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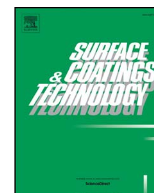

Antireflection and passivation property of aluminium oxide thin film on silicon nanowire by liquid phase deposition

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ABSTRACT

To improve the silicon nanowires solar cell of conversation efficiency is one of the most important and challenging problems, the antireflection coatings and surface passivation technique were very important. In this investigation, aluminium oxide coatings were deposited on silicon nanowires by using liquid phase deposition. The deposition solution of aluminium sulfate and sodium bicarbonate were used for aluminium oxide deposition. The Al_2O_3 film can cause different surface passivation at different annealing temperatures, allowing the Al_2O_3/SiNWs interface to form different amounts of negatively charged AlO_4 and positively charged SiO_x, that the mutually suppressing action of the two oppositely charged structure. Under the optimal condition, the reflectance and effective minority carrier lifetime of liquid phase deposited aluminium oxide film were 0.97% and 31 μs, respectively. The aluminium oxide films were used herein to fabricate antireflection coating and passivation film to ensure low cost, good uniformity, favorable adhesion, mass producibility, and the formation of large-area thin film; thus, the liquid phase deposition-antireflection coating film was highly favorable for silicon-based solar cells.

1. Introduction

Recently, one-dimensional nanostructure have received increasing attention for extremely low reflectivity on a wide wavelength range and simplicity of producing mesoporous nanostructures makes it promising for photovoltaic, photodetectors, photodiodes, and gas sensors applications. Several studies have investigated one-dimensional nanostructures. This technology may be produced both by "bottom-up" and "top-down" approaches such as vapor-liquid-solid process [1,2], laser-assisted catalytic growth [3], hydrothermal synthesis method [4,5], and electroless etching [6,7]. The mechanism of high temperature vapor–liquid–solid process growth in a furnace requires a long process time and the growth conditions cannot be easily controlled. Laser-assisted catalytic growth requires expensive laser devices to grow the nanowires. Moreover, the hydrothermal synthesis method was preferred to prepare a seed crystal as it has a long process time and produces nanowires of large diameter. The electroless etching process was used for fabricating silicon nanowires (SiNWs) in this study due to its great advantages such as low-cost, simplicity, mass producibility, uniformity, large-area thin films and achieving high efficiencies in mass production.

SiNWs with excellent antireflection properties are widely used in high efficiency solar cells [8–10]. However, SiNWs exhibit a surface recombination phenomenon and have uneven pore structures as they possess a high specific surface area and different etching rate, wherein numerous dangling bonds tend to exist, which increases the reflectance [11–13]. At present, antireflective coating (ARC) passivation films are most widely used in crystalline silicon solar cells due to the high effective minority carrier lifetime (τ_{eff}) that can be obtained, which prevents carrier recombination behavior in some high recombination regions (e.g., the cell surface, the contact region at the cell surface, and the metal electrode) and minimizes the front reflection, thereby improving the conversion efficiency of the cell. H.Y. Liu et al. used the ultrasonic spray pyrolysis deposition to deposit the Al_2O_3 films on the TiO_2 layer as the passivation and antireflection layer and UV photodetectors were fabricated. A.M. Albadri used the atomic layer deposition (ALD) to deposit the Al_2O_3 films on the silicon substrate as the passivation layer and solar cells were fabricated [14,15]. Herein, the Al_2O_3 thin films were applied as the surface passivation layer and ARC for the SiNWs-based solar cell due to the excellent antireflection properties, which can inhibit the recombination of photogenerated electrons and holes.

Al_2O_3 thin films are generally formed using vacuum processes, such as evaporation [16], sputtering [17], ALD [18], and plasma-enhanced

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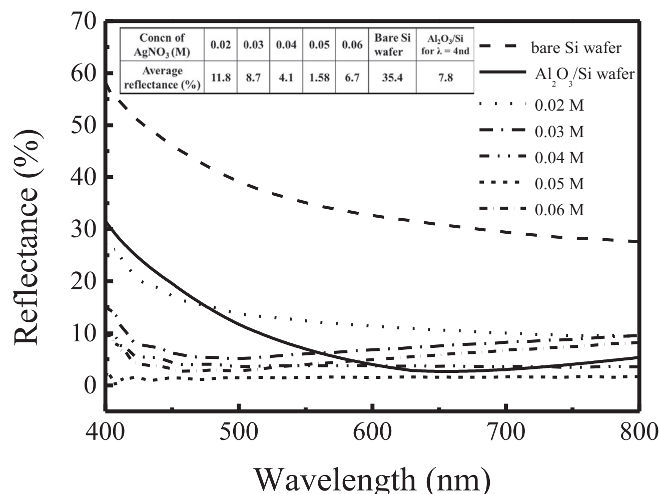
chemical vapor deposition (PECVD) [19]. All of these methods can be used to produce films exhibiting uniform thickness and favorable electrical properties. However, conventional vacuum deposition processes are expensive and unsuitable for continuous mass production, particularly for forming coatings for use in low-cost solar cells. Recently used non-vacuum processes for depositing Al_2O_3 thin films 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 Al_2O_3 thin films to ensure low costs, uniformity, favorable adhesion, mass producibility, and the formation of large-area thin films.

LPD mainly includes hydrolysis and a direct deposition reaction of the metal–fluoro complex at low ambient temperature (including room temperature) without any heating process, which has advantages such as high selectivity, large area, simplicity, ease of change of the film composition, and ease of mass production [20–23]. However, there are absence studies of the passivation and antireflection properties of Al_2O_3 thin films on the SiNWs solar cell using LPD. To achieve the optimal passivation and antireflection of Al_2O_3 thin films on SiNWs, the precursor concentration of $AgNO_3$ for controlling the Si substrate etching and $NaHCO_3$ for controlling the Al_2O_3 film deposition should be adjusted. In this study, the passivation and antireflection properties of Al_2O_3 thin films on the SiNWs substrate using LPD were investigated.

2. Experiment

A boron-doped, p-type (100)-oriented silicon wafer with a resistivity of 0.5–3 Ω·cm was used as the substrate in this study. The Si substrate was degreased in a solvent, chemically etched in a solution ($HF:H_2O$ = 1:10) for 30 s, and then rinsed in deionized (DI) water. The etching and deposition system contains (1) a temperature-controlled water bath that provides uniform etching and deposition temperature at an accuracy of ± 0.1 °C and (2) a Teflon vessel containing the etching and deposition solution. SiNWs fabrication using metal-assisted wet chemical etching, first, the SiNWs etching solution was prepared using a mixture of silver nitrate and hydrofluoric acid (HF) solution with the combined proportions of 40 mL of 0.05 M silver nitrate and 32 mL of 0.4 M HF. The etching temperature was maintained at 40 °C during the etching process. After the necessary etching process was completed, the SiNWs was immersed in the nitric acid and HF solution to remove the residual silver particle and native oxide layer, respectively, and the SiNWs structure was thus obtained. LPD-Al_2O_3 thin films were orderly deposited on a SiNWs substrate using LPD. The 20 mL growth solution of the $Al(OH)_3$ (pH = 3.3) solution that was produced by the aluminium sulfate ($Al_2(SO_4)_3{\cdot}18H_2O$) and sodium bicarbonate ($NaHCO_3$), with which 200 mL of DI water was added for depositing LPD-Al_2O_3 films. The deposition temperature was maintained at 40 °C during the deposition. After the deposition of the 40 nm LPD-Al_2O_3 thin films, the substrate was rinsed in DI water and dried using purified nitrogen gas. Finally, post-deposition annealing was performed in a quartz furnace at a temperature of 500 °C for 30 min under nitrogen ambient to increase the film density, adhesion, and passivation properties.

The surface morphologies of the LPD films and SiNWs were analyzed using field-emission scanning electron microscopy (FE-SEM; JEOL JSM-7000F) at an accelerating voltage of 15 kV. The Al_2O_3/Si interface was analyzed using field emission transmission electron microscope (FE-TEM, JEOL JEM-2100F) equipped with a 200 kV field-emission gun. The structure of Al_2O_3 thin films in the were characterized by fourier transform infrared (FTIR) spectroscopy. The reflectance spectra of the samples at wavelengths from 400 to 800 nm were obtained using a UV–Vis spectrophotometer with integrating sphere. Chemical compositions of the LPD films were obtained by X-ray photoelectron spectroscopy (XPS; PHI 5000 VersaProbe) with an Al Kα radiation (photon energy of 1486.6 eV). The energy resolution of this instrument was 0.5 eV full-width at half maximum. The measurement was conducted at a base pressure of 7.4 × 10^{-7} Pa in an analyzer chamber. A 2 kV Argon ion beam with a current density of 100 A/cm^2 was used to acquire the depth profiles, and the binding energy of each element was self-calibrated to C 1s (284.5 eV) reference peak states. The τ_{eff} of the LPD-Al_2O_3 thin films were measured using a Sinton Instruments WCT-120 system in the QSSPC mode. The τ_{eff} of LPD-Al_2O_3 thin films on the Si substrate using different annealing temperature were measured under photo-excitation, which was mainly the recombination time of the sample exciting electrons and holes after illumination.



Concn of AgNO3 (M)	0.02	0.03	0.04	0.05	0.06	Bare Si wafer	Al2O3/Si for λ = 4nd
Average reflectance (%)	11.8	8.7	4.1	1.58	6.7	35.4	7.8

Fig. 1. The reflectance spectra of the SiNWs as a function of $AgNO_3$ concentration, conventional antireflection coating of Al_2O_3/Si (Al_2O_3 film thickness must satisfy the λ = 4nd condition) and bare silicon wafers at wavelengths from 400 to 800 nm. The inset table shows the average reflectance at wavelengths from 400 to 800 nm.

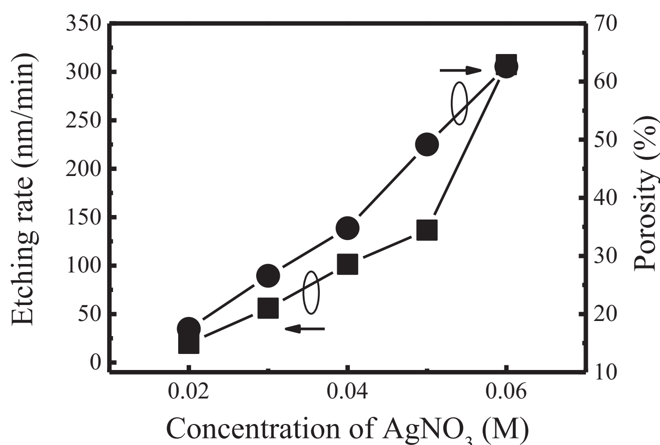


Fig. 2. Etching rate and porosity of SiNWs as a function of $AgNO_3$ concentration.

3. Results and discussion

To obtain a SiNWs structure with the best antireflection, we studied the effect on SiNWs length by changing the concentration of $AgNO_3$, thereby producing SiNWs with different reflectance. Fig. 1 shows the reflectance changes in silicon wafers etched by different $AgNO_3$ concentrations resulting from a fixed HF concentration, conventional quarter-wavelength single antireflection coating, and bare silicon wafers. The high refractive index of a silicon wafer is well known, and studies have shown that the average reflectance of the untreated silicon wafer is as high as 35.4%. When silicon wafers are etched into SiNWs, the reflectivity in the wavelength range 400–800 nm has overall shown a decreasing trend. The lowest average reflectance is 1.58% (0.05 M) because after the silicon wafer is soaked in an etching solution of HF and $AgNO_3$, it is etched into SiNWs with a matrix structure. The spaces among the SiNWs structure is smaller than or close to the wavelength of

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