Properties of double-layer Al2O3/TiO2 antireflection coatings by liquid phase deposition

Dong-Sing Wuu, Che-Chun Lin, Chao-Nan Chen, Hong-Hsiu Lee, Jung-Jie Huang

A R T I C L E   I N F O

Available online 29 January 2015

Keywords:
Antireflection coatings
Liquid phase deposition
Titanium dioxide
Aluminum oxide

A B S T R A C T

In this investigation, Al2O3/TiO2 double-layer antireflection coatings were deposited on polished silicon substrate by using liquid phase deposition. The deposition solution of ammonium hexafluoro-titanate and boric acid was used for TiO2 deposition. Aluminum sulfate and sodium bicarbonate were used for Al2O3 deposition. The concentration of the sodium bicarbonate and boric acid in the deposition solution controls the rate of deposition of Al2O3 and TiO2 films. Under optimal conditions, the average refractive index of liquid phase deposited Al2O3 and liquid phase deposited TiO2 films was 1.58 and 1.76, respectively. The average reflectance was 3.3% at wavelengths from 400 to 800 nm for liquid phase deposited Al2O3 and liquid phase deposited TiO2 film thicknesses of 59 and 89 nm, respectively. This antireflection property was comparable to other vacuum deposition methods, such as plasma-enhanced chemical vapor deposition and sputtering; thus, the liquid phase deposition of antireflection coatings was highly favorable for silicon-based solar cells.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Antireflective coatings (ARCs) were required to reduce the optical loss of numerous optical devices, such as optical lenses, flat panel displays, and solar cells [1,2]. Reflection occurs at the interface where the refractive index changes abruptly. Several transparent materials have already been used as ARCs. These materials include SiO2 (n = 1.44), Si3N4 (n = 1.9), TiO2 (n = 2.3), Al2O3 (n = 1.86), Ta2O5 (n = 2.26), and SiO2–TiO2 (n = 1.8–1.96) [3–8]. These ARC films were most widely used for crystalline silicon (Si) solar cells as single-layer ARCs. However, low reflectance can be obtained from only a single-layer ARC at a specific wavelength. To minimize the front reflection of solar cells further, double-layer ARCs consisting of two materials (e.g., MgF2/ZnS, SiO2/TiO2, SiO2/Si3N4, and Al2O3/TiO2) have been developed because of their low reflectance at a relatively wide wavelength range [9–12].

ARCs were generally formed using vacuum processes, such as evaporation [13], sputtering [14], and plasma-enhanced chemical vapor deposition (PECVD) [15]. All of these methods can be used to produce films exhibiting uniform thickness and favorable optical properties. However, conventional vacuum deposition processes were expensive and unsuitable for continuous mass production, particularly for forming coatings for use in low-cost solar cells. Recently used nonvacuum processes for depositing an ARC film on a substrate include sol–gel dip coating, spin coating, spray pyrolysis, and liquid phase deposition (LPD).

This study applied the LPD method for fabricating ARC films to ensure low costs, uniformity, favorable adhesion, mass producibility, and the formation of large-area optical films.

LPD was a low-temperature (including room temperature) growth process that has other advantages such as high selectivity, a large area, simplicity, ease of change of the film composition, and ease of mass production [16,17]. However, there was absence of the antireflection properties of double-layer Al2O3/TiO2 ARC by LPD. For an optimal ARC design, the refractive index and thickness of each layer must be controllable to achieve the highest performance along the desired spectrum. In this study, double-layer LPD-Al2O3/LPD-TiO2 ARCs on a polished Si substrate by using LPD were investigated.

2. Experiment

A p-type Si (100) wafer was used as the substrate, and its resistivity was 10 to 20 Ω-cm. The Si substrate was degreased in solvent, chemically etched in a solution (HF:H2O = 1:10) for 30 s, and then rinsed in deionized (DI) water. The deposition system contains (1) a temperature-controlled water bath that provides a uniform deposition temperature at an accuracy of ±0.1 °C and (2) a Teflon vessel containing the deposition solution. Fig. 1 shows a flow chart of the ARC synthesis process performed using LPD. LPD-TiO2 and LPD-Al2O3 layers were deposited on a p-type Si (100) wafer substrate orderly by using LPD. An LPD-TiO2 film was the first layer on the p-type Si (100) wafer substrate by a 20 mL of 0.2 M ammonium hexafluoro-titanate ([(NH4)2TiF6] solution that was saturated with TiO2 powder and mixed.
with 20 mL of 0.5 M boric acid (H₃BO₃) for depositing LPD-TiO₂ films. The deposition temperature was maintained at 60 °C during the deposition. After the deposition, the Si wafer was rinsed in DI water and dried using purified nitrogen gas. Finally, the samples were annealed at 700 °C in air for 1 h to convert the amorphous phase to the crystalline anatase structure [18]. The LPD-Al₂O₃ film was the second film to be deposited on the LPD-TiO₂ film by using the 20 mL growth solution of the Al(OH)₃ (pH = 3.3) solution that was produced by the aluminum sulfate (Al₂(SO₄)₃ · 18H₂O) and sodium bicarbonate (NaHCO₃), with which 200 mL of DI water was added for depositing LPD-Al₂O₃ films. The deposition temperature was maintained at 40 °C during the deposition. After the deposition, the Si wafer was rinsed in DI water and dried using purified nitrogen gas. Finally, the samples were annealed at 300 to 700 °C in nitrogen for 1 h to increase the film density. The final film thicknesses of LPD-Al₂O₃ and LPD-TiO₂, measured using field-emission scanning electron microscopy (FE-SEM), were 99 and 89 nm, respectively. Fig. 2 shows the schematic structure of the LPD-Al₂O₃/LPD-TiO₂ double layers on a polished Si substrate.

The surface morphologies and thickness of the LPD films were analyzed using FE-SEM (JEOL JSM-7000F) at an accelerating voltage of 15 kV and atomic force microscopy (AFM; Dimension Icon AFM) using tapping mode. The refractive index of the LPD-Al₂O₃ and LPD-TiO₂ thin films was measured using an n&k analyzer (model: 1280). Chemical compositions of the LPD films were obtained with X-ray photoelectron spectroscopy (XPS; PHI 5000 VersaProbe) using an Al Kα radiation (1486.6 eV). The reflection spectra of the samples at wavelengths from 400 to 800 nm were obtained using an UV–VIS–NIR spectrophotometer.

3. Results and discussion

Single-layer LPD-TiO₂ ARCs were optimized based on our previous studies that indicated the LPD-TiO₂ film become denser as the H₃BO₃ concentration at 0.5 M with the mean reflectance of 5.3% [18]. In order to reduce the reflectance, the LPD-Al₂O₃/LPD-TiO₂ double layer structure was designed to improve the reflection property. Fig. 3 shows the deposition rate of LPD-Al₂O₃ films on the Si substrate as a function of the pH value of the growth solution. Smooth LPD-Al₂O₃ films on a polished Si substrate can be obtained. The deposition rate increases as the pH value of the growth solution increases and was linearly related to the pH value of the growth solution within the range of 3.1 to 3.4. However, a thick powder is covered with the film surface as the pH value for the growth solution at 3.4, causing a fast reaction rate in the precipitation of Al₂O₃ in the deposition solution. Thus, the optimal growth conditions for the most effective film determined a pH value of 3.3 for the growth solution.

Fig. 4 shows the surface morphologies of the LPD-Al₂O₃ film on the polished Si substrate with a pH value of 3.3 for the growth solution.
after annealing at 300 to 700 °C (Fig. 4(b)–(f)) in nitrogen for 1 h and as-deposited LPD-Al2O3 by FE-SEM (Fig. 4(a)). The surface morphology of the annealed LPD-Al2O3 films was denser and more uniform compared with the as-deposited film. In addition, the surface roughness of the LPD-Al2O3 film was observed using AFM, as shown in Fig. 5(a). The surface roughness of the LPD-Al2O3 film slightly decreased from 1.1 nm to 0.58 nm as the annealing temperature increased. These results indicated that an extremely flat and uniform LPD-Al2O3 film was obtained using LPD, which was suitable for application in optical films, as shown in Fig. 5(b). Fig. 6 shows the content of aluminum and oxygen of the LPD-Al2O3 film observed using XPS after annealing at 300 to 700 °C in nitrogen for 1 h. The oxygen content of the LPD-Al2O3 film was decreased as the annealing temperature increasing, due to the hydroxyl group (OH) which was desorbed from the LPD-Al2O3 film as temperature increasing [19]. This result indicated that the LPD-Al2O3 film after annealing at 700 °C in nitrogen for 1 h was close to the stoichiometry; therefore, this was the upper layer ARC condition.

Fig. 7 shows the refractive index of the annealed LPD-TiO2 and LPD-Al2O3 films on the polished Si substrate as a function of wavelength. The average refractive indices of the LPD-Al2O3 and LPD-TiO2 ARCs at the wavelengths from 400 to 800 nm were 1.58 and 1.76, respectively. To optimize the parameters of the ARCs (refractive index and thicknesses)
for double-layer LPD-Al2O3/LPD-TiO2 ARCs, the thickness adopted the
\( \lambda/4 \)-\( \lambda/4 \) film design at the wavelengths from 400 to 800 nm. The optimal ARC thickness for the minimal reflection of double-layer LPD-Al2O3/LPD-TiO2 ARCs can be determined using the following equation [20]:

\[
\frac{n_1 d_1}{\lambda} = \frac{1}{2 \tan^{-1} \left\{ \frac{(n_n - n_0)(n_0 n_1 - n_0 n_2)}{(n_0 n_2 - n_0 n_1)} \right\}^{1/2}}
\]

(1)

\[
\frac{n_2 d_2}{\lambda} = \frac{1}{2 \tan^{-1} \left\{ \frac{(n_n - n_0)(n_0 n_1 - n_0 n_2)}{(n_0 n_2 - n_0 n_1)} \right\}^{1/2}}
\]

(2)

where \( n_0, n_n, n_1, \) and \( n_2 \) were the refractive index of air, substrate, outer and inner layers, respectively; \( d_1 \) and \( d_2 \) were the thickness of the outer and inner layers, respectively. The minimal value of reflectance can be obtained as each layer must meet Eqs. (1) and (2), and the thickness of each layer can be calculated by using the equation of \( n_1 d_1 = n_2 d_2 = \lambda/4 \) (n: refractive index, d: thickness, \( \lambda \): wavelength).

Fig. 8 shows the measured reflectance spectra of the double-layer LPD-Al2O3/LPD-TiO2 ARCs on the polished Si substrate. Bare Si was well known to have a high refractive index, which leads to an average reflectance of approximately 37%. The high reflection loss can be reduced substantially by applying a suitable ARC. Following the deposition of double-layer LPD-Al2O3/LPD-TiO2 ARCs on the polished Si substrate, the minimal value of reflectance of 0.2% can be obtained at the wavelength of 515 nm. The average reflectance of approximately 3.3% between 400 nm and 800 nm was obtained as the thickness of the double-layer ARCs was 99 nm (LPD-Al2O3) and 89 nm (LPD-TiO2).

The cross-sectional image of the \( \lambda/4 \)-\( \lambda/4 \) structure double-layer LPD-Al2O3/LPD-TiO2 ARCs was analyzed using FE-SEM, as shown in Fig. 9. The coating layers consisted of two layers, LPD-Al2O3 at the top and LPD-TiO2 at the bottom. The interfaces of air/LPD-Al2O3/LPD-TiO2/Si substrate were clearly observed. The LPD-Al2O3 and LPD-TiO2 films were dense and uniform. The thickness of the LPD-Al2O3 and LPD-TiO2 films was approximately 99 and 89 nm. Optimal results were obtained using the aforementioned data analysis, which was applied to the mass productivity test. Fig. 10 shows the picture of the batch-type LPD process flow chart for the double-layer LPD-Al2O3/LPD-TiO2 ARCs on a 6-inch c-Si substrate. The uniformity of the double-layer LPD-Al2O3/LPD-TiO2 ARCs were measured at five positions (a, b, c, d and e) by n8k analyzer. The film thickness at five locations were 186, 187, 190, 186 and 185 nm, respectively. The uniformity of the double-layer LPD-Al2O3/LPD-TiO2 film was calculated as 1.33% by \( U\% = \left[ \frac{\text{max} - \text{min}}{\text{max} + \text{min}} \right] \times 100\% \). The max and min were maximum and minimum thickness of measurement positions. Thus, the surface morphology of the double-layer LPD-Al2O3/LPD-TiO2 ARCs was dense and uniform. This antireflective property was comparable to other vacuum deposition method, such as PECVD [4] and sputtering [21], which makes the LPD-ARC film be very favorable for Si-based solar cells.

4. Conclusions

In summary, this study deposited double-layer LPD-Al2O3/LPD-TiO2 ARCs on a polished Si substrate by using LPD, which was a low-cost and simple method that can be used at a low deposition temperature and was suitable for coating over a large area. Under an optimal reflection condition, the average reflectance was 3.3% at wavelengths from 400 nm to 800 nm for LPD-Al2O3 and LPD-TiO2 thicknesses of 99 nm and 89 nm, respectively. A minimal value of reflectance of 0.2% can be obtained at 515 nm. According to these results, the LPD-ARC films exhibit a favorable antireflective property, which was comparable to other vacuum deposition methods, such as PECVD and sputtering; thus, the LPD-ARC films were highly favorable for Si-based solar cells.
Acknowledgment

The authors thank the National Science Council Taiwan, for financially supporting this research under Contract No. NSC 102-2221-E-451-005.

References


