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Solution growth of polycrystalline silicon on Al-Si coated borosilicate and quartz glass substrates for low cost solar cell application

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저가태양전지에 응용을 위한 용액성장법에 의한 Al-Si층이 코팅된 유리기판상의 다결정 실리콘 박막성장에 관한 연구

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Abstract We investigated solution growth of silicon on borosilicate and quartz glass substrates in the temperature range of 800℃~520℃. A thin Al-Si layer evaporated onto the substrate serves to improve the wetting between the substrate and the Al/Ga solvent. Nucleation takes place by a reaction of Al with SiO_2 from the substrate. We obtained silicon deposits with a grain size up to a few 100 μm. There was a perferential (111) orientation for the case of quartz glass substrates while there is a strong contribution of other orientations for the deposition of Si on borosilicate glass substrates.

요 약 보로실리케이트 유리기판과 석영기판을 사용하여 800℃~520℃의 온도 범위에서 용액 성장법에 의한 다결정 실리콘 박막의 성장에 관해 조사하였다. 기판상에는 용액과의 젖음성을 좋게 해주기 위해 박막의 알루미늄층과 실리콘층이 증착되었으며, 용매로는 알루미늄과 갈륨의 합금을 사용하였다. 핵생성은 기판의 표면에서 알루미늄과 실리콘옥사이드와의 반응에 의해서 일어난다. 결정립 크기가 수백 마이크론까지 이르는 실리콘을 얻을 수 있었으며, 석영기판의 경우에는 보로실리케이트 유리기판보다 강한 (111) 우선 성장 방향을 보여주고 있다.

1. Introduction

A lot of experimental work has been done to prepare polycrystalline silicon thin films on foreign substrates in order to fabricate inexpensive thin film solar cells. The present status of crystalline Si thin film solar cells is described in two recent overview articles [1,2]. Substrate materials can be classified as high temperature resistant substrates such as graphite, quartz or ceramics and low temperature substrates such as glass. While polycrystalline Si thin film solar cells with efficiencies around 15 % have been realised using high temperature processing, no solar cells have yet been realised on commercial float glass. Glass is of special interest as a foreign substrate material for solar cell applications, since it is (i) cheap, (ii) transparent, (iii) insulating and (iv) chemically inert. It thus allows for the use as a supporting superstrate of monolithically interconnected solar cells. The drawback of glass as a substrate material is it's low strain point of typically around 600℃. In order to deposit Si at low temperatures, liquid phase epitaxy (LPE) has attracted considerable interest during the last years. Silicon grown from the liquid phase has superior quality [3] and solar cells with efficiencies up to 14.7 % have been made from epitaxial Si grown on monocrystalline Si substrates [4]. Solution growth of ploycrystalline Si on foreign substrates, however, is still in a development stage. The deposition of large Si grains on glass substrates at temperatures below 800℃ has recently been demonstrated by other authors [5, 6]. In these experiments, Si-particle seeded growth led to the formation of isolated Si grains and Si deposition on glass substrates coated with amorphous Si led to the formation of Si deposits with 50 μm grain size. Solution growth on bare and sandblasted glass at temperatures near the softening point of the glass led to the formation of deposits with grain sizes ranging from 50~350 μm.

Earlier work by other authors using chemical vapour deposition indicated [7,8], that a grain size enhancement of the crystallising semiconductor material can be obtained by introducing liquid intermediate layers, such as Sn, Pb, In, Bi or Tl on insulating substrates. With the molten surface of such an interlayer on a rigid substrate, crystallites were about an order of magnitude larger than without interlayer. The high surface mobility of adatoms in a liquid film facilitates the aggregation of the atoms in a cluster and subsequent cluster coalescence. Thus it seems interesting to employ an interlayer in order to improve the nucleation of Si in the case of solution growth.

Our work aims at the deposition of Si at comparatively low temperatures on glass substrates. The present paper describes the solution growth of polycrystalline silicon films on borosilicate and quartz glass substrates. While we recently published some of our results on quartz glass substrates [9], we present here new results on the deposition of Si on borosilicate glass and compare the results on both types of substrates. In this series of experiments we use growth temperatures in the range of 800~520℃. The surface substrates is coated with a thin Al-Si alloy layer prior to the solution growth process. This interlayer improves the wetting between the solvent and the

surface of the substrate and provides a silicon rich surface.

2. Substrate preparation

We use quartz glass and borosilicate glass as substrates. While quartz glass consists of pure amorphous SiO_2 and has a high strain point of $T_S = 1100℃$ [10], Duran 8330 glass consists of 86 % SiO_2, 13 % boric acid and 1 % calcium and sodium compounds and has a strain point of $T_S = 550℃$. Amorphous silicon is initially deposited onto the substrates by electron beam gun evaporation, followed by the deposition of aluminium by high vacuum evaporation. The rate of evaporation is 2 Å/s and 60 Å/s, respectively for Si and Al. The Al-Si alloy system exhibits a eutectic point of 577℃ and 12.2 at% Si content. We deposit 220 nm of Si and 500 nm of Al and thus obtain a hyper-eutectic composition of about 28 at% Si. This Si content corresponds to the solubility of Si in Al at the temperature of 800℃ used during the annealing process of 30 min in hydrogen ambient prior to the solution growth process [11].

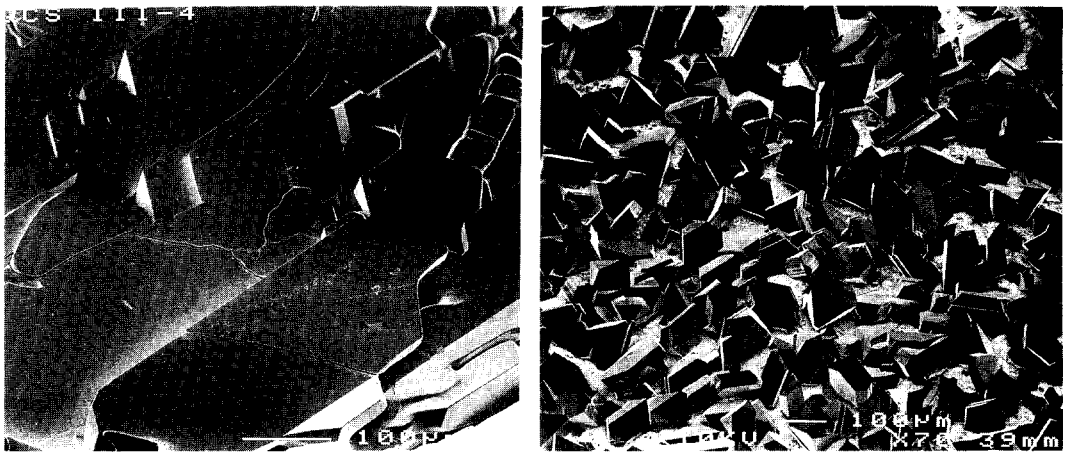
3. Solution growth process

The solvent alloy is prepared from Al and Ga of 4 N purity and 6 N purity, respectively. The silicon solubility of the 10 at% Al/Ga alloy is 2.6 at% at 700℃ and 6 at% at 800℃ [12]. Using a lower Al content in the solution results in a bad nucleation, while a solvent with a higher Al content attacks the graphite boat. Growth takes place in a tipping boat, in which the solution-substrate contact is achieved by tipping the solvent onto the substrate [13]. In order to enhance the wetting of the substrates by the solvent, we use a graphite cover on top of the solvent. Details of the growth process are outlined in a recent publication [9].

4. Results

4.1. Growth morphology

Fig. 1 shows scanning electron micrograph plan views of our samples. By deposition Si in the temperature interval of 800℃ to 765℃, large and flat Si grains have formed on a part of a quartz glass substrate as can be seen in Fig. 1a. These grains extend a few 100 μm with a morphology typical for (111) faceted crystallites. The occurrence of (111) oriented crystallites can be expected due to the fact that the (111) faces have the lowest surface energy in the silicon structure. The orientation of the Si grains varies over the sample surface. During cooling of the furnace, cracks occur between the deposited Si and the quartz glass substrate. These cracks are visible on the surface of the large crystallites depicted in Fig. 1a and are a consequence of the large difference in the coefficients of the thermal expansion of Si and quartz of $4.3 \times 10^{-6}/℃$ [14] and $0.5 \times 10^{-6}/℃$ [10] respectively at 800℃. Fig. 1b shows impinging Si grains on a Duran glass substrate using a growth temperature interval of 700℃ to 520℃. We obtain grain sizes exceeding 100 μm, however, the surface mor-



(a) (b)

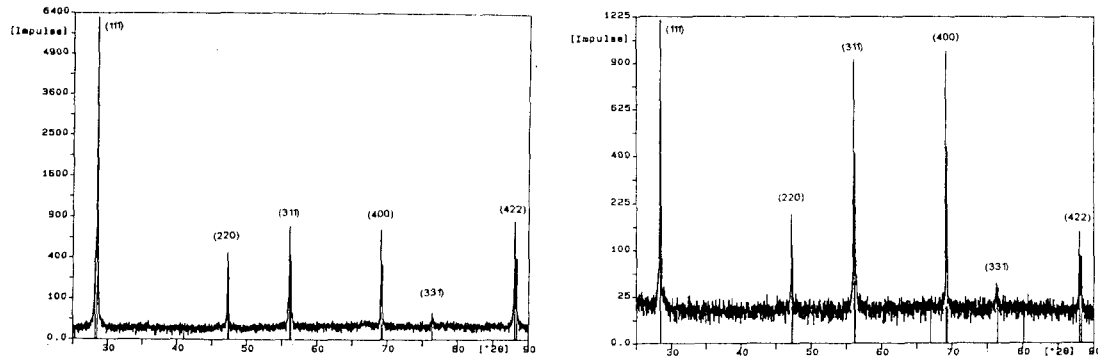
Fig. 1. Plan view of Si deposited on Al-Si coated substrates. Low magnification scanning electron micrograph. Growth from 10 at% Al/Ga solution. (a) Deposition on quartz glass, growth temperature interval from 800 to 765℃, initial supersaturation 5℃, cooling rate 0.3℃/min. (b) Deposition on Duran glass substrate, growth temperature interval from 700℃ to 520℃, initial supersaturation 20℃, cooling rate 1.5℃/min.

phology is very rough. At some areas we also observe needles in various orientations relative to the surface. The development of needles in the Al-Si system has already been explained by other authors [15].

The occurrence of crystallites with a (111) orientation parallel or near parallel to the substrate surface has been confirmed on our samples by X-ray diffraction measurements. Fig. 2 shows a comparison of the X-ray diffraction spectra obtained from Si grown on the two substrate types. While the (111)-peak is dominant for Si deposited on quartz glass, as can be seen from Fig. 2a, grains formed on Duran glass show strong contributions of (220), (311) and (400) peaks in addition to the (111) diffraction peak, see Fig. 2b. It should, however, be emphasized, that no strict quantitative conclusions can be drawn from these spectra, since the surface morphology of the sample is very rough. Shading of the incomming beam caused by large crystallites may influence the measured peak intensity ratios. A quantitative analysis of the grain distribution would require a planarisation of the Si surface. This is not possible at the present stage due to an insufficient adhesion of Si to the substrate.

4.2. Substrate-Interlayer-Solution interaction

The deposition of an Al-Si layer prior to the solution growth process and the addition of Al to the Ga melt improve the wetting between the solvent and the substrate. This is due to a chemical reaction between the solvent, the interlayer and the substrate [9]. Fig. 3a shows a cross section of a part of the sample depicted in Fig. 1a. Beneath the deposited Si there is an area of chemical reaction between the solvent and the substrate that extends up to approxi-

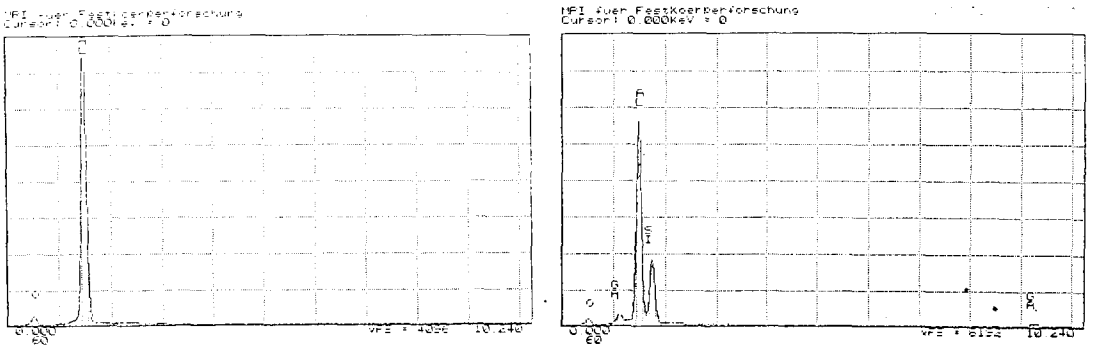


(a) (b)

Fig. 2. X-ray diffraction spectra of Si grown from a 10 at% Al/Ga solution. (a) Spectrum of Si grains deposited on quartz glass substrate. Largest diffraction peak originates from grains oriented in a (111) orientation, growth temperature interval from 800 to 745℃, initial supersaturation 10℃, cooling rate 0.4℃/min. (b) Spectrum of Si grains deposited on Duran glass substrate. Apart from the (111) oriented grains, there is a strong contribution of other crystallographic orientations like (220), (311) and (400). Growth from 10 at% Al/Ga solution, growth temperature interval from 700 to 665℃, initial supersaturation 5℃, cooling rate 0.3℃/min.

(a) (b)

Fig. 3. Cross sections of silicon films grown on quartz glass from 10 at% Al/Ga solution, cleaved samples. Scanning electron micrograph. (a) The brighter and darker areas directly underneath the Si result from a reaction of the solvent with the substrate. Growth temperature interval from 800℃ to 765℃, initial supercooling 5℃, cooling rate 0.3℃/min. (b) In this case, the Al-Si interlayer has not significantly changed its thickness of 0.75 μm. Area of the cross section polished after cleaving. Growth temperature interval from 700℃ to 580℃, initial supercooling 15℃, cooling rate 1℃/min.



(a) (b)

Fig. 4. Energy dispersive X-ray analysis (EDAX) of the areas between solution grown Si and the quartz substrate shown in Fig. 3. (a) The brighter area contains Al and O. (b) The darker area contains a compound of Al, Ga, Si and O.

mately 100 μm into the substrate and is subdivided into a dark and a bright area. Extensive energy dispersive X-ray analysis (EDAX) shows, see Fig. 4, that there is -independent of the substrate type- a tendency for Si to nucleate in those areas, where the Al_2O_3 content of the interlayer is larger than the SiO_2 content, while there is no strong perference of chemical composition in areas with no Si nucleation. The presence of Al both in the solution and on the surface of the substrate plays an important role in reducing the oxygen from the surface of the substrates. Aluminium is one of the elements which has a higher affinity for oxygen than silicon. According to other authors [16], an reaction between aluminium and silica occurs below the melting point of aluminium with the formation of aluminium oxide and silicon. The activation energy for the reaction decreases at the melting point of the aluminium, and a volatile oxide, probably Al_2O, is formed. Gallium also has the ability to reduce oxygen from the surface of silicon dioxide at a temperature as low as 800℃ [17]. A reaction between the pre-deposited Al-Si thin layer and the substratre is almost negligible at temperatures around 700℃, as can be seen from Fig. 3b. Here, the thickness of the interlayer between the pre-deposited Al-Si and the substrate after solution growth is 0.75 μm. This sample is grown at a temperature interval from 700℃ to 580℃. Unfortunately it was not possible up to this point to achieve a continuous nucleation of Si on the whole area of the interlayer.

5. Conclusions

We have deposited silicon on borosilicate and quartz glass substrates containing crystallites of a few 100 μm diameter using solution growth with a 10 at% Al/Ga alloy as a solvent in the temperature range of 800℃ to 520℃. The wetting between the substrate and the solvent has been dramatically improved by the pre-deposition of a thin Al-Si layer on the sub-

strate prior to the solution growth process. While for Si grains deposited on quartz glass the (111) orientation is dominant in the X-ray diffraction spectra, a mix of orientations is revealed in case of Si grains on borosillicate glass substrates. The development of a relatively thick interlayer between the solution grown Si and the quartz substrate during the growth process is due to the formation of an Al-Ga-O-Si compound. The large grain size obtained in this study make the solution growth process very attractive for solar cell application. However, at this stage of the investigations the control of the grain morphology is still insufficient for the fabrication of pn-junctions for solar cell manufacturing.

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