Growth rate of AL₂O₃ Thin Film by Liquid Phase Deposition as an Anti-reflection Coating Layer on Crystalline Silicon for Solar Cell Applications


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**ABSTRACT**

The fabrication of photovoltaic (PV) device requires that surface reflectance of solar cells has to be minimized to achieve higher photo-conversion efficiency (PCE). Antireflection coating layer is deposited on the surface of a p-type crystalline silicon material to reduce the surface reflections of solar radiation and increase its absorption for efficient solar cell application. In this work, aluminum oxide thin film by liquid phase deposition (LPD-AL₂O₃) is synthesized from combined solution of aluminum sulfate octadecahydrate (Al₂(SO₄)₃·18H₂O) and sodium carbonate (NaHCO₃) with pH of 3.1. Some samples of p-type (100) crystalline silicon (c-Si) wafers of resistivity 1–10 mΩ were immersed inside the growth liquid of LPD-AL₂O₃ thin film for 1hr – 2.5 hours. This is followed by annealing the samples at a temperature of 450°C, the deposition rate is faster in the range 1 – 1.5 hours is about 35nm/hr. As the growth time increases, the growth rate of the film decreases and remains nearly constant at about 10 nm/hour at 1 – 2 hours. When the growth time exceeds 2 hours, the film thickness remains unchanged showing that the liquid has lost in growth ability. The weighted average reflection (Ravg%) of planar c-Si is reduced from 44.9 % to 29.6 % after deposition of the LPD-AL₂O₃ for 2.5 hours growth time, indicating a 34.1 % reduction in reflection within wavelength region of 300–1100 nm. While the root means square (RMS) surface roughness of 36.5 nm was also recorded at the highest growth time of 2.5 hours. This shows the effect of thicker LPD-AL₂O₃ thin film layer increases the anti-reflecting coating property of the material.

**Keywords:**
Aluminum oxide thin film, Weighted average reflection, RMS surface roughness, Anti-reflecting coating.

**INTRODUCTION**

Solar energy has emerged as a global alternative energy source in recent years due to its abundance, accessibility, environmental friendliness, and renewable nature. This energy has been harnessed using modern technologies (Lin et al., 2016). It lessens the impact of global warming, in contrast to certain other energy sources. Photovoltaic (PV) cells are among the most widely used semiconductor technologies for converting thermal energy from solar radiation into electrical energy or electricity. Crystalline silicon (c-Si) is the most utilized semiconductor material in the photovoltaic manufacturing business. This is because it is a plentiful element that can be found both on and below the surface of the Earth, and it has the capacity to absorb solar energy (Jia et al., 2017; Özkol et al., 2020). In the 300–1100 nm wavelength range, it still has an average reflectance rate of roughly 35% despite its noticeable degree of broadband light absorption (Wang et al., 2021). A variety of ARC materials are available, such as organic ARC layer (Chai et al., 2020), metamaterials ARC (Fan et al., 2021), dielectric ARC material (Viswanath, 2001), and multilayered ARC structures (Barreda et al., 2019). In order to increase solar cell efficiency, ARC is required to decrease reflection losses that occur at the Si-air contact. This is accomplished by maximizing light absorption in the semiconductor material’s active layer, which raises the efficiency of solar cell conversion. Light emitting diodes (LEDs), integrated circuits, solar cells, photosensors, transistors,
and other semiconductor devices are among the devices that use it (Hou et al., 2021). Silicon dioxide (SiO$_2$), silicon nitride (Si$_3$N$_4$), and aluminum oxide (Al$_2$O$_3$) are the most frequently reported ARC materials that suppress reflection in b-Si (Özkol et al., 2020). High temperatures are needed to create SiO$_2$, which makes the process costly. Additionally, the inherent positive fixed charges of SiO$_2$ or SiNx might induce poor passivation for p-type silicon surfaces due to the resultant depletion that increases the likelihood of minority carriers recombining (Lee et al., 2018).

Because of its chemical and field effect capabilities, Al$_2$O$_3$ is now thought to be an excellent ARC material (Castillo et al., 2017; Balaji et al., 2020). With its high refractive index (~1.6) at 600 nm, wide band gap (E$_g$ ~ 9 eV), good thermal conductivity, great transparency in the ultraviolet and visible spectra throughout a wavelength range of 200 – 800 nm, and good electrical insulation, Al$_2$O$_3$ is a promising resource (Dingemans and Kessels, 2012; Hsu et al., 2019). Al$_2$O$_3$ has many uses, such as in transparent ceramics (Singh et al., 2018), integrated circuit baseboards (Angarita et al., 2017), cosmetic fillers (Li et al., 2020), polishing materials (Ding et al., 2017), and others. In terms of radiation resistance and impurity inhibition, including sodium ions, it outperforms SiO$_2$ and Si$_3$N$_4$ (Chen et al., 2021). It is more resilient to basic corrosion and a variety of acids than SiO$_2$. Hence, it is utilized in semiconductor electrical devices as an enhanced dielectric as an ARC layer (Lin et al., 2016).

![Figure 1: Conventional diagram of antireflection coating of Al$_2$O$_3$/Si (Lin et al., 2016)](image)

The primary techniques described in the literature for preparing Al$_2$O$_3$ thin films on semiconductor material include electron beam evaporation (Nabhan et al., 2023), magnetron sputtering (Yan et al., 2013), atomic layer deposition (ALD) (Fukushima et al., 1994; Hannebauer et al., 2015; Musil et al., 2010), and plasma-enhanced chemical vapour deposition (PECVD) (Getz et al., 2021). While Al$_2$O$_3$ films made with these methods are usually of great quality, they necessitate extremely high temperatures and costly equipment. As a result, we provide LPD-Al$_2$O$_3$, or liquid phase deposition, as a straightforward, inexpensive, large-area coverage thin film, and non-toxic technique for depositing Al$_2$O$_3$ (Ghiraldelli et al., 2008). Zhang et al. report that to examine the impact of annealing temperature on the optical and structural properties, an Al$_2$O$_3$ thin film with a thickness of approximately 80 nm was formed as an ARC layer on p-type b-Si using the chemical liquid phase deposition technique (CLD) (Zhang et al., 2017). Al$_2$O$_3$ ARC was also deposited via RF sputtering and annealing on p-type Si wafers. As a result, the Al$_2$O$_3$'s refractive index increased from 1.69 to 1.74 with an annealing temperature of 300 to 600°C. The annealing temperature also induced a rise in coat density because it rearranges the Al$_2$O$_3$ atoms (Repo et al., 2011). Al$_2$O$_3$ film of thickness 40nm is deposited on Si nanowires on c-Si, SiNWs/Si as both ARCs and passivation layer using LPD to decrease reflectivity of 1.57 % to 0.98 %, improving absorption by ~63 % (Jia et al., 2017).

In this work, four samples of p-type (100) c-Si are immersed in a growth liquid of LPD-Al$_2$O$_3$ thin film of pH 3.1 as an ARC layer by dip coating method from 1 hour to 2.5 hours and annealed at 400°C for 1 hour. The optical and morphological properties of the substrates are characterized and the relationship between R$_{avg}$ and potential short circuit current J$_{sc(max)}$ is used to determine the reflectivity performance of LPD-Al$_2$O$_3$ ARC layer on Si within the wavelength 300 – 1100 nm. The values of J$_{sc(max)}$ enhancement is generated from the expected results for each substrate. The research also shows that as growth time of the LPD-Al$_2$O$_3$ thin film increases, the R$_{avg}$ on the surface of the c-Si decreases and potential J$_{sc(max)}$ increases for improving solar cell efficiency.

**MATERIALS AND METHODS**

**RCA cleaning of c-Si**

In this research, p-type monocrystalline silicon (c-Si) wafer <100> of 250 μm thickness and a resistivity of 1–10 Ωcm is used. The standard Radio Corporation of
America (RCA) technique is used to clean the c-Si. A mixture of 50ml of deionized water (DI H₂O), 10ml of hydrogen peroxide H₂O₂ and 10ml of ammonium hydroxide NH₄OH in the ratio 5H₂O:1H₂O₂:1NH₄OH in a glass beaker is heated until 75°C. The samples of the p-type c-Si are immersed in the heated solution and maintained at 80°C for 10 minutes. The samples are rinsed in DI H₂O and then immersed in a solution of 50 ml of DI H₂O and 1ml of hydrofluoric acid HF (50H₂O:1HF) for 10 – 15 sec. each to make them hydrophobic. These samples are then immersed in another solution of 60ml of deionized water (DI H₂O), 10 ml of hydrogen peroxide H₂O₂ and 10 ml of hydrochloric acid HCl in the ratio 6H₂O:1H₂O₂:1HCl in a glass beaker and then heated until 75°C. The samples are heated for another 10 minutes and then transferred into a beaker of DI H₂O for few minutes before drying with nitrogen gas N₂.

**Figure 2: Diagrammatic Process of RCA cleaning of c-Si**

**Synthesizing of LPD-Al₂O₃ thin film**

Sodium carbonate (NaHCO₃) and aluminum sulfate octadecahydrate Al₂(SO₄)₃·18H₂O are the precursor chemicals needed to manufacture LPD- Al₂O₃ thin film. In a Teflon beaker, dissolve 50g of Al₂(SO₄)₃·18H₂O in 50 ml of DI H₂O at room temperature and mix well. A slightly viscous translucent liquid with a pH of 2.86 is obtained by filtering away the undissolved particles using filter paper. A magnetic stirrer is used to mix the Al₂(SO₄)₃·18H₂O solution once it has been transferred into a different beaker. Before adding further powder, slowly add 13.5 g of NaHCO₃ powder to the solution until the foamy CO₂ goes away. The particles were completely dissolved using an ultrasonic instrument, yielding a transparent, colorless, viscous solution with a pH of around 2.91. Filter sheets measuring 5 μm were used to filter the mixture. To prevent the long-term production of aluminum sodium vanadium, this combination was diluted right away with 150 milliliters of DI water. The growing fluids had a pH of roughly 3.1. The reaction as it appears in equations (1) and (2) is shown below.

\[
\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + 6\text{NaHCO}_3 \rightarrow 2\text{Al(OH)}_3 + 3\text{H}_2\text{SO}_4 + 6\text{CO}_2 \uparrow + 18\text{H}_2\text{O} + 6\text{Na}_2\text{SO}_4 \quad (1)
\]

\[
2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \quad (2)
\]

The four samples of c-Si substrates were immersed into the thin film of Al₂O₃ produced through the LPD technique (LPD-Al₂O₃) for 1, 1.5, 2 and 2.5 hours each. The growth liquid was deposited, rinsed with DI water, and then dried with a N₂ atmosphere. The substrates were annealed in a furnace at a temperature of 400°C for 1 hour in an ambient N₂ environment to ensure proper adhesion, increase the density of thin film and efficient passivation property. This step can also eliminate the possible existence of hydrogen element although negligible.
Samples Characterization and Measurement
Using field emission scanning electron spectroscopy (FESEM; Model: FEI Nova NanoSEM 450), the thickness and surface morphology of the LPD-Al₂O₃ thin film, which has a mirror-like surface, are characterized on the substrates. The atomic force microscope (AFM; Model: Dimension Edge, Bunker) was used to measure the height and root means square (RMS) surface roughness of the substrates over a scan range of 10 × 10 μm². Using an integrating sphere (Model: Agilent Cary 500) and a UV-vis-NIR spectrophotometer, the optical characteristics of the substrate were measured between 300 and 1100 nm. The LPD-Al₂O₃ thin film deposit thickness was examined using the Image J computer application program. By integrating the product of absolute reflectance $R(\lambda)$ and the spectral photon density under standard AM 1.5G solar spectrum $S(\lambda)$ within the wideband of 300 – 1100 nm, equation (1) was utilized to calculate the weighted average reflection ($R_{avg}$ %) of the substrates, as illustrated below (Song et al., 2013).

$$R_{avg} = \frac{\int_{300nm}^{1100nm} R(\lambda)S(\lambda)d\lambda}{\int_{300nm}^{1100nm} S(\lambda)d\lambda}$$  \hspace{1cm} (3)

where $R(\lambda)$ represents absolute reflectance, $S(\lambda)$ represents spectral photon density under standard AM 1.5G solar spectrum and $\lambda$ represents the wavelength of light. The absorption (A) of light through the samples can be obtained from the equation $A = (100 - R - T)\%$ (Özkol et al., 2020). From the equation, the transmission (T) is zero because the c-Si is an opaque body, which cannot allow light to transmit through it. Therefore, the equation becomes $A = (100 - R)\%$. The result from the absorption, the light-coupling performance of the LPD-Al₂O₃ on the samples can be achieved using the potential $J_{sc}(\lambda)$. The equation (4) below can be used to calculate the value of potential $J_{sc}(\max)$ for the wavelength region of 300 – 1100 nm (Wang et al., 2021).

$$J_{sc}(\max) = q \int_{\lambda=300nm}^{\lambda=1100nm} EQE(\lambda).S(\lambda)d\lambda$$  \hspace{1cm} (4)

RESULTS AND DISCUSSION
Morphological characterization
Figure: 4 (a) – (e) describes the images from AFM tilted at 45° of c-Si, LPD-Al₂O₃/c-Si 1hr, LPD-Al₂O₃/c-Si 1.5 hours, LPD-Al₂O₃/c-Si 2 hours and LPD-Al₂O₃/c-Si 2.5 hours respectively. From the images displayed by the AFM, it can be deduced that the RMS surface roughness increases with the growth rate and is affected by the annealing temperature of 400°C for 1 hour in the blue furnace. The root mean square (RMS) roughness of pure c-Si is 2.18 nm, the LPD-Al₂O₃/c-Si deposition for 1 hour is 26.7 nm while deposition for 1.5 hours is 27.2 nm. Also, the RMS surface roughness for deposition of 2 hours is 36.5 nm and that of 2.5 hours is 29.8 nm. This indicates that at deposition of LPD-Al₂O₃ on c-Si reaches its optimal growth limit at 2 hours and remain constant until 2.5 hours.
Figure 4: AFM images of (a) planar c-Si (b) LPD-Al₂O₃/c-Si 1 hour (c) LPD-Al₂O₃/c-Si 1.5 hours (d) LPD-Al₂O₃/c-Si 2 hours (e) LPD-Al₂O₃/c-Si 2.5 hours deposition time and annealed at 400°C for 1 hour.

Also Figure 5: (a and b) illustrates the FESEM results showing the top view of the c-Si and LPD-Al₂O₃/c-Si substrates. The top view (10,000 magnification) of the planar c-Si shows no sign of deposition as seen in Figure 5(a). Proper observation on the top view FESEM image of LPD-Al₂O₃/c-Si in figure 5(b) shows a uniformly and continuous spread of LPD-Al₂O₃ thin film with few bumps. Generally, a smooth insulating layer of the thin film is preferable because of the good interface contact with the c-Si wafer, which can improve the stability and electrical performance of the solar cell. The cross-sectional FESEM image of LPD-Al₂O₃/c-Si in Figure 5(c) shows a smooth layer of the thin film deposited which thickness is 30 nm. This thickness corresponds to [5].

Figure 5: Top view of (a) pure c-Si (b) LPD-Al₂O₃/c-Si and (c) cross-sectional view of LPD-Al₂O₃/c-Si showing a thickness of 30 nm thin film.
Figure 6: Explains the EDX spectrum of the LPD-Al₂O₃ thin film deposited Si substrate with a scan range of 0 to 10 keV, 400°C annealing temperature. The figure shows that the apparent signals of Al and O are located at 1.50 and 0.50 keV, respectively. There are no other peaks found, indicating that the LPD-Al₂O₃ thin film chemical composition process is impurity-free. This is in addition to the Si peak. The atomic ratio of the O element to the Al element is estimated to be roughly 7:3, which deviates from the predicted 3:2 ratio based on the peak values found. Because of the excess oxygen in the thin film, the presence of LPD-Al₂O₃ results in a negative fixed charge Qf between the LPD-Al₂O₃/c-Si interface. This suggests that the LPD-Al₂O₃ thin film has a low thickness. This supports reference (Cibert et al., 2008).

**Optical characterization**

Figures 7: (a) and (b) show the total reflection and absorption of all the substrates from the UV-vis-NIR characterization. The equation (3) above is used to calculate $R_{avg}$ of total reflection obtained from the curve within the wavelength 300 – 1100 nm region. The c-Si and LPD-Al₂O₃/c-Si of several growth film deposition time samples are compared. The $R_{avg}$ of the c-Si at a wavelength of 600 nm is 44.9% while the $R_{avg}$ of LPD-Al₂O₃/c-Si 1hr is 35.0 %. Also, the $R_{avg}$ of LPD-Al₂O₃/c-Si 1.5 hours deposition is 35.3 % while that of LPD-Al₂O₃/c-Si 2 hours is 34.7 %. lastly, the $R_{avg}$ of LPD-Al₂O₃/c-Si 2.5 hours is 29.6 %. The trends show that the increase in growth time of the thin film on the substrates causes a reduction in reflection of the c-Si. Hence, improve absorption of light energy for better efficiency and performance of solar cell applications. The percentage reduction or improvement in reflectivity is calculated with the equation $\left(\frac{Abs(b-a)}{b}\right)100\%$, where b and a are the weighted average reflectance of substrates before and after the deposition of the LPD-Al₂O₃ film respectively.

Figure 7: (a) Total reflection and (b) Total absorption curves of all samples annealed at 400°C for 1 hour
Figure 8: exhibits the XRD patterns of LPD-Al₂O₃ films deposited on c-Si and annealed at 400 °C for 1 hr. It can be seen that after the LPD-Al₂O₃ film is annealed at 400 °C, only the diffraction peaks α-Al₂O₃ (220) located at 89.9°C is observed. This makes the emergence of (400) and (440) planes indicate the structure of Al₂O₃ becomes γ-Al₂O₃. It means the film can crystallize to be γ-Al₂O₃ at a relatively low temperature. Although, no other peak corresponding to the α-Al₂O₃ (220) was observed, suggesting amorphous γ-Al₂O₃ thin films were obtained almost over the entire range of the annealing temperature. The amorphous nature of γ-Al₂O₃ dielectric is preferable because grain boundaries in poly-crystalline structure act as preferential paths for impurity diffusion and leakage currents, and certainly cause an inferior dielectric reliability (Zhang et al., 2017).

The Table 1 below show the relationship between the potential $J_{sc(max)}$ and $R_{avg}$ of the samples immersed in the growth film for different deposition time ranging from 1 – 2.5 hours and the pure c-Si, after annealing at 400°C for 1 hour. The Equation (4) above is used to achieve the potential $J_{sc(max)}$ and potential $J_{sc(max)}$ enhancement (%) by comparing the improvement of the other samples to the planar c-Si which represents the reference sample with $R_{avg}$ of 44.9 % and potential $J_{sc(max)}$ of 22.5 mA/cm². The LPD-Al₂O₃/c-Si 1 hour sample with $R_{avg}$ 35.0 %, has an increased potential $J_{sc(max)}$ value of 23.8 mA/cm² and an enhancement of 5.8 % because of low light reflection within a wavelength of 300 – 1100 nm. Also, the LPD-Al₂O₃/c-Si 1.5 hours and LPD-Al₂O₃/c-Si 2 hours sample of $R_{avg}$ are 35.3 % and 34.7 % exhibit a potential $J_{sc(max)}$ of 23.4 mA/cm² and 24.7 mA/cm² with an enhancement of 4.0% and 9.8% respectively compared to pure c-Si. Finally, LPD-Al₂O₃/c-Si 2.5 hours with the lowest $R_{avg}$ of 29.6 %, has potential $J_{sc(max)}$ and potential $J_{sc(max)}$ enhancement of 27.2 mA/cm² and 20.9 % respectively. This can be attributed to the improved broadband light absorption by the LPD-Al₂O₃ roughness on the surface of the planar c-Si wafer.

Table 1: Relationship between $R_{avg}$ and potential $J_{sc(max)}$ for all the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{avg}$ (%)</th>
<th>Potential $J_{sc(max)}$(mA/cm²)</th>
<th>Potential $J_{sc(max)}$ enhancement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si</td>
<td>44.9</td>
<td>22.5</td>
<td>-</td>
</tr>
<tr>
<td>LPD-Al₂O₃/c-Si 1 hour</td>
<td>35.3</td>
<td>23.8</td>
<td>5.8</td>
</tr>
<tr>
<td>LPD-Al₂O₃/c-Si 1.5 hours</td>
<td>35.0</td>
<td>23.4</td>
<td>4.0</td>
</tr>
<tr>
<td>LPD-Al₂O₃/c-Si 2 hours</td>
<td>34.7</td>
<td>24.7</td>
<td>9.8</td>
</tr>
<tr>
<td>LPD-Al₂O₃/c-Si 2.5 hours</td>
<td>29.6</td>
<td>27.2</td>
<td>20.9</td>
</tr>
</tbody>
</table>
CONCLUSION
In this work, the growth rate of LPD-Al2O3 thin film deposition on c-Si was studied. The LPD-Al2O3 thin film was prepared from precursor chemicals mixtures of Al2(SO4)3-18H2O and NaHCO3 dissolved in DI H2O at room temperature and obtained a pH of 3.1. Four samples of c-Si were immersed in the LPD-Al2O3 thin film for 1, 1.5, 2 and 2.5 hours and annealed in the furnace at a temperature of 400°C for an hour in N2 ambient. From the UV-vis curve, the Ravg of the samples including planar c-Si, LPD-Al2O3/c-Si 1hr, LPD-Al2O3/c-Si 1.5 hours, LPD-Al2O3/c-Si 2 hours and LPD-Al2O3/c-Si 2.5 hours are 44.9%, 35.3%, 35.0%, 34.7% and 29.6% respectively. Also, the values absorption is 55.1%, 64.7%, 65.0%, 65.3% and 70.4% respectively. The AFM images show RMS surface roughness of each sample. The reference sample (planar c-Si) has a smooth RMS surface roughness of 2.18 nm because no deposition of LPD-Al2O3 on its surface. The RMS surface roughness increased because of growth rate of LPD-Al2O3 thin film and annealing at 400°C for 1 hour. The RMS surface roughness of LPD-Al2O3/c-Si at 1, 1.5, 2 and 2.5 hours are 26.7 nm, 27.2 nm, 36.5 and 29.8 nm respectively. Moreso, the potential Jsc(max) of the planar c-Si without any deposition is 22.5 mA/cm², while LPD-Al2O3/c-Si 2.5 hours has a potential Jsc(max) of 27.2 mA/cm² resulting in Jsc(max) enhancement by 20.9% compared to the reference substrate (planar c-Si). It can be deduced that the deposition of LPD-Al2O3 thin film on b-Si substrate followed by annealing at a temperature of 500°C for 1 hour, decreases Ravg, increases the RMS surface roughness and increases the potential Jsc(max) of the substrate.

REFERENCES


