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Evolution of Al/Al_2O_3 Layer on Glass Substrates during N_2 Anneal

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Abstract

Light trapping is essential for thin film solar cells to decrease the solar electricity cost. Aluminum induced texturing (AIT) is an alternative and effective method for light trapping. Various parameters effects the final surface morphology in AIT. However, surface morphology obtained by AIT method on glass is mostly formed in annealing process which occurs at temperatures above 500 °C. In this study, annealing process under N_2 ambient is investigated. A relevant model of evolution is formed. In addition, diffusion of Na during this process is covered.

Keywords: Aluminum induced texturing (AIT); thin film solar cells; texturing; evolution of Al film; c-Si cluster

1. Introduction

Thin film solar cells have advantages like using less materials, being easy to produce, applicable with different substrates like glass and plastic (polyimide, PET) [1], [2]. However, due to low efficiencies and usage of critical materials (Te, In, Cd, Se [3]–[5]) leads c-Si wafer based solar cells becomes dominant in the market [6]. The opportunity of thin film solar cells is that efficient light trapping scheme can lead more efficiency or thinner absorber layer in substrate and superstrate configurations by increasing optical path as shown in Figure 1. This results with decreasing solar electricity costs [7]. Texturing of transparent conductive oxide (TCO) on flat substrate is used commercially for light trapping [8]. However, texturing flat substrate, glass, can give the opportunity to obtain more efficient light trapping scheme. Aluminum induced texturing (AIT) is one of the texturing techniques used to modify glass surface [9]. In AIT process, texture mainly depends on the reaction between Al and SiO_2 occurs at the interface of Al and glass. To induce this reaction, annealing process, carried out at temperatures above 500 °C, is necessary.

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Reaction starts randomly at the interface and this cause formation of Al_2O_3 nodule through the glass while produced elemental Si dissolves into Al [10]. Removing reaction products by wet etching reveal surface texture with some modification on surface according to used chemicals.

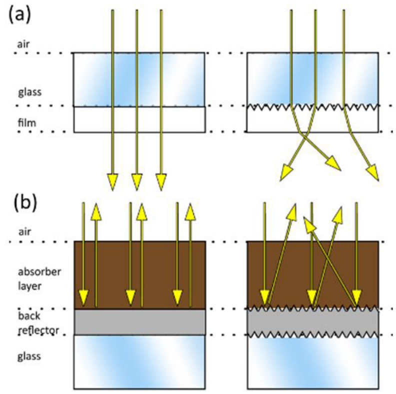

Figure 1. Schematic representation of effect of textured interface on optical path in (a) supertrate configuration and (b) substrate configuration. Refractive indexed are assumed to be as follows: $n_{air}<n_{glass}<n_{film}$

Due to the fact that the texture is mainly formed in annealing process, having a better understanding of thermodynamic mechanism during annealing is crucial. In this present study, the attempt of explanation of evolution of Al/Al_2O_3 film during annealing under N_2 ambient is done.

2. Experimental

4 mm soda-lime low iron glasses (Türkiye Şişe ve Cam Fabrikaları A.Ş.) were used for annealing experiments. Before Al coating, all samples were cleaned by a chemical detergent in ultrasonic bath. Al was coated with thermal evaporation system under 3 x 10^{-5} torr vacuum with a thickness of 350 nm. Annealing process was carried out at 600 °C in a classical tube furnace (10 cm diameter) under 4 slm N_2 flow. Annealing for each sample was done with different durations as given in Table 1.

Table 1. Annealing durations with respect to sample names

Sample Name	A00	A10	A15	A20	A30	A60	A120	A240
Annealing Duration	No anneal	10 min.	15 min.	20 min.	30 min.	60 min.	120 min.	240 min.

Surface characterization of those samples were made by Nade metallurgical microscope (NMM-800TRF) and a QUANTA 400F field emission scanning electron microscope (FE-SEM) coupled with an Ametek EDAX energy dispersive X-ray spectroscope (EDX). Elemental analysis is made by PHI Versaprobe 5000 Scanning X-Ray Photoelectron Spectrometer (XPS) with Al k-alpha X-ray source for Al, Si and Na.

3. Results and Discussion

It is expected that reaction is near to be completed at 60 min. of annealing. In A60, there are bright, peanut-like structures as seen in Figure 2a. However, in Figure 2b, light is transmitted through the area around peanut-like structures. Those areas which are transmitting the light are strongly compose of Al_2O_3 which have bandgap higher than 3 eV for different forms of it [11]. The dark regions in transmission mode are probably made of compounds having smaller bandgap because no light is passing through those regions. The bright spot on the Figure 2b is a defect occurred during sample preparation process, which do not contribute this discussion.

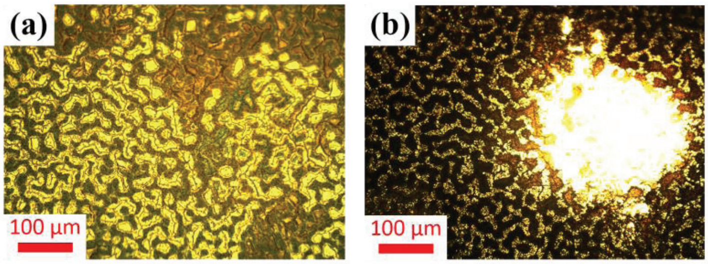

Figure 2. Optical microscope images of A60 measured by (a) reflected light and (b) transmitted light

To identify peanut-like structures, EDX is employed for sample A120 which is annealed excessively. It is seen that peanut-like structures are composed of mostly Si which highlighted by pink color in FE-SEM image given in Figure 3.

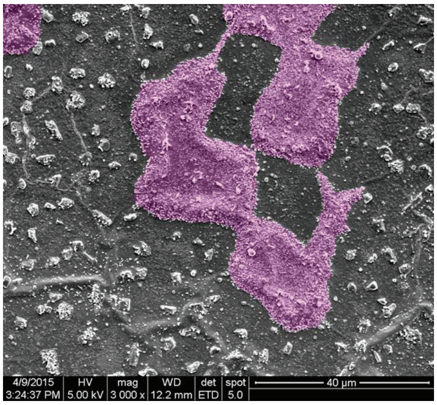

Figure 3. FE-SEM image of A120 with emphasizing of Si rich region

Observing the evolution of Al film from elemental form to the structure describe in the discussion of Figure 2 and Figure 3 is necessary to understand the mechanism. Samples are prepared to see this evolution. In Figure 4, evolution is observed by optical microscope while in Figure 5, by FE-SEM.

Sample A10 have dark dots on the surface when it is observed by reflected light in optical microscope (Figure 4). Those dots appears as bright with transmitted light, on the other hand. It is probable that those dots are first areas where reactions is started and Al_2O_3 is formed. After 20 min. of annealing, peanut-like structures are started to be formed. Those can be seen more clearly after 20 min. of annealing with reflected light in optical microscope. With increasing the annealing time to 30 min., it can be seen that peanut-like structures becomes distinguishable with both reflected light and transmitted light. Increasing annealing time more leads to more separation between peanut-like structures and the rest. Those structures have more contrast in A60. It is probably coming from remaining elemental Al on top of the elemental Si which is identified by EDX because solubility of Al in Si is significantly low [12]. After 120 min. of annealing, those bright peanut-like structures becomes darker due to oxidation of Al.

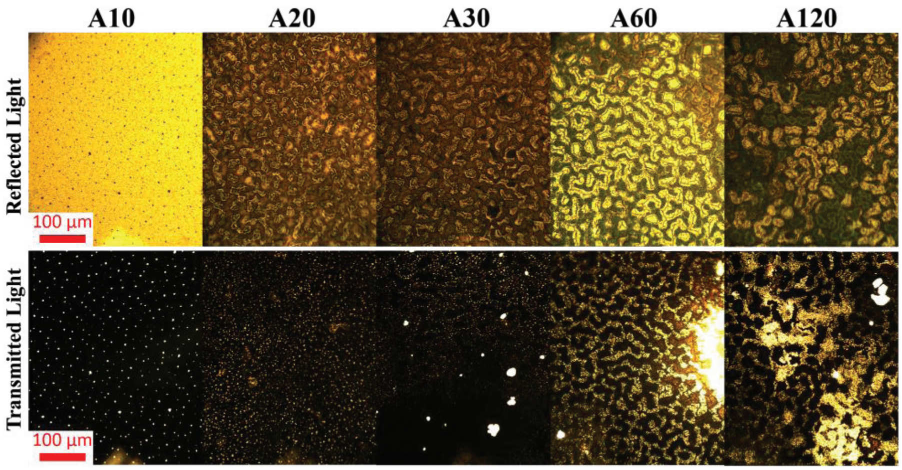

Figure 4. Optical microscope images with reflected and transmitted light for samples annealed at different durations

In FE-SEM images given in Figure 5, evolution of surface can be seen more explicitly with different magnifications. In A10, dark regions seen with reflected light in optical microscope can be seen in FE-SEM. EDX signal coming from inside of this dark region says that there are more Si and O than in other regions. It is known that density of Al_2O_3 is much higher than elemental Si, elemental Al and SiO_2, where densities of Si, Al and SiO_2 are very close to each other. The reason of that more signal from glass is coming might be related with density of Al_2O_3 which leads to decrease on film thickness and with that starting reaction causes formation of mixture of Al_2O_3 and Si. After 5 more minute further annealing, those dark regions disappears, probably becomes base of A15 where bumps are present. EDX shows that those bumps are mostly includes Al. However, there are some regions where Si is dominant as shown in Figure 6. Those regions lies at Al/Al_2O_3 boundary. In previous studies it is shown that Si dissolve into Al and precipitate in crystalline form [10]. It can be concluded that Si firstly dissolved into Al and forms Al-Si alloy at 600 °C. After certain concentration Si precipitate in crystalline form. Because of the fact that there is existing low energy surface, which is Al_2O_3, Si precipitate around it. With increasing annealing time, those Si precipitates becomes distinguishable by FE-SEM and Al bumps seize to exist. In this case, reaction carried out and most of the Al converted into Al_2O_3. By difference in density, c-Si structures revived. The detailed EDX analyses can be seen in Figure 7.

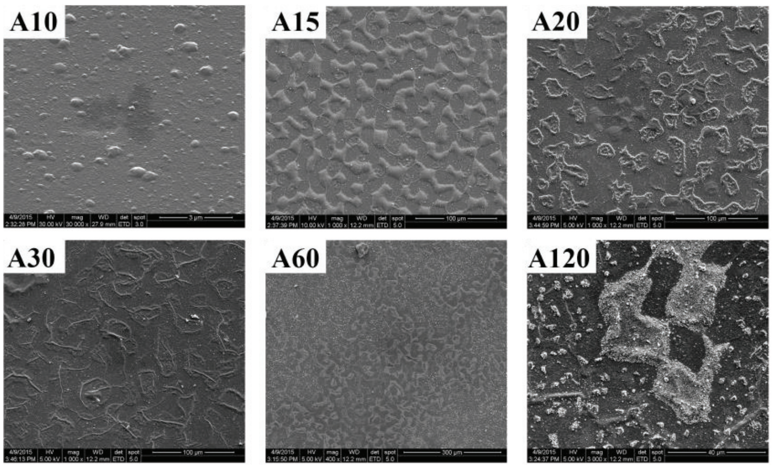

Figure 5. FE-SEM micrographs of annealed samples

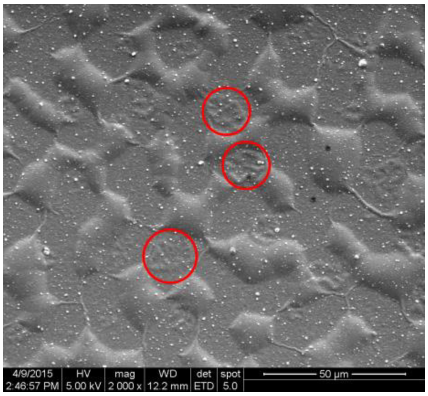

Figure 6. FE-SEM micrograph of A15. Circulated areas are Si rich regions

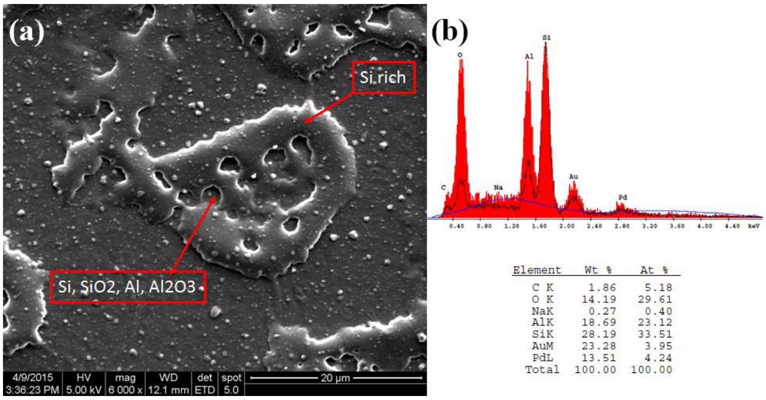

Figure 7. FE-SEM image of A20 and EDX analyze results. Black lines indicate the signal coming from Si rich region, while red filled graph composite.

After 30 minute annealing, pipes are formed on the surface of peanut-like structures as seen in Figure 5. Those lines are composed of Al. The formation of those lines probably result of deformation of elemental Al on top of peanut-like structure by heat. In A60 which was annealed for 60 min., peanut-like structures have high contrast. In addition, there are dark region in the middle of those Si rich regions. EDX analyze shows that in those dark regions, Na is dominant which present in the glass at the beginning of process (Figure 8a). Diffusibility of Na in Si is much higher than in Al_2O_3 which is used as diffusion barrier. Si crystals acts as "diffusion highways" for Na. Detailed image with formation of small Na agglomerates can be seen in Figure 8a. It is seen that small Na agglomerates are started to be formed around Si rich regions.

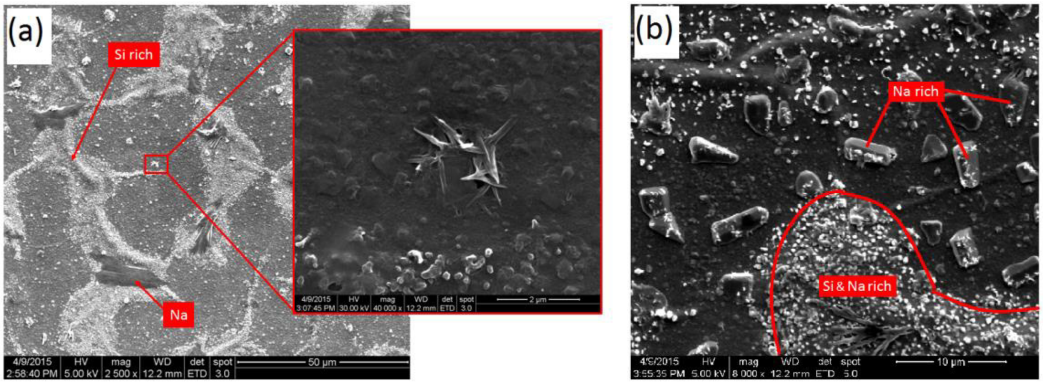

Figure 8. FE-SEM image of (a) A60 with 2500x magnification with 40000x magnification of formed small Na agglomerate and (b) A240 with 8000x magnification showing Na rich regions.

With increasing annealing time, it is seen that more Na diffuse to the surface but there is less chance in surface morphology. Na agglomerates have started to appear on non-Si rich regions also and Si rich regions contains highly Na signal in EDX (Figure 8b).

To understand structure form of components, depth profiling with 40 layers by XPS is conducted for elements Na, Al and Si (Figure 9). Those data do not show layers taken from glass. Because of the fact that there is no SiO_2 signal, it is assumed as 40th layer is somewhere inside the film. It is seen that Na is agglomerated on the surface which corrects EDX measurement. While Al shows relatively constant concentration through deeper layers, Si concentration which is in elemental form is increased. This shows that precipitate Si grows towards the surface of film also and reaction finished due to the absence of elemental Al.

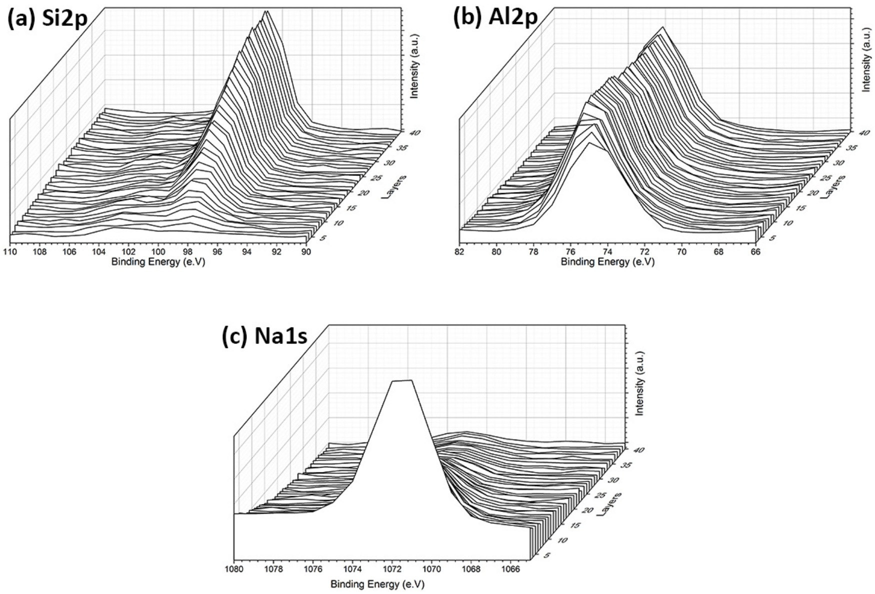

Figure 9. Depth profile of A120 obtained by XPS

With the data presented above a model for mechanism can be described. Figure 10 describe formed model for annealing and formation of texture. As mentioned before, reaction between Al and glass starts at random places on the interface, which causes formation of Al_2O_3 nodules as shown in Figure 10. With continuous annealing, Si reaches critical concentration and starts to precipitate around Al_2O_3 nodules. After all Al is converted into Al_2O_3, Si clusters takes their final form and concentrate inside the film.

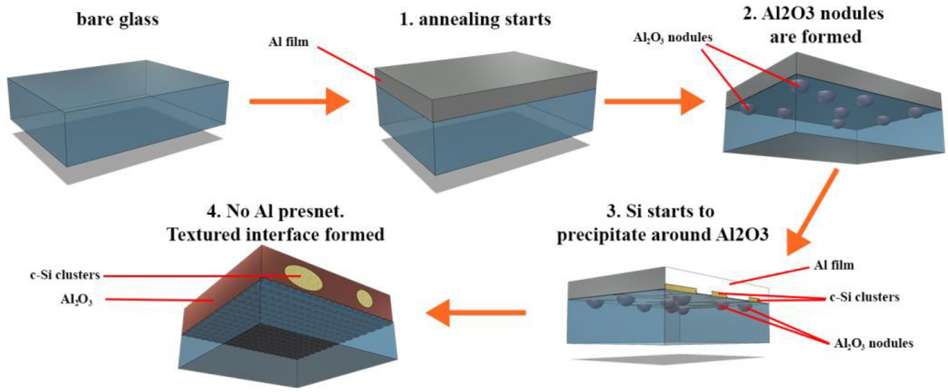

Figure 10. Schematic representation of the evolution of Al film through annealing process and formation of texture

4. Conclusion

In this study, a rough model for annealing is built. It is seen that reaction starts at 10 min of annealing at 600 °C however, critical concentration of Si in Al is reached after 15 min of annealing. With increasing annealing time Si precipitates which are formed around Al_2O_3 nodules, gets bigger and can be seen easily by FE-SEM. Then, after all Al is converted into Al_2O_3, it is seen by depth profile that Si precipitates can be found mainly inside of Al_2O_3 film. Increasing annealing time more than the necessary to complete the reaction is just leads to diffusion of Na to the surface of the film. The reason is that Si clusters gets big enough to make connection between surface of glass and surface of film/sample. This connection and high diffusion coefficient of Na inside Si lead to formation of "diffusion highways" and Na agglomerates are formed mainly on Si rich areas.

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