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Al_2O_3 thin films deposited by thermal atomic layer deposition: Characterization for photovoltaic applications

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ABSTRACT

Al_2O_3 thin films with thickness between 2 and 100 nm were synthetized at 250 °C by thermal atomic layer deposition on silicon substrates. Characterizations of as-deposited and annealed layers were carried out using ellipsometry, X-ray reflectivity, and X-ray photoelectron spectroscopy. A silicon-rich SiO_x layer at the interface between Si and Al_2O_3 was introduced in the optical models to fit the experimental data. Surface passivation performances of Al_2O_3 layers deposited on n-type float-zone monocrystalline silicon were investigated as a function of thickness and post-deposition annealing conditions. Surface recombination velocity around 2 cm.s − 1 was measured after the activation of the negative charges at the Si/Al_2O_3 interface under optimized annealing at 400 °C for 10 min. The evolution of the interface layer and of the material properties with the thermal treatment was studied.

1. Introduction

Passivation of silicon surfaces is essential to achieve high solar cell performances. Several trends in photovoltaics have played an important role in the popularity of Al_2O_3 for efficient surface passivation. Firstly, the photovoltaic (PV) industry has been looking to improve the rear side of conventional screen printed p-type Si solar cells by replacing the standard Al-back surface field (BSF) by a dielectric-passivated rear side with localized BSF. Secondly, the use of n-type Si which does not suffer from light induced degradation and is less sensitive to common metal impurities, has become an attractive option for the fabrication of high solar cell efficiencies. The high density of negative charges in Al_2O_3 is well suited for the passivation of p+ emitters on n-type substrate [1]. A very high conversion efficiency of 23.9% for an n-type Passivated Emitter Rear Locally Diffused solar cell with a front side B-doped emitter and an Al_2O_3 passivation layer has been reported [2,3]. Recent works [4,5] have demonstrated that Al_2O_3 could also be efficient for passivation of n-type silicon substrates.

Along with Al_2O_3, atomic layer deposition (ALD) was introduced in the field of Si PV. ALD differs from conventional (plasma enhanced) chemical vapor deposition methods by strict separation of precursors in the reaction chamber. As the precursors can only react with the wafer surface in a self-limiting way, film growth proceeds layer by layer and a very precise thickness control is possible. This technique is ideal for depositing high-quality, uniform, and conformal thin films at relatively low temperatures (100–250 °C). The passivation of high aspect ratio surface texturation (nanowires, "black silicon"), used to improve the optical confinement in advanced solar cells, requires a very conformal thin passivation layer. Al_2O_3 deposited by thermal ALD (more conformal than plasma enhanced ALD) becomes the ideal candidate for this passivation layers.

Given the multiple advantages of Al_2O_3 deposited by ALD, this material has become widely used for photovoltaic applications [6] where the commonly used thickness is less than 15 nm. Therefore, an important need in very thin film characterization has appeared. However, very thin films (<10 nm) are difficult to characterize precisely as interfaces play a major role in the data analysis. For example, thickness and refractive index are difficult to measure separately by optical techniques like ellipsometry as they are highly correlated [7]. Consequently, various characterizations techniques and optical models should be used and compared in order to determine very thin film properties.

In this study, Al_2O_3 layers with thicknesses in the range 2–100 nm were deposited by thermal ALD on n-type crystalline Si substrates. Fast, non-destructive and accurate characterization techniques were chosen to analyze the Al_2O_3 layers and the interfaces. Optical and geometrical properties of the Al_2O_3 layers were studied by ellipsometry and X-ray reflectivity (XRR). Stoichiometry was measured by X-ray photoelectron spectroscopy (XPS) to analyze the material and the interface structure. The surface passivation of the Si wafers was evaluated by photo-conductance measurements. Characterization of the Al_2O_3 layers

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and of the interfaces was performed before and after the thermal treatment that is required to improve the surface passivation of silicon.

2. Sample preparation

We used 250 μm thick float zone (FZ) n-type double sided polished Si (100) substrates with a resistivity of 10 Ω.cm. Sapphire substrates A-Plane (11–20) polished on the front side were also used for additional ellipsometry measurements. Prior to deposition, the wafers were cleaned using standard chemical process (Piranha [H_2O_2, H_2SO_4] and diluted HF). Al_2O_3 films were deposited by ALD in an Ultratech Fiji F200 reactor. Trimethylaluminium (Al $(CH_3)_3$) and water (H_2O) were used as reactants. The chuck and chamber temperature was set to 250 °C during deposition. Substrates were positioned on quartz holders to coat both surfaces in the same run. This was particularly interesting for minority carrier lifetime measurements that required passivation on both surfaces. For the present study, the number of cycles was varied between 20 and 1000, leading to film thicknesses between 2 and 100 nm. More precisely, we measured previously a growth per cycle (GPC) of 0.098 nm per cycle at 250 °C on Si substrates [8]. After as-deposited characterizations, the samples were annealed in the ALD chamber in direct contact with the chuck. A range of temperatures (350–450 °C) and annealing times (5–15 min) were applied. The argon pressure was kept at around 670 Pa. The annealing step is essential for photovoltaic applications to activate the surface charges and improve the surface passivation.

3. Results and discussion

In order to investigate the interface properties, different optical models were considered. These models account for an abrupt transition between the Si substrate and Al_2O_3 (Model 1), surface roughness (Model 2) or a SiO_x interface layer (Model 3) at the Si/Al_2O_3 interface, and a carbon surface layer due to surface contamination (Model 4). Negligible surface roughness at the interface Al_2O_3/air was evidenced by atomic force microscope [8] and was therefore not included in the models.

3.1. Characterization of Al_2O_3 thin films by ellipsometry

The thickness and wavelength-dependent refractive index n (λ) of the Al_2O_3 coatings were deduced from spectroscopic ellipsometry measurements in the 1.5–5 eV range, using a Jobin Yvon Horiba apparatus. The incident angle relative to the surface was 20°. The Al_2O_3 layer thickness was extracted from the data analysis and compared with the value expected from the GPC. The refractive index of the layers was calculated using a simplified Sellmeier formula for transparent media (Eq.(1)) that is supposed to be more accurate than Cauchy dispersion law for characterizing a material across a wide spectral range. The B and λ_1 parameters were fixed for the analysis at the following values: $B = 1.32$ and $\lambda_1 = 121.59$ nm, according to Kumar et al. [9].

$$n(\lambda) = \sqrt{A + \frac{B\lambda^2}{\lambda^2 - \lambda_1^2}} \tag{1}$$

Refractive indexes calculated with the most relevant models and for different film thicknesses are plotted in Fig. 2. All refractive index values are given for a wavelength of 630 nm. The fitted parameters are reported in Table 1 that gives the film thicknesses (e), refractive indexes (n), the Sellmeier coefficient A and the mean square error (MSE) to indicate the fit quality (a smaller value indicates a better fit to the experimental data).

First, a simple optical model was assumed with an abrupt transition between the Al_2O_3 layer and the Si substrate (Model 1 in Fig. 1). In this case, the refractive index of Al_2O_3 was found to depend strongly on the film thickness as shown in Fig. 2 (black hollow squares). A significant increase of the refractive index with decreasing thickness was observed below 50 nm ($n = 1.65$ for a 50 nm-thick film and $n = 2.15$ for a 3.9 nm-thick film). Furthermore, the fit accuracy decreased for thicknesses below 15 nm. Above 50 nm, the extracted value of the refractive index ($n = 1.65$) was constant and in agreement with the literature [1]. From these results, it was assumed that the simple optical model (Model 1) was not suitable for thin films below 50 nm and that the contribution of interfaces had to be taken into account.

Table 1
Fitted parameters from ellipsometry measurements using Model 1 and Model 3: thickness (e), refractive index at 630 nm (n), A parameter from Sellmeier law and fit quality (MSE).

Number of ALD cycles		30	50	100	150	500	1000
Thickness from GPC (nm)		2.9	4.9	9.8	14.7	49	98
Model 1	e (Al_2O_3)	3.9	5.5	10.6	15.8	50.9	101.2
	n	2.15	2	1.84	1.76	1.66	1.65
	A	3.25	2.65	2.01	1.8	1.37	1.37
	MSE	2.76	2.84	2.58	1.67	4.14	8.81
Model 3	e (Al_2O_3)	3.4	5.2	10.8	15.8	50.4	100
	e (SiO_x)	0.8	0.8	0.8	0.8	1.2	1.2
	n	1.74	1.7	1.66	1.66	1.65	1.65
	A	1.66	1.54	1.4	1.41	1.38	1.38
	MSE	2.6	2.14	2.3	1.11	4.19	5.15

As proposed by Petrik et al. [10], roughness at the Si/Al_2O_3 interface was taken into account in the ellipsometry data analysis. An interface layer was introduced as a Bruggeman effective medium composed of 50% Si substrate and 50% Al_2O_3 layer (Model 2) to simulate the surface roughness. Calculations lead to a negligible interface roughness of only 0.02 nm thickness and higher MSE values. Consequently, in our case, interface roughness does not explain the high refractive index values calculated for small Al_2O_3 thicknesses. Thermal ALD process leads to more conformal deposition than plasma enhanced ALD that was used by Petrik et al. That may explain the rougher interfaces observed in their case.

The presence of a Si-rich oxide layer with Si—Si and Si—O bonds has been reported in the literature to explain the refractive index measurements of very thin oxide film grown on Si substrates [11–13]. A Si-rich oxide layer (SiO_x, $x < 2$) was introduced in our optical model at the interface between the Si substrate and the Al_2O_3 layer (Model 3 in Fig. 1). The refractive index of SiO_x is expected to be intermediate between crystalline Si ($n \sim 3.87$) and SiO_2 ($n \sim 1.46$). The best fits for the whole data range were obtained when introducing a SiO_x layer of thickness close to 1 nm with a refractive index of 3.17. The new values of Al_2O_3 refractive index extracted with Model 3 are shown in Fig. 2 (full red circles) as a function of thickness. Clearly, the introduction of a SiO_x layer at the Si/Al_2O_3 interface reduces the calculated value of Al_2O_3 refractive index which is now close to the expected value of 1.66 for film thicker than 10 nm, in agreement with the literature [1]. Table 1 summarizes the results obtained with Model 1 and Model 3. Note that although the fit accuracy is improved by the introduction of the sub-oxide interface for thin film, MSE increases for thicker Al_2O_3 layers (500 and 1000 cycles). This phenomenon was already described by Petrik et al. [10] and may indicate a slight inhomogeneity in thickness or refractive index or other non-ideality of the layer that are not taken into account by these models. Based on ellipsometry studies of the Si/SiO_2 interfaces [12,14] and on the high value of the extracted refractive index (3.17), the composition of the SiO_x interface layer could be roughly estimated to $x < 0.4$.

However, even with a SiO_x interface layer, an increase of the extracted Al_2O_3 refractive index is observed for thickness below 10 nm. This effect is attributed to the larger influence of the interface for very thin films and the strong correlation between the refractive index and thickness in the optical models and measurements [7,10].