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

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ABSTRACT

To improve a high-efficiency silicon nanowires solar cell, using the antireflection coatings and surface passivation technique were very important. In this investigation, titanium oxide antireflection coatings were deposited on silicon nanowires by using liquid phase deposition. The deposition solution of $(NH_4)_2TiF_6$ and H_3BO_3 were used for titanium oxide deposition. The concentration of the H_3BO_3 in the deposition solution play important roles in the formation of $Ti–Si_{1-x}O_y$ interface layer between the titanium oxide/silicon nanowires interface and to control the trace amount of hydrofluoric acid in the solution. The titanium oxide films modification decreases and increases the reflectance and effective minority carrier lifetime of the silicon nanowires arrays. Under the optimal condition, the reflectance and effective minority carrier lifetime of liquid phase deposited titanium oxide film were 3.6% and 1.29 μs, respectively. The titanium 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-based solar cell surfaces have received increasing attention for two reasons: (i) fabrication of mesoporous nanostructures is simple and cost effective and (ii) the one-dimensional array nanostructures effectively decrease reflectance with increasing absorption of sunlight. 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, and formation of large-area thin films.

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. Herein, the TiO_2 thin films were applied as the surface passivation layer and ARC for the SiNWs-based solar cell due to the excellent antireflection properties and fluorine doping, which can inhibit the recombination of photogenerated electrons and holes.

Titanium oxide thin films are generally formed using vacuum processes such as atomic layer deposition [13] and chemical vapor deposition [14–16]. These methods can be used to produce films with 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. Sol-gel dip coating [17,18], hydrothermal process [19–21], spray pyrolysis [22], and liquid phase deposition (LPD) [23] are some of the non-vacuum processes currently used for depositing

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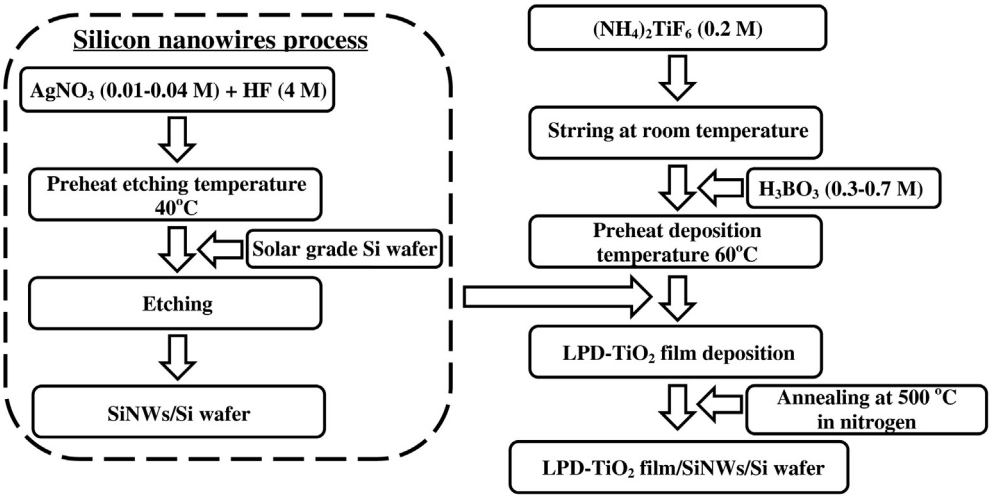

Fig. 1. Flow chart of LPD-TiO_2 thin film deposition on SiNWs.

TiO_2 thin films on a substrate. Among these processes, in this study, LPD has been used for fabricating TiO_2 thin films due to its various advantages, including low costs, uniformity, favorable adhesion, mass producibility, fluorine passivation and 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 [24–26]. However, there are absence studies of the passivation and antireflection properties of TiO_2 thin films on the SiNWs solar cell using LPD. To achieve the optimal passivation and antireflection of TiO_2 thin films on SiNWs, the precursor concentration of $AgNO_3$ for controlling the Si substrate etching and H_3BO_3 for controlling the TiO_2 film deposition should be adjusted. In this study, the passivation and antireflection properties of TiO_2 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. Fig. 1 shows a flow chart of the SiNWs and LPD-TiO_2 thin films fabrication process using metal-assisted wet chemical etching and LPD. 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 0.04 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 silicon substrate 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. Titanium oxide thin films were orderly deposited on a SiNWs substrate using LPD. 20 mL of $(NH_4)_2TiF_6$ (0.2 M) solution that was saturated with TiO_2 powder was mixed with 20 mL H_3BO_3 (0.3–0.7 M) for depositing the TiO_2 thin films. The deposition temperature was maintained at 60 °C during the deposition. After the deposition of the LPD-TiO_2 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 reflection spectra of the samples at wavelengths from 400 to 800 nm were obtained using a UV–vis spectrophotometer. 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-TiO_2 thin films were measured using a Sinton Instruments WCT-120 system in the QSSPC mode. The τ_{eff} of LPD-TiO_2 thin films on the Si substrate using different H_3BO_3 concentration were measured under photo-excitation, which was mainly the recombination time of the sample exciting electrons and holes after illumination. Furthermore, τ_{eff} depends on both bulk minority carrier lifetime (τ_{bulk}) and surface recombination velocity

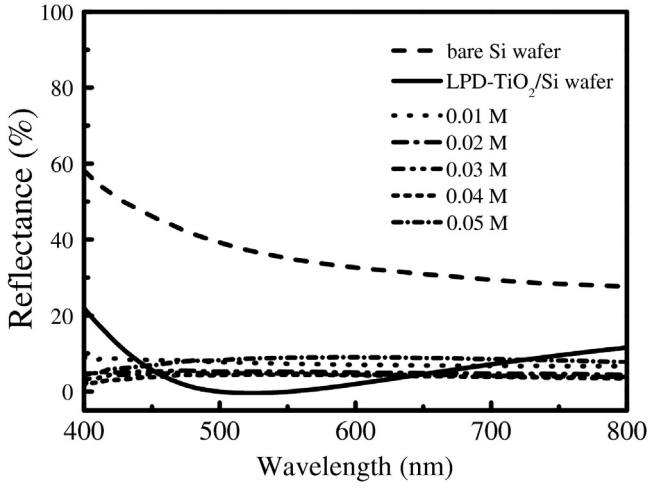

Fig. 2. The reflectance spectra of the SiNWs as a function of $AgNO_3$ concentration at wavelengths from 400 to 800 nm.

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