J. King Saud Univ., Vol. 15, *Eng. Sci.* (2), pp. 235-248, Riyadh (1423/2003)

Crystallization of PECVD-deposited Amorphous Silicon Thin Films Using the Aluminum-induced Crystallization Technique

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(Received 14 November, 2001; accepted for publication 19 March, 2002)

Abstract. The investigation of polycrystalline silicon made on glass and carbon coated nickel substrates by aluminum-induced crystallization of amorphous silicon (a-Si) is reported. Aluminum was sputtered onto a-Si films deposited in an ultra-high-vacuum plasma-enhanced chemical vapor deposition (PECVD) system to form Al/a-Si substrate structures. These samples were then vacuum annealed for 30 min. at temperatures in the range 150°C -350°C. X-ray diffractometry (XRD) and transmission electron microscopy (TEM) were utilized to determine the crystallization temperature. Annealing at 200°C resulted in the formation of crystalline Si as observed by TEM, and at 275°C as observed by XRD. These different results obtained by these two techniques are discussed and explained. Scanning electron microscopy (SEM) was used to study the surface morphology. SEM pictures of the interacted film surface of Al/a-Si structures annealed above the crystallization temperature clearly show hillocks or bumps distributed all over the surface. The presence of these hillocks or bumps after annealing at 275°C and above confirms that the a-Si has been crystallized.

Introduction

The crystallization of amorphous silicon (a-Si) is increasingly gaining interest for polycrystalline silicon devices such as thin film transistors (TFTs) and thin-film solar cells [1,2]. In relation to solar cell devices, the crystallization of a-Si offers the opportunity for using low temperature, and therefore low-cost substrates which is vitally important for the reduction of the overall costs of solar cells. However, most attention in the field of crystallization has been given to solid phase crystallization (SPC) [3, 4] and laser crystallization (LC) [1, 5]. But SPC suffers from long annealing times and rather high temperature (~ 600°C, which is still too high for large-area substrates) while laser

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crystallization remains an expensive and complex process. Due to these problems, metal-induced crystallization (MIC) has recently been investigated as an alternative crystallization process for thin-film device fabrication [6-9], although the interaction of metal and a-Si has been studied for many years. Aluminum-induced crystallization (AIC) is one of the most techniques because it has the following advantages: simple processing, process temperature below 600°C, standard industrial fabrication technique, short crystallization time, and also due to the fact that Al has a low resistivity and a good adhesion to a-Si [10-13]. Regarding the crystallization temperature, using AIC, Haque et al. [11] reported as low as 150°C for a-Si:H. It has also been shown that AIC of a-Sibelow the eutectic temperature is a solid phase process [14]. In this work, AIC of a-Si has been investigated in the form of Al/a-Si substrate structures for a wide range of annealing temperatures. The crystallization process has been investigated by three different techniques, namely X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM).

Experiments

Intrinsic amorphous silicon (a-Si) films of approximately 50nm thick were deposited onto carbon coated nickel substrates using an ultra-high-vacuum plasma enhanced chemical vapor deposition (PECVD) system. After deposition of the a-Si films, the samples were transferred to another chamber where a 50nm thick film of Al was sputter deposited over the a-Si film, using the same system without breaking the vacuum. The thicknesses of both the a-Si and the Al were intentionally kept low to enable us to view the structure under TEM. On the other hand, another set of substrates were used for XRD and SEM. Corning 7059 glass was used for this purpose. The a-Si and Al thicknesses on the glass substrate were 300nm and 200nm, respectively. In all the experiments, the base pressure, sputtering pressure, substrate temperature and rf power density were maintained at $5x10^{-8}$ torr, 500 mtorr, 240°C and 2 W/cm^2, respectively, except the substrate temperature was kept at 40°C during Al sputtering. These nickel and glass substrates were then annealed in vacuum (2 mtorr) at 150°C, 200°C, 250°C, 275°C, 290°C, 300°C or 350 °C for 30 minutes in a clean optically heated quartz tube furnace. A Phillips model A Jeol 100Cx transmission electron microscope (TEM) was used to observe the microstructure and electron diffraction pattern (EDP). X'pert system using a pw 3710 diffractometer control unit was used for XRD measurements. Cu K_α radiation was provided by a rotating anode x-ray source operating at 45 kV and 40 mA. X-ray diffraction spectra were taken both under regular θ-2θ and thin- film optics configurations (glancing-angle, parallel-beam geometry). Under the thin-film optics configuration, a 2θ-only scan was performed at a very small fixed θ value of 2.5^o. A Xenon-filled proportional counter detector was used for data collection in both configurations. A Hitachi (Model S-2300) scanning electron microscope (SEM) was applied to analyze the surface morphology.

Results and Discussion

Figures 1-6 show TEM electron diffraction patterns (EDP) of the as-deposited and annealed films. For every annealing temperature, the annealing time was fixed at 30 min. The micrographs and halos in the ED pattern clearly show the amorphous nature (short-range order) of the as-deposited films, as well as those annealed below 200°C. At 200°C, the ED patterns show that crystallization has started in the samples. The radiuses of the circular EP patterns for the polycrystalline silicon were indexed and found to correspond to the d-spacing of silicon corresponding to the orientation of (111), (220), (311), (400), and (331) crystal planes. At higher annealing temperatures the rings became very sharp, superimposed with a certain dot pattern. This may either be due to growth of individual crystal grains to a relatively larger size, relative to the electron beam size, or the development of a preferential orientation of the Si crystallites. A new ring appeared in the EDP after annealing the Al/a-Si substrate samples at 350°C or higher. This may be due to the formation of an oxide layer on the exposed Al surface.

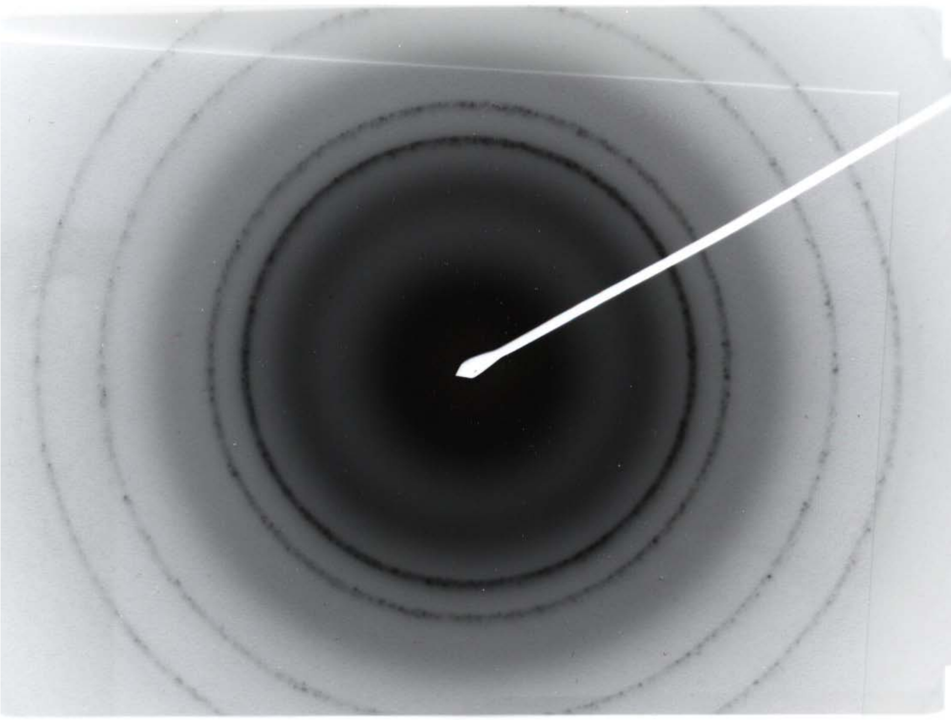

Fig. 1. Electron diffraction pattern of as-deposited Al/a-Si film.

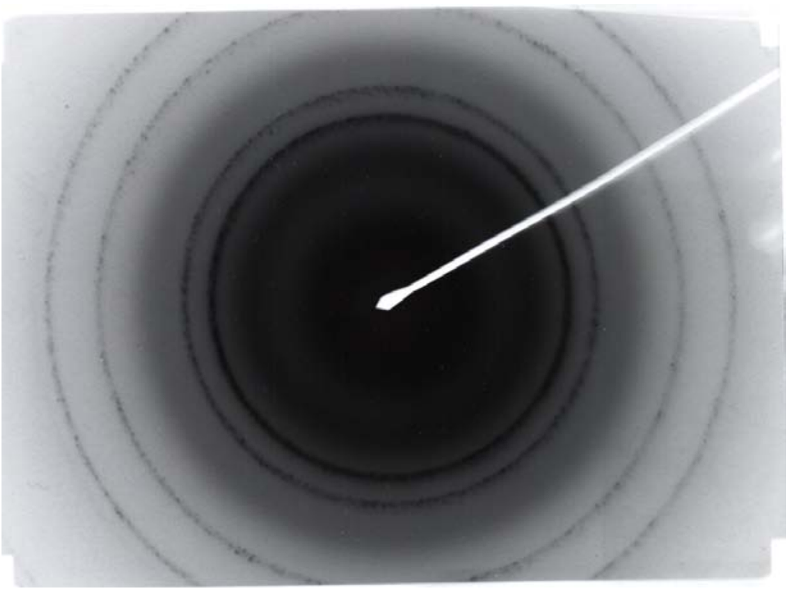

Fig. 2. Electron diffraction pattern of the Al/a-Si film annealed at 150°C for 30 minutes.

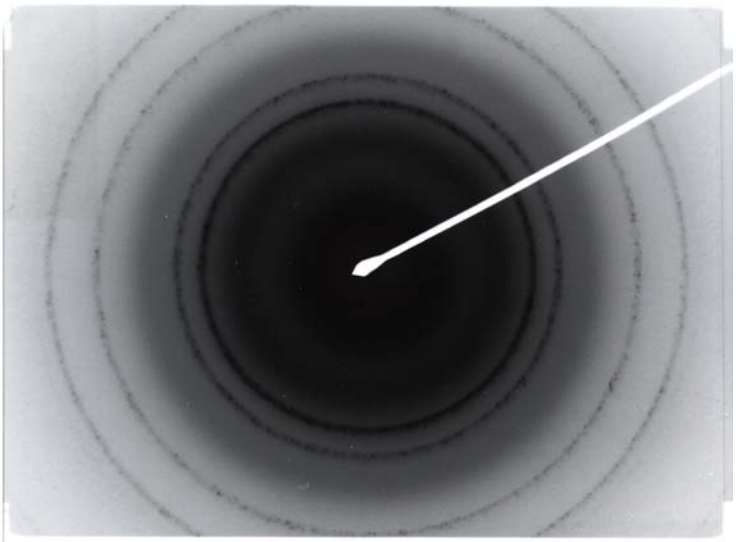

Fig. 3. Electron diffraction pattern of the Al/a-Si film annealed at 175°C for 30 minutes.

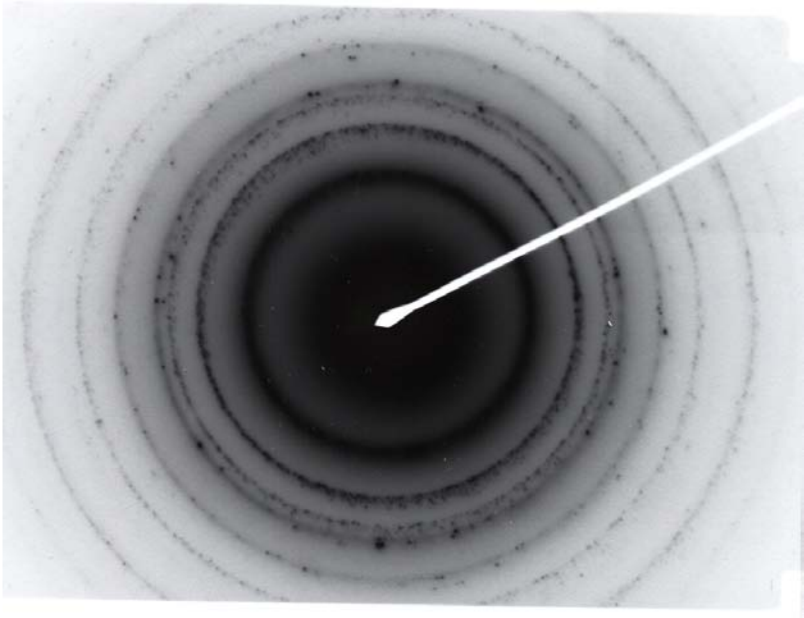

Fig. 4. Electron diffraction pattern of the Al/a-Si film annealed at 200°C for 30 minutes.

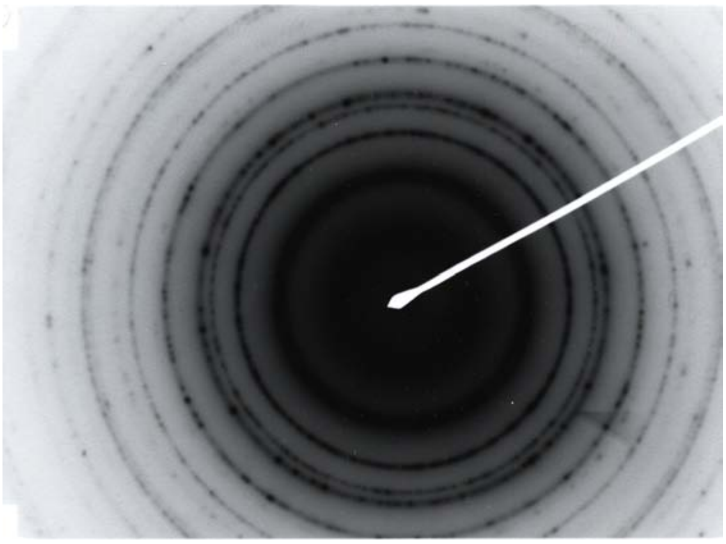

Fig. 5. Electron diffraction pattern of the Al/a-Si film annealed at 250°C for 30 minutes.

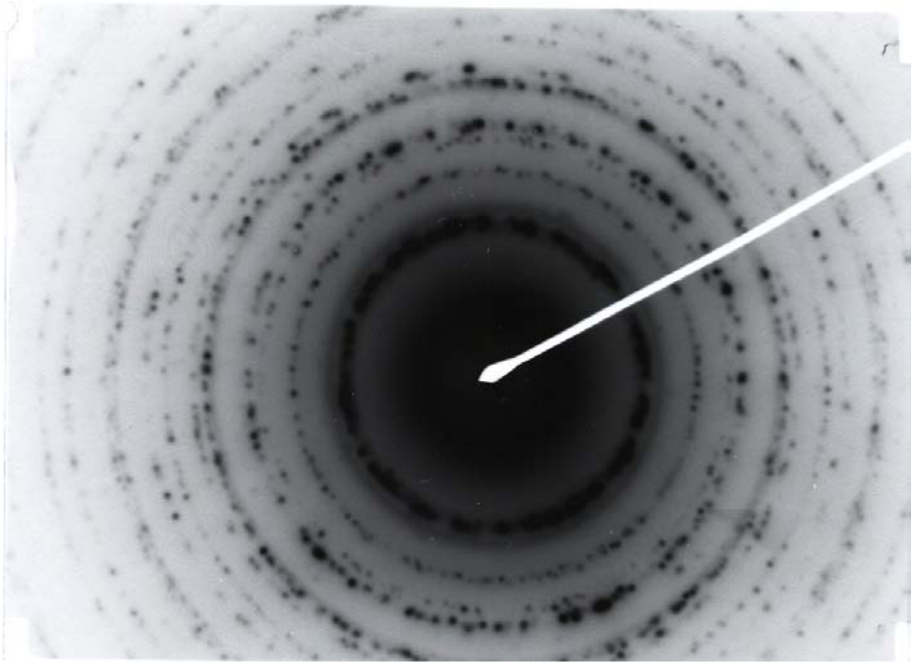

Fig. 6. Electron diffraction pattern of the Al/a-Si film annealed at 350°C for 30 minutes.

Figures 7-12 show XRD spectra of samples annealed at various temperatures for 30 minutes. No crystallization was observed for annealing temperatures of 150°C, 200°C, and 250°C. At 275°C annealing temperature, a small peak appears at a 2θ of 28.5° corresponding to (111) planes, indicating the start of the crystallization of the amorphous silicon. Complete crystallization was achieved at temperatures above 300°C, with crystalline Si peaks appearing at 2θ values of 28.5, 47.3, 56.1, and 69.2° corresponding to the (111), (220), (311), and (400) planes, respectively, as shown in figures 10, 11, and 12. The polycrystalline Al peaks are also shown in the figure at 2θ values of 38.5, 44.8, 65.1 and 78.2°, which are from the (111), (200), (220), and (311) planes, respectively. Similar results have been reported for the configuration where a sputtered a-Si film was deposited onto evaporated Al. In that case crystallization was also observed to occur at temperatures above 300°C [17].

It has also been reported that the crystallization temperature will be slightly higher (310°C) when the configuration takes the form a-Si/Al substrate [15]. It has previously been reported that aluminum assisted crystallization of sputtered a-Si films does not start until the sample is annealed at 300°C for 30 minutes, when the Al is evaporated onto the amorphous silicon films (Al/a-Si) and full crystallization is achieved at 400^{o}C [12]. However, for the case where hydrogenated amorphous silicon was plasma-deposited on evaporated Al (a-Si:H/Al), crystallization required at higher annealing temperatures compared to the other configuration (Al/a-Si:H) [16]. The evaporated Al is exposed to room ambient during its transfer from the evaporator to the cluster tool where either sputtered or plasma deposited amorphous silicon is fabricated.

It seems, therefore, that the native aluminum oxide, which acts as a barrier for crystallization in the plasma deposited sample, is removed during the early phase of sputter deposition of a-Si film. This possibly explains why the crystallization of the sputtered a-Si/sputtered Al and sputtered a-Si/ evaporated Al samples commences at similar temperatures of 300°C when observed by XRD. It may be noted here that although the glancing-angle XRD patterns show no significant crystallization for samples annealed below 275°C, their EDP show significant levels of crystallization at temperatures above 200°C. This may be due to several reasons. The sensitivity of XRD may be much smaller than TEM/EDP. The electron beam may focus on the crystallized area where the nucleation starts. Or, the initial crystal growth may have some level of preferential orientation, which could not be detected by the thin-ilm optics using glancing-angle diffraction.

For the case of evaporated Al on plasma-deposited hydrogenated a-Si films (Al/a-Si:H), however, the crystallization was reported to start at temperatures just above 150°C. Hydrogen may be playing a significant role in lowering the crystallization temperature in Al-induced crystallization [7]. Generally, there are a few models for the AIC crystallization process. Haque et al [13] reported that a metal-rich Al-Si mixed phase Al_xSi is formed at the interface at early stage of annealing. Silicon atoms diffuse into the aluminum and aluminum atoms diffuse into the silicon through this defect-rich metastable material. Eventually, atoms which diffuse through the aluminum grain boundaries begin to precipitate on top of the aluminum pad.

Nast and Wenham [17] showed that the Si nuclei formed at Al grain boundaries and that the growth proceeded within the aluminum layer until adjacent Si grains impinged. The overall crystallization process results in the exchange of the layer positions and the formation of a continuous poly-silicon film.

Figure 13 shows the SEM picture of the interacted film surface of Al/a-Si structure annealed above the crystallization temperature, clearly depicting hillocks or bumps distributed all over the surface. The presence of these hillocks after annealing at 275°C and above confirms that the a-Si has been crystallized. On the other hand, annealing the films below the crystallization temperature of 275°C shows a very smooth surfaces (Fig. 14).

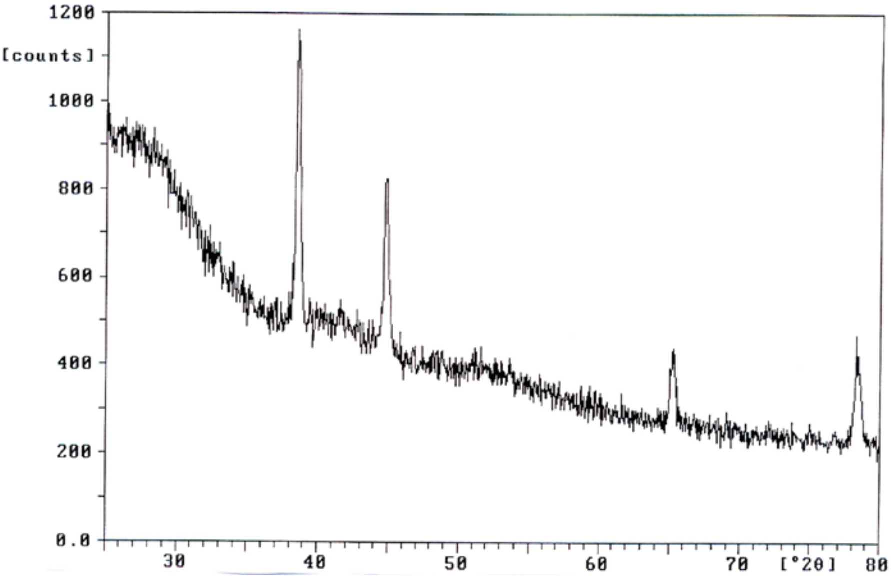

Fig. 7. X-ray diffraction spectra of as-deposited Al/a-Si film.

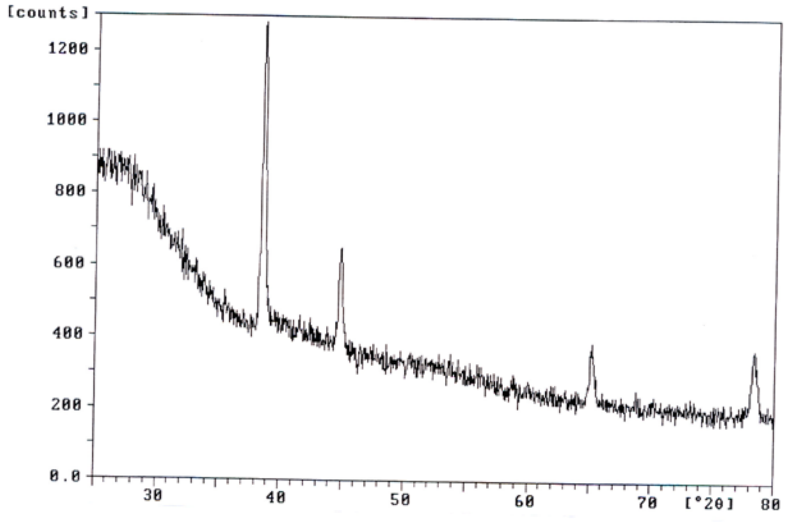

Fig. 8. X-ray diffraction spectra of the Al/a-Si film annealed at 250°C for 30 minutes.

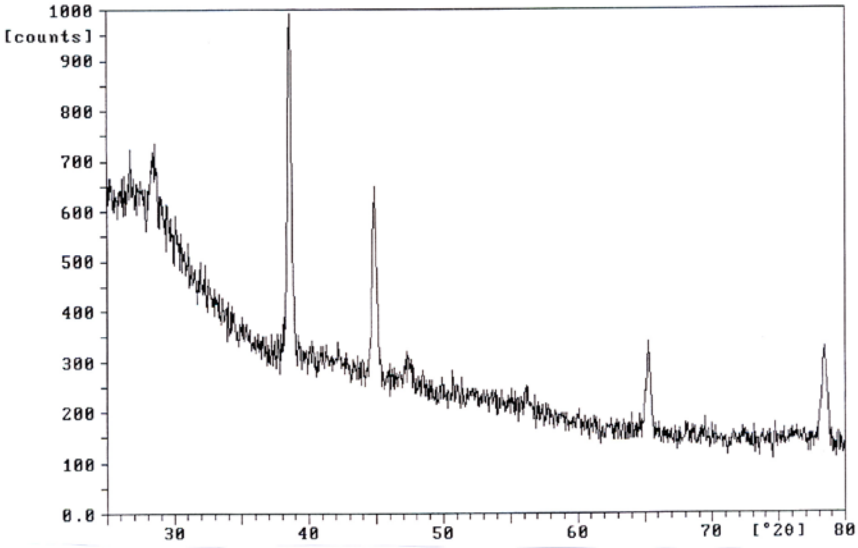

Fig. 9. X-ray diffraction spectra of the Al/a-Si film annealed at 275°C for 30 minutes.

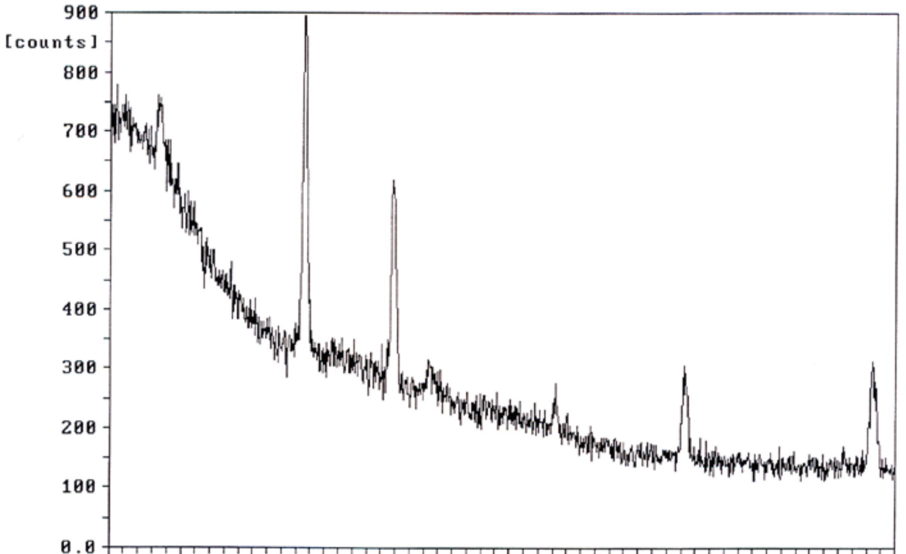

Fig. 10. X-ray diffraction spectra of the Al/a-Si film annealed at 290°C for 30 minutes.

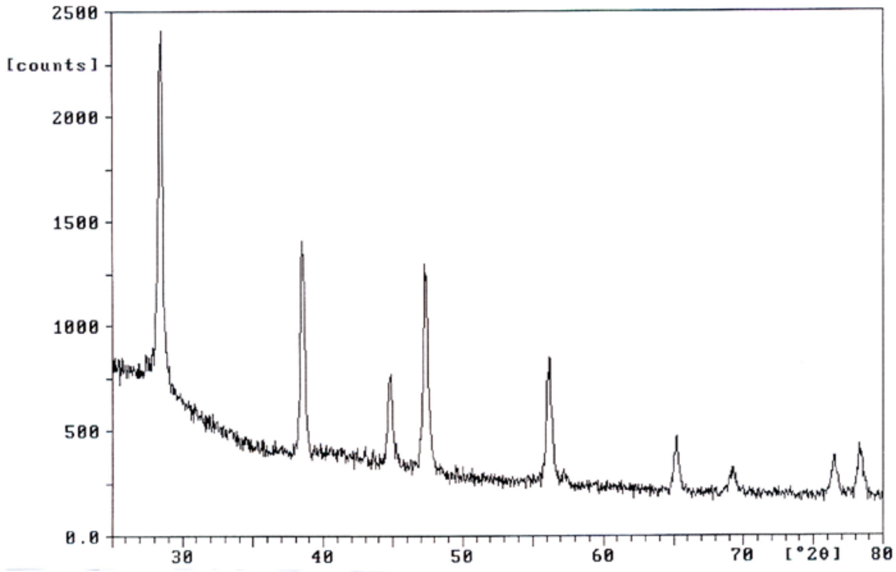

Fig. 11. X-ray diffraction spectra of the Al/a-Si film annealed at 300°C for 30 minutes.

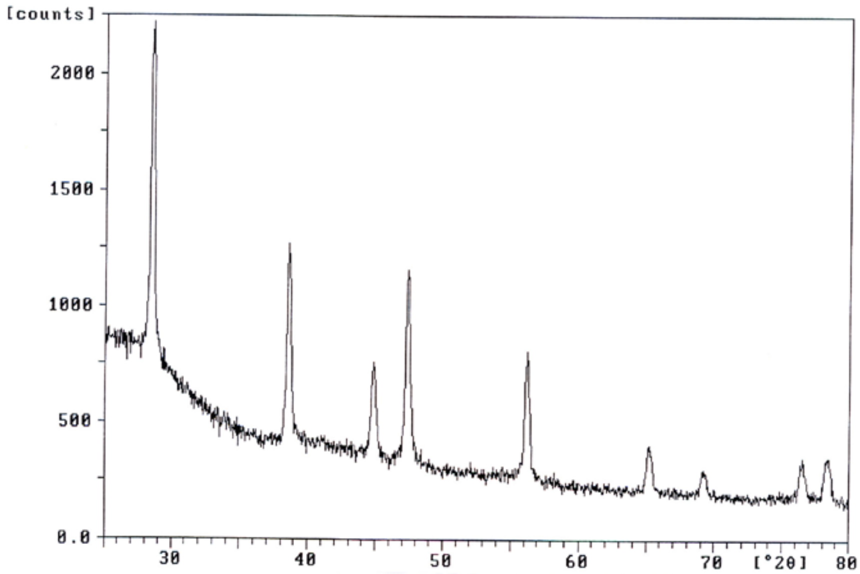

Fig. 12. X-ray diffraction spectra of the Al/a-Si film annealed at 350°C for 30 minutes.

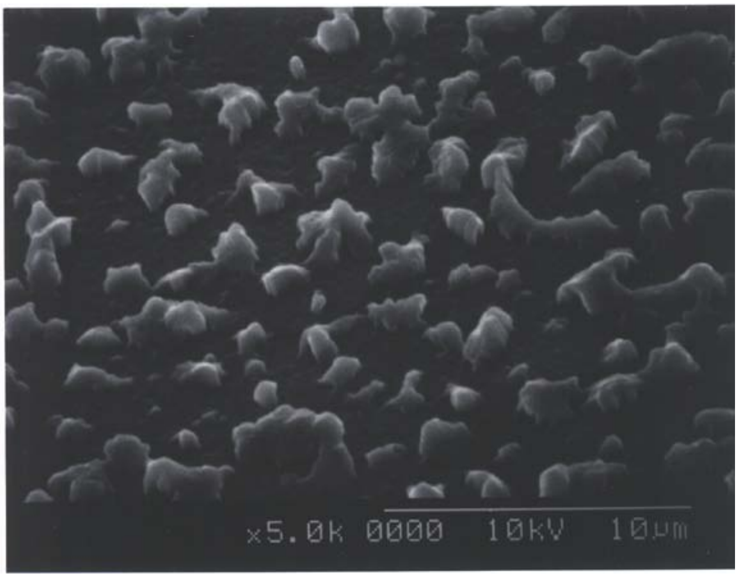

Fig.13. SEM micrograph showing the interacted film surface of an Al/a-Si / glass structure annealed above the crystallization temperature.

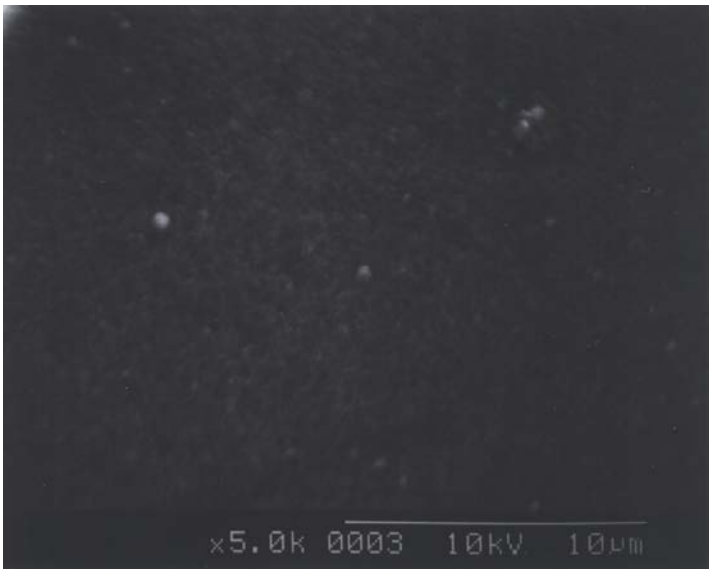

Fig.14. SEM micrograph showing the interacted film surface of an Al/a-Si / glass structure annealed below the crystallization temperature.

Conclusion

Al-induced crystallization of a-Si on two different substrates, glass and carbon coated nickel is investigatyed in this paper. The interaction between the Al and the a-Si layers is studied in the temperature range 150°C-350°C. Annealing at 200°C resulted in the formation of crystalline Si as observed by TEM, and 275°C as observed by XRD. These different results obtained by two techniques are discussed and explained. A new ring appeared in the EDP after annealing Al/a-Si at 350°C or higher. The SEM picture of the interacted film surface of Al/a-Si samples annealed above the crystallization temperature clearly shows hillocks or bumps distributed all over the surface. The combination of SEM and XRD results confirms that a 30 min. annealing ≥ at 275°C crystallizes the a-Si.

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تبلور السليكون المبخّر بطريقة PECVD باستخدام تقنية الألمنيوم المحث على التبلور

عبد الله بن محارب الظفيري

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الرياض ١١٤٥١، المملكة العربية السعودية

(قدم للنشر في ٢٠٠١/١١/١٤م؛ وقبل للنشر في ٢٠٠٢/٠٣/١٩م)

ملخص البحث. يعرض البحث طريقة تبخير السليكون غير المتبلور على قاعدتين الأولى زجاجية والأخرى قاعدة من الكربون المغطى بالنيكل. تستخدم القاعدة الأولى لدراسة الأشعة السينية ولدراسة المجهر والماسح الإلكتروني بينما تستخدم القاعدة الثانية لدراسة المجهر النافذ الإلكتروني. تم تبخير السليكون بواسطة طريقة الرش الكيميائي تحت ضغط منخفض جدا ومن ثم استخدمت نفس الطريقة لتبخير الألمنيوم فوق السليكون سخنت العينات عند درجات حرارة مختلفة من ١٥٠° م إلى ٣٥٠° م ولمدة ٣٠ دقيقة وجد أن السليكون يبدأ في التبلور عند درجة حرارة ٢٠٠° م عند استخدام المجهر النافذ الإلكتروني وعند درجة ٢٧٥° م عند استخدام الأشعة السينية. تم تفسير هذا الاختلاف طبقا لكل طريقة. درس سطح العينات باستخدام المجهر الماسح الإلكتروني ووجد أن العينات التي سخنت عند درجات حرارة أكبر من ٢٧٥° م تمتاز بوجود أشكال هرمية مما يؤكد تبلور السليكون بينما تمتاز العينات التي سخنت عند درجات حرارة أقل من ٢٧٥° م في وجود سطح أملس تم عرض ومناقشة وتفسير كل تلك النتائج بناء على التغيرات التركيبية والدراسات السابقة.