Optical and Electrical Properties of $Ti_xSi_{1-x}O_y$ Films

Jung Wook Lim, Sun Jin Yun, and Je Ha Kim

$Ti_xSi_{1-x}O_y$ (TSO) thin films are fabricated using plasma-enhanced atomic layer deposition. The Ti content in the TSO films is controlled by adjusting the sub-cycle ratio of TiO_2 and SiO_2. The refractive indices of SiO_2 and TiO_2 are 1.4 and 2.4, respectively. Hence, tailoring of the refractivity indices from 1.4 to 2.4 is feasible. The controllability of the refractive index and film thickness enables application of an antireflection coating layer to TSO films for use as a thin film solar cell. The TSO coating layer on an Si wafer dramatically reduces reflectivity compared to a bare Si wafer. In the measurement of the current-voltage characteristics, a nonlinear coefficient of 13.6 is obtained in the TSO films.

Keywords: TiSiO, refractive index, AR coating, solar cell, nonlinear I-V curve.

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I. Introduction

TiO_2 has attracted attention due to its high dielectric constant (κ) and high refractive index (n). However, TiO_2 has disadvantages of a high leakage current and a low crystallization temperature below 400°C [1]. One way of overcoming these problems is fabricating a mixture of TiO_2 and a low κ material, such as SiO_2 and Al_2O_3 [2]. It is expected that a mixed material like $Ti_xSi_{1-x}O_y$ (TSO) film will show improved leakage current and breakdown voltage. If the compositions of the mixture are controlled accurately, the dielectric constant and refractive index can be tailored, which will be useful in fabricating optical and electronic devices. Plasma-enhanced atomic layer deposition (PEALD) is a powerful method to deposit thin films with precise controls of the mixed material composition and film thickness [2], [3]. Tailoring the refractive index and film thickness provides many advantages, particularly in the fabrication of antireflection (AR) coating films used as solar cells. In the field of thin film solar cells, AR coating with the designed optical thickness (a product of refractive index and film thickness) is required to enhance solar cell efficiency [4], [5]. High κ materials such as TiO_2 and ZnO have been used as AR coated films in Si thin film solar cells [6]-[8]. However, ZnO shows a photo induced variation of electrical properties under visible illumination [9].

Multilayer AR coating with refractive index variation effectively enhances the solar cell efficiency [10], [11]. Precise control of the optical thickness of TSO films grown using PEALD will be useful for the light-capturing structure of thin film solar cells.

To secure a wide refractive index range, a low n material (such as SiO_2 and Al_2O_3) and a high n material (such as TiO_2) should be selected to fabricate an AR coating for a thin film solar cell. In this study, SiO_2 and TiO_2 have been selected and refractive indices between the values of SiO_2 and TiO_2 could be controlled. For the application of the AR coating layer of an Si-based solar cell, TSO with various refractive indices was deposited on an Si wafer. Then, a reduction in reflectivity was observed.

In current-voltage (I-V) measurements, TSO films showed a nonlinear I-V behavior. High nonlinearity is important to realize protection devices. This protection function is possibly due to the nonlinear electrical property that is given by the following relation:

$$I = KV^{\alpha}, \tag{1}$$

where α, V, I, and K are the non-linearity coefficient, the applied voltage, the current, and a constant, respectively [12].

II. Experiments

TSO films with the thickness of around 70 nm were grown using PEALD at 250°C. The precursors for TiO_2 and SiO_2 were titanium isopropoxide [TTIP; $Ti(OCH(CH_3)_2)_4$] and tetraethoxysilane [TEOS; $Si(OC_2H_5)_4$], respectively. The formation of one cycle for SiO_2 is TEOS/source purge (SP)/O_2 gas (plasma)/reactant gas purge (RP), and that for TiO_2 is TTIP/SP/O_2 gas (plasma)/RP. The plasma power density was about 0.4 W/cm^2, and the plasma was turned on only during the supply of O_2 reactant gas. The purging gas was Ar, and the reactant gases were O_2+Ar. The formation of one cycle for the TSO film is N_{Ti} subcycles of TiO_2, and N_{Si} subcycles of SiO_2, which designates the cycle coordinates (N_{Ti}, N_{Si}).

For example, TSO (1, 2) designates one cycle of TiO_2 and two cycles of SiO_2 [13]. TSOs of (1, 2), (1, 1), (2, 1), and (3, 1) were fabricated; thus, the Ti content varied with the cycle coordinates. To obtain reflection spectra curves, TSO films were deposited on a p-type Si (100) wafer as shown in Fig. 1(a), and for I-V measurement, a metal/TSO/ITO/glass structure was fabricated as shown in Fig. 1(b). The I-V measurement was performed with a voltage mode, which means that voltages were supplied and then currents were measured. In addition, the I-V curves were measured by a precision semiconductor parameter analyzer HP 4156B. The Mo metal used as a top electrode was deposited using a sputtering method. The diameter of a dot is 0.04 cm; thus, the dot area is 0.001256 cm^2. The elemental composition of the film was determined using auger electron spectroscopy (AES). The film thickness and refractive index were obtained using ellipsometer measurements. The Ti content can be controlled as a variation of cycle coordinates in fabricating TSO films.

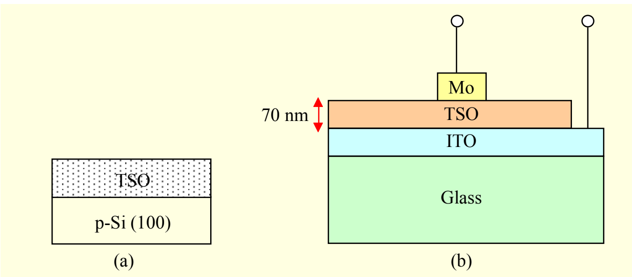

Fig. 1. Schematic diagram of (a) a TSO/p-Si structure for reflection spectra and (b) an Mo/TSO/ITO/glass structure for I-V measurement.

Table 1. Thicknesses, refractive indices, and compositions of TiSiO films.

Sample	Thickness (nm)	Refractive index	Compositions (at. %)		
			O	Ti	Si
TSO (1, 2)	71	1.93	61.8	19.1	19.1
TSO (1, 1)	66	2.03	62.8	21.2	16.0
TSO (2, 1)	68	2.14	63.9	24.5	11.6
TSO (3, 1)	66	2.21	65.4	26.3	8.3

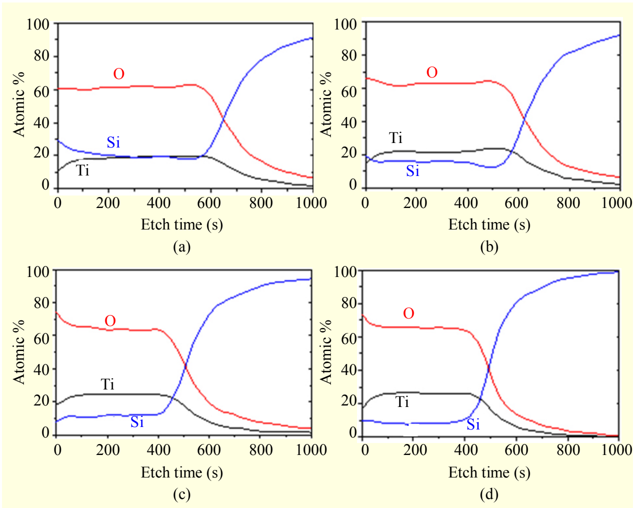

Fig. 2. AES depth profiles of (a) TSO (1,2), (b) TSO (1,1), (c) TSO (2,1), and (d) TSO (3,1) films.

III. Results and Discussion

1. Composition Control

The Ti composition was controlled by adjusting the sub-cycles of TiO_2 and SiO_2 using PEALD. As N_{Ti} increases, the Ti content gradually increases as does the refractive index. The thicknesses, refractive indices, and compositions of TSO films are listed in Table 1.

From the results of the composition data, the atomic ratios of Ti to Si were 1.00, 1.33, 2.11, and 3.17. Note that, as the results of Table 1 show, the oxygen content increases from 61.8 at.% for TSO (1, 2) to 65.4 at.% for TSO (3, 1) with the Ti content.

In the cases of TSO (1, 2) and TSO (3, 1), $Ti_{0.5}Si_{0.5}O_{1.62}$ and $Ti_{0.76}Si_{0.24}O_{1.89}$ films were obtained. Thus, the valence of Ti or Si may increase from 3 to 4 as the Ti content increases. This result indicates that nonstoichiometric compounds were formed in the TSO films. In the case of AlTiO film grown using PEALD, similar nonstoichiometric compounds were found [2]. The nonstoichiometric compounds may generate nonlinear I-V characteristics.

Figure 2 shows the AES depth profile for TSO (1, 2), (1, 1), (2, 1), and (3, 1) films. From the figures, with the exception of the surface and interface, good composition controllability was obtained through the depth of the TSO films. Hence, physical properties such as refractive index and dielectric constant could be tailored, which is powerful in optimizing the optical and electrical properties.

2. Optical Properties of TSO Films

In our previous study, an equation for the relation between the refractive index and the Ti to Al cycle ratio was derived in AlTiO films [2]. In a similar way, the relation between the refractive index and the Ti/Si atomic ratio can be obtained, and it will be helpful to control the refractive index of TSO films by adjusting the cycle ratio. Figure 3(a) shows the refractive indices as a function of the Ti/Si atomic ratio. The reason for the nonlinear relation was explained in our previous work [2]. In the deposition of TSO films, the refractive index increases with a negative curvature as the Ti composition increases. Therefore, optical thickness can be controlled, and this can be a powerful technique in fabricating AR coating. In the field of thin film solar cells, a method for improving cell efficiency is essential to lowering the price of a cell. Our technique of tailoring the optical thickness of TSO films will prevent reflection in the visible and near-infrared regions and improve cell efficiency in thin film solar cells [14]. To investigate the AR characteristics of TSO films, TSO (1, 2), (1, 1), (2, 1), and (3, 1) films were each deposited on an Si substrate. Figure 3(b) shows the reflection spectra of TSO/Si samples, where the minimum reflectivity is nearly zero for all samples.

When an AR coating layer with thickness t and index of refraction n_{AR} is placed on a substrate with an index of refraction n_{sub}, the reflectivity would be zero for normal incident light when the following conditions are satisfied:

$$t = \frac{\lambda}{4n_{AR}} + J\frac{\lambda}{2n_{AR}}, \qquad n_{AR} = \sqrt{n_{sub}}, \tag{2}$$

where J is an integer, and λ is the wavelength of incident light in a vacuum [15], [16]. Hence, the wavelength of minimum reflectivity is $4n_{AR}t$ when J is zero. Using the results of Table 1, the theoretical wavelengths of minimum reflectivity are

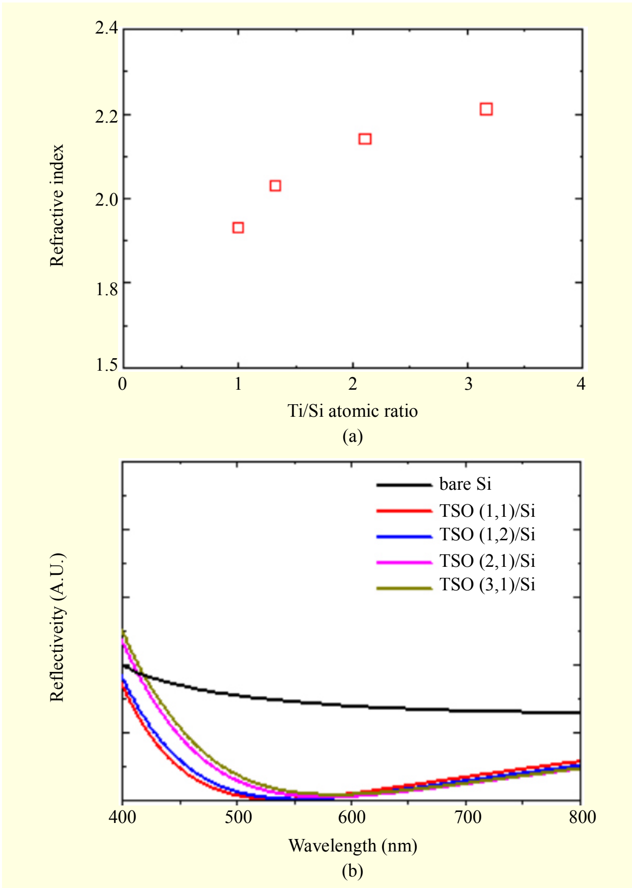

Fig. 3. (a) Refractive indices versus Ti/Si atomic ratio and (b) reflection spectra for TSO/Si samples.

548 nm, 536 nm, 582 nm, and 583 nm for TSO (1, 2), (1, 1), (2, 1), and (3, 1), respectively. The experimental data of wavelengths of minimum reflectivity from Fig. 3(b) were 553 nm, 539 nm, 578 nm, and 586 nm for TSO (1, 2), (1, 1), (2, 1), and (3, 1), respectively, which are very close to those obtained by theoretical calculation. The refractive index of the Si wafer is about 3.5; thus, the ideal refractive index of the AR coating layer should be 1.87 from (2), which is close to that of TSO (1, 2). As shown in Fig. 3(b), the minimum reflectivity was below 0.1% for TSO (1, 2)/Si samples, while the minimum reflectivity was more than 2% for TSO (3, 1)/Si samples.

When a TSO AR coating layer is used in an Si-based solar cell, high transmittance should be confirmed. Since the band gap of TiO_2 is above 3 eV, which falls to about 413 nm, light absorbance of TSO samples in the visible range may be quite small. Thus, transmittance will be higher with a decrease of reflectivity. Figure 4 shows reflection spectra of TSO/glass samples. For TSO (1, 2)/glass and TSO (1, 1)/glass samples, lower reflectivities over the entire visible range were obtained compared to TSO (2, 1)/glass and TSO (3, 1)/glass samples. Ti compositions of TSO (1, 2) and TSO (1, 1) are lower than

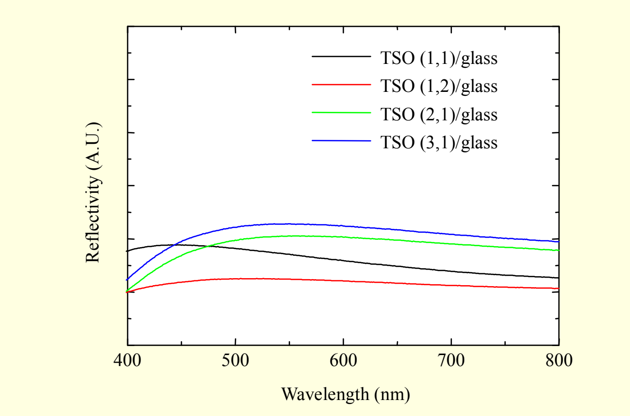

Fig. 4. Reflection spectra of TSO/glass samples.

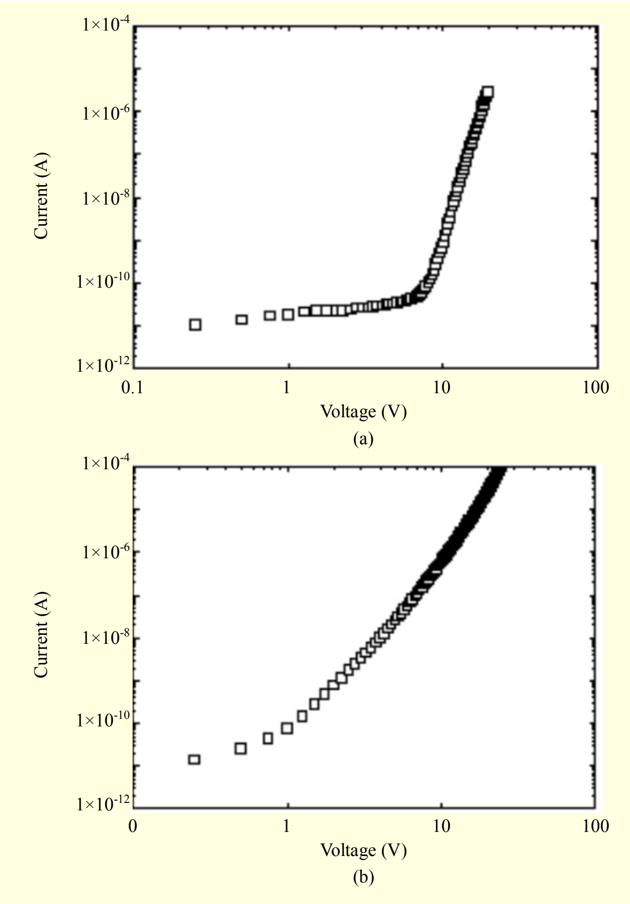

Fig. 5. Current-voltage curves of TSO (1,2) sample with (a) forward bias and (b) reverse bias.

those of TSO (2, 1) and TSO (3, 1). This implies that an AR coating layer with a lower refractive index is advantageous for obtaining high transmittance in thin film solar cells.

3. Electrical Properties of TSO films

In an I-V measurement, TSO films show nonlinear I-V curves. For all TSO samples, different curves were obtained, namely, asymmetric curves, with both polarities, as different electrodes, Mo and ITO, were used as top and bottom electrodes. The equation of I-V curves indicates a power law relation, which may be related to deep traps [17].

Figures 5(a) and (b) show I-V curves of the TSO (1, 2) sample with forward bias and reverse bias, respectively. The TSO (1, 2) sample has the highest Si content among the four samples. The nonlinearity in the I-V curve is clearly shown with a forward bias. The nonlinear coefficients of 13.6 and 4.2 were obtained for forward bias and reverse bias, respectively. These values were obtained from the slope of the log-log plot of the I-V curves, which show a linear relationship between current and voltage. In I-V curves for other TSO compositions, nonlinear coefficients exhibited smaller values than that for the TSO (1, 2) sample.

IV. Conclusion

TSO films were grown using PEALD. The Ti content can be controlled by adjusting the cycle ratio of TiO_2 and SiO_2, and as a result, the refractive index and film thickness can be controlled. The controllability of the Ti content and film thickness is useful to tailor the optimal optical thickness of TSO films. The TSO films with various refractive indices show nearly zero reflectivity at a certain wavelength range. The TSO films can be applied as AR coating layers in thin film solar cells to improve conversion efficiency. In the measurement of I-V characteristics, a nonlinear coefficient of 13.6 was obtained in TSO (1, 2) films.

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