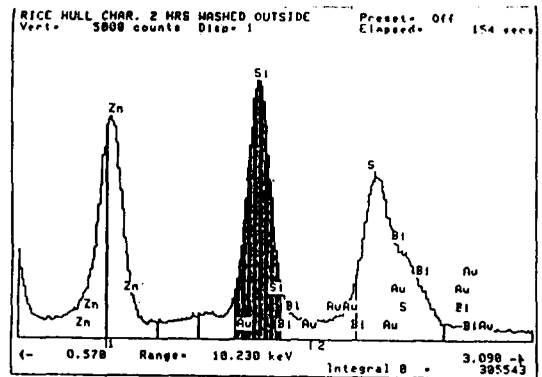

Fig. 3. EDX-analysis plot of surface layer on ZnS coated glass substrate.

strate.

In the present work, all of the intermediate layers were prepared by the vacuum evaporation method except sputtered Si and SiO_2 layers. The results of these experiments are shown in Table 1. Some positive and successful results came from these experiments, although most of the cases gave negative results.

The solution growth of silicon on the ZnS coated substrate produced quite thin (<1 μm) and smooth surface layers. However, this thin layer was completely etched away when the sample was dipped into aqua regia (1 HNO_3 + 3 HCl) to remove the remnant solvent on the thin film. Thus, another sample's surface layer was investigated by the EDX-analysis without chemical treatment. The result is shown in Fig. 3. The constituents of this surface layer on the ZnS-coated substrate are Zn, S, Si, Au and Bi as might be expected. In this condition, there is no obvious way for the application of this layer.

4.1. Deposition on Al-coated substrate

The purpose of this experiment is to explore the possibility of making a silicon layer on a glass substrate by using an Al intermediate layer as an oxygen reducing agent.

A 790 nm thick layer of Al was deposited by vacuum evaporation onto glass substrates, the surfaces of which had been roughened by sand-blasting or scribing with a diamond scriber. The apparent colour of this evaporated aluminium on the glass substrate was shiny tin-white. The role of Al in this experiments is to deplete oxygen from the surface of the glass substrate, thus making a silicon rich surface for improving wettability between the melt and the substrate. Al is one of the elements which has a higher affinity for oxygen than silicon. Its oxide formation energy (-1045 kJ/1 mol oxygen at 273 K) is much lower than that of silicon (-836 kJ/1 mol oxygen at 273 K) [13].

The Al-coated glass substrate was sintered at the growth temperature (550℃) for 2~3 hours before moving under the melt. The surface colour of this sintered Al coated layer was almost the same as the evaporated layer, but it was no longer reflective. During this sintering process, the Al layer was expected to become Al_2O_3. Next, this sintered Al-coated substrate was moved under the melt and was left for 10 ~ 20 minutes at the growth temperature. Subsequently the temperature of the furnace was increased (5 ~ 15℃ above the growth temperature-550℃) in order to induce melt-back.

This melt back process is necessary to dissolve the thin aluminium oxide layer and other surface contaminants from the glass surface, and to let them float to the top of the melt. The growth was started by cooling down the furnace. The growth temperature was from 550 ~ 400℃ with the cooling rate above 3℃/min. After crystal growth of silicon, it was observed that the initially Al coated layer had almost vanished from the glass surface. The sample was dipped into aqua regia solution to remove the remaining solvent. However, during this chemical process, most of the silicon crystallites were removed from the glass substrate. This indicates that the adhesion of silicon to glass seems poor.

As an alternative, another sample was prepared by repeating the same experimental method as above except that the substrate was not dipped into aqua regia to remove the remaining solvent. This substrate, on which silicon crystallites were deposited, was sintered at 810 ~ 820℃ for 30 ~ 60 minutes. Only after this sintering process were the samples dipped into the aqua regia solution to remove the remaining solvent. This method prevented the silicon crystallites from being removed by the aqua regia solution. These crystallites would have attached to the soft substrate surface more strongly when the glass substrate was sintered near its softening point. The nucleation pattern of silicon crystallites on the borosilicate glass is shown in Fig. 4. Some crystals are beginning to impinge on their neighbours to make a continuous layer. The crystal size varies from about 60 μm to 130 μm. These grain sizes are almost the same as obtained on appropriately coated quartz substrates in previous work [3]. In this work, which used a solution growth method, typical grain sizes ranging from 25~150 μm were reported. However, no

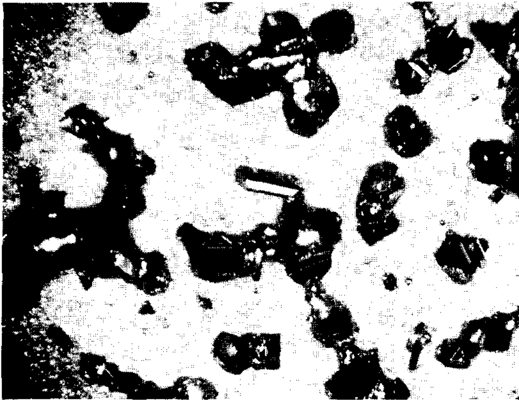

Fig. 4. Silicon nucleation pattern on Al-coated borosilicate glass Mag. ×59 (Growth temperature : 550 - 400℃).

other details of the coating materials was provided. The crystallographic orientation of silicon on this borosilicate glass is predominantly (111) as determined by crystal shape. This technique may be useful when highly doped p-type layer is required.

4.2. *Deposition on Si-coated substrate*

This substrate was prepared by initially sputtering 700 nm of silicon onto the glass substrate, the surfaces of which had been roughened by sandblasting or scribing with a diamond scriber. Samples were furnace annealed at 820℃ for 2 hours. After this annealing process, the samples were used as substrates for solution growth. The purpose of the annealing process is to make fine grain polycrystalline silicon from the amorphous silicon prepard by sputtering. The aggregated polycrystalline silicon on the sand blasted glass substrate after annealing was observed by Scanning Electron Microscope. This polycrystalline silicon was used as seeds to make continuous layers. The growth temperature was from 550～420℃ with the cooling rate above 3℃/min. The melt-back step was employed as in the previous section.

The above thin film was orginally bonded to the substrate but separated when the substrate was subjected to mechanical shock. This is primarily due to the contraction of the remnant solvent on the thin film when the furnace cools down. Since the thermal expansion coefficient of the solvent is 3 times larger than that of silicon, the solvent contraction force exceeded the thin film adhesive force to the substrate when the furnace was cooled down and the film was jolted.

The surface morphology of these layers is shown in Fig. 5. This morphology is very similar to typical Si deposition on a (111) silicon substrate (Fig. 6). The crystal type has nearly hexagonal symmetry which shows the (111)

Fig. 5. The surface morphology of Si layer on the borosilicate glass substrate. Mag. ×59 (Growth temperature : 550 - 420℃).

Fig. 6. The surface morphology of silicon layer on the (111) silicon substrate Mag. ×59.

preferred orientation. All the crystal facets seem to be aligned. Some of this growth (A in Fig. 5) would occur after the slider moved (420℃-R.T.) because some remnant melt still covered this area. No grain boundaries could be discerned after etching in Sirtl etch [14].

The entire growth morphology appears to be terrace growth. This growth may be due to the roughened surface of the glass substrates.

The circular area (B in Fig. 5) was probably due to the presence of depressions or other impurities on the substrate which seem to disturb the crystal growth front.

Even though the surface was treated as a silicon rich surface, the borosilicate glass substrate is composed of many compounds (e.g., B_2O_3, Na_2O, Al_2O_3, K_2O).

The crystal size is much larger than the result reported in reference [3] and also larger than that of the Al-coated substrate. No influence from the original silicon coating of the substrate could be observed. It might be concluded that the polycrystalline silicon which was supposed to act as a seed merely contributed to the formation of the silicon rich layer of the galss substrate similar to a pure silicon substrate. If the polycrystalline silicon acted as a seed, the surface morphology of the thin film should be influenced by it. However, no evidence could be found for this seeding effect in Fig. 5. This silicon rich layer may act merely to improve wettablility between the melt and substrate.

Furthermore, the surface colour where sintered polycrystalline Si was deposited was almost the same as Mg-treated glass substrate described below. This indicates that the aggregated polycrystalline silicon was oxidized. By employing the melt back step, the silicon oxide layer might have been largely removed bofore crystal growth.

4.3. *Deposition on Mg-treated substrate*

The affinity of magnesium for oxygen (-1162 kJ/1 mol oxygen at 273 K) [13] has been used in several applications. These include the de-oxidizing of metals, such as Cu and brass, and as an oxygen "getter" in thermionic valves. A number of metals such as thorium, titanium, uranium and zirconium are prepared by thermal oxidizing reaction with magnesium [15, 16]. This affinity could be used for reducing the oxide at the glass surface, thus making a silicon rich layer.

The Mg (300 nm thickness) was deposited on the sand blasted or scratched surface of a borosilicate glass substrate followed by annealing the sample at about 500℃ for two hours. After cooling the furnace, the samples were

taken out. After this annealing step, the colour of the surface of the sample where Mg was deposited was dark brown. After dipping the samples in diluted nitric acid for a few seconds, the surface colour changed to almost yellow. Judging from the EDX analysis result (Fig. 7), and the measurement of the layer refractive index by ellipsometry, this yellow coloured layer appears to be a silicon rich oxide layer (SiO_x). The growth temperature was from 550 ~420℃ with a cooling rate above 3℃/min. The melt-back step was employed. Fig. 8 shows the surface morphology of the silicon layer grown on Mg-treated borosilicate glass substrate. This is very similar to the morphology of Si grown on Si-coated substrate.

The surface undulation is very obvious. Roughened glass surface would be one of the reasons for this rough surface morphology. The semi-circle area was formed probably with the same reason as described for the previous silicon-coated substrate. The crystal growth habit of the film shows mainly the (111) preferred orientation confirmed by X-ray diffraction.

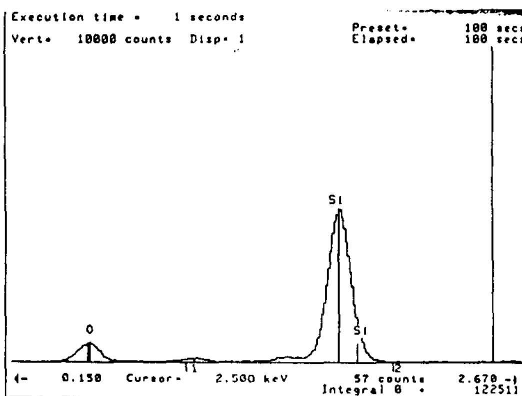

Fig. 7. EDX-analysis plot at 6 keV of Mg-treated glass surface.

5. Discussion of results on glass

The surface morphology of layers grown on Mg-treated glass substrate is almost the same as that of the Si-coated substrate. These results seem to come from the following factors:

1. The same amorphous glass substrates, solvent and growth conditions are used in both cases. The surface of these two substrates was roughened by sandblasting or by scribing with a diamond scriber.

2. These amorphous glass substrates would be expected to exhibit only weak interactions with the deposit and exert little influence on the crystallographic structure of the deposited films;

3. Both these two substrates have similar silicon rich surfaces. One is made by employing a powerful oxygen reducing metal (Mg), and the other is made by depositing amorphous silicon and subsequently sintering to make polycrystalline Si crystals. The crystal grain size would be expected to be very small (few hundred Å).

Figs. 5 and 8 show that (111) orientation is the preferred orientation on the glass substrates, confirmed by X-ray diffraction. Several different seed planes are expected to be present on the surface treated glass substrates. This solution growth of Si on the glass substrates may be treated as the same as conventional Czochralski (CZ) growth. The (111) planes are most closely packed in silicon lattice. In general, the crystal planes that grow most

slowly are those with the closest packing [17]. The closest packing plane would be the planes to expand laterally along interfaces.

Even though there were some (110), (100) planes on the surface treated glass substrates as Si seed area, these planes were etched quickly compared to (111) planes during the melt-back. Eventually, only nucleation sites of (111) orientation would be distributed over the surface. This may be attributable to faster etch rate of (100) and (110) plane, as previously noted. For example, a commonly used orientation-dependent etch for silicon consists of a mixture of KOH in water and isopropyl alcohol. In this solution at 80°C, the ratio of etch rates for (100), (110) and (111) planes is 100 : 16 : 1 [18].

Some factors that influence nucleation of silicon of glass substrates are as follows.

Firstly, supersaturation and high silicon content are important in encouraging nucleation on glass.

In the present work, the cooling rate was above 3°C/min. This fast cooling rate is sufficient to induce supersaturation of the solvent and encourage silicon nucleation on the glass substrate.

As an alternative, the supercooling method was also employed to induce supersaturation of the solvent. In the work described here, the solvent was cooled by 20°C to 30°C before contacting the glass substrate. No melt-back was employed in this experiment. This inital supercooling places the solvent in a supersaturated state. Following this, the substrate was moved under the solvent and subsequently the cooling rate was above 3°C/min. after contact with the substrate. The surface morphology of these deposited layers is the same as Fig. 8.

The silicon solubility in Au-60 wt% Bi solvent is about 2.2 at% at 414°C, 4.5 at% at 513 °C and 5.9 at% at 613°C. Compared to tin solvent (2 at% at 950°C), this alloy has a high content of silicon at even much lower temperature.

Secondly, surface treatments probably just improved wettablility between the melt and the substrate. Good wetting is a prerequisite condition for fabricating continuous layers.

In the present work, it was found that both Mg-treatment and Si-coating on the surface of the glass substrates was a more effective method than an Al-coating treatment to fabricate large Si crystals. The surface preparation needs to produce a silicon rich condition as much as possible in order to ensure the growth of a continuous silicon crystal layer on the glass substrates.

Fig. 8. The surface morphology of Si layer on the Mg-treated borosilicate glass substrate (Growth Temperature : 550-420°C) sample # EG-37.

In conclusion, continuous silicon thin films on glass substrates were successfully deposited in these experiments. However, better bonding between thin film and substrate would be desirable. The main reasons for the separation of the thin film from the substrate observed in this work are due to the remnant solvent on the thin film. The contraction force of the solvent exceeded the thin film adhesive force and the films separated from the glass substrate on cooling. This is because the thermal expansion coefficient of solvent is more than 3 times that of silicon and the solid solvent layer is quite thick.

6. Comments on growth apparatus

One problem was found to occur throughout the whole of this work. The wiping action of the slider in the graphite boat was not satisfactory even though elaborate clearance adjustments of the slider bar to prevent leakage of molten melt were made.

This phenomenon was present, to varying degrees, for silicon deposition on silicon substrate, sapphire substrate and glass substrate. In the case of other work [19,21], remnant solvent was reported. These groups removed this excess metallic solvent (Sn) by dipping the samples in the aqua regia (1 HNO_3 + 3 HCl). In the present work, this single chemical process for the removal of remnant solvent (Au-60 wt% Bi) usually takes 2 ~ 3 hours. Also, in other techniques such as dipping [20] and tipping [22] methods, remnant solvent could be found.

Among the many techniques investigated to date, the only apparatus which can remove remnant solvent completely from the substrate is a centrifugal technique which utilizes centrifugal forces for the transport of the solution [23]. This centrifugal LPE growth technique has proven to be a convenient way for producing layers with planar interfaces. However, this technique needs a more complicated system in comparison with the above three techniques. As described above, all the techniques for LPE growth have some advantages and disadvantages. For the preparation of single layers, dipping and tipping methods are suitable.

For silicon single layer deposition on glass substrate, probably the dipping method is the most effective way even though some remnant solvent would probably be found in the bottom edge of the substrate as reported elsewhere [20]. Dawson [24] reported that smooth GaAs films from which the melt drained completely as the substrate was withdrawn were grown by using the dipping technique. The greatest use is made of gravity and surface tension for complete drainage when the melt and substrate are separated after growth by withdrawing the substrate through the top surface of the melt [24]. Baliga [25] also indicated that one of the advantages of this technique is the avoidance of the mechanical problem of a sliding boat arrangement. Judging from the above situation, a dipping system may be more suitable for investigating the growth of silicon layers on glass substrates.

7. Conclusion

To deposit silicon on borosilicate glass substrates, 18 different substrate combinations were investigated because of the difficulty of direct deposition of Si. Successful results were obtained from Al-and Mg-treated glass and glass onto which furnace annealed sputtered silicon has been deposited. Continuous large area silicon thin films were obtained at lower temperature. The role of the deposited Al and Mg layers was to reduce oxide from the glass surface to produce silicon rich layers at this surface.

However, these thin films were easily separated from the glass by physical shock. This is primarily because of the remnant solvent contraction on the thin film when the furnace cools down because the thermal expansion coefficient of solvent is larger than 3 times than that of silicon. The contraction force of the solvent exceeded the thin film's adhesive force causing separation upon jolting. Better bonding between thin film and substrate would be desirable. The results of this research could contribute significantly to the development of low cost photovoltaic cells and also silicon-on-insulator (SOI) technology.

Acknowledgements

This work was supported by the Australian National Energy Research, Development and Demonstration Program and the New South Wales Department of Minearals and Energy. The Center for Photovoltaic Devices and System is supported by the Australian Reaearch Council Special Research Centers Scheme and Pacific Powers.

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