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## Variation of the layer thickness to study the electrical property of PECVD Al<sub>2</sub>O<sub>3</sub> / c-Si interface

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### Abstract

This paper focusses in particular on the influence of the layer thickness on the passivation quality, the charge density and the interface defects of PECVD Al<sub>2</sub>O<sub>3</sub> passivation layers on c-Si surfaces. The surface recombination velocity and the interface defect density are observed to increase by decreasing the layer thickness. However, the density of negative charges remains almost constant with values around  $3 \cdot 10^{12} \text{ cm}^{-2}$ . An optimal passivation quality is obtained for thicknesses of 15 nm and higher. A linear relation between surface recombination velocity and  $D_{it}$  was established, allowing the estimation of the electron capture cross section ( $\sigma_n \sim 10^{-13} \text{ cm}^2$ ).

Additionally, we measured the capture cross section of holes and electrons using DLTS measurement. The results are found to be very similar to reported values for silicon dioxide. This supports the idea that the chemical passivation of crystalline silicon by Al<sub>2</sub>O<sub>3</sub> is performed by the interstitial SiO<sub>2</sub> layer.

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Surface passivation, Al<sub>2</sub>O<sub>3</sub>, PECVD, capture cross section, DLTS.

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### 1. Introduction

Aluminium oxide is becoming more and more important for crystalline-silicon-based solar cells. It offers a combination of low interface defect density and fixed negative charges that give the highest passivation quality of *p*-type Si surfaces. The determination of the property of this material is of great interest for the photovoltaic industry and for the scientific community. As Al<sub>2</sub>O<sub>3</sub> already proved its value as a passivation layer, the application of this material in the industry will mainly depend on the cost and

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the suitability of the deposition process. Particularly the thickness of aluminium oxide layers can have a substantial impact on the cost and the throughput of the deposition process. In this paper we are studying aluminium oxide prepared using plasma-enhanced chemical vapour deposition (PECVD).

## 2. Passivation quality as a function of Al<sub>2</sub>O<sub>3</sub> layer thickness

### 2.1. Sample preparation

The Si wafers used for this experiment are float zone (FZ) grown and *p*-type doped. The specific resistivity is 1 Ω.cm, and the thickness is 250 μm. The surfaces were shiny etched.

Prior the deposition of aluminum oxide the samples were cleaned using a wet chemical treatment consisting of a hot HNO<sub>3</sub> followed by an HF dip.

Shortly after cleaning the samples were coated with Al<sub>2</sub>O<sub>3</sub> using PECVD. As demonstrated in previous papers PECVD can be used to deposit high-quality aluminum oxide layers with a high deposition rate[1]. In this paper we used an inline deposition system (SiNA, Roth & Rau) already applied for the deposition of antireflection SiN<sub>x</sub> in industrial solar cell production. The samples were deposited on both sides symmetrically, with Al<sub>2</sub>O<sub>3</sub> layers of different thicknesses.

After deposition, the samples were annealed at 450°C for 10 min under N<sub>2</sub> atmosphere.

### 2.2. Characterization

The thickness of the aluminum oxide layers has been measured using spectral ellipsometry measurements in a range of wavelength between 250 nm and 1200 nm. The measured signals are fitted using a Cauchy model.

The carriers' lifetimes in the symmetrically deposited samples have been measured using a lifetime tester (Sinton consulting WCT-120). The use of symmetric samples allow a simple relation between the measured effective lifetime ( $\tau_{\text{eff}}$ ), the bulk lifetime limit ( $\tau_{\text{lim}}$  – Auger[2] and radiative recombination) and the surface recombination velocity (*SRV*) *S*

$$\tau_{\text{eff}}^{-1} = \tau_{\text{lim}}^{-1} + 2 S_{\text{eff}} / W. \quad (1)$$

where *W* is wafer thickness. All the lifetimes reported in this paper are calculated or measured at an injection density  $\Delta n = 10^{15} \text{ cm}^{-3}$ .

The charge density ( $Q_{\text{tot}}$ ) and the interface state density ( $D_{\text{it}}$ ) have been measured using a technique involving corona charging and surface-photovoltage (SPV) measurement. This technique that doesn't require any particular sample preparation could be interpreted as a contact-less CV measurement technique (COCOS, Semilab SDI) [3].

### 2.3. Thickness variation: results and discussion

We measured the lifetime as a function of the aluminum oxide layer thickness (see figure 1 (a)). The lifetimes have a stable value ranging around 2.5 ms for thicknesses higher than 20 nm. This corresponds to a *SRV* of quasi null. Between 10 and 15 nm, the lifetime decreases showing that a minimal aluminum oxide thickness is necessary to obtain an excellent surface passivation.

The density of charges in the aluminium oxide and the density of defects at the interface are presented in figure 2 (b). The density of charges is almost constant, ranging  $- 3 \times 10^{12} \text{ cm}^{-2}$ . This shows that the

negative charges in the Al<sub>2</sub>O<sub>3</sub> are situated very close to the interface with the Si, in at least the first 6 nm. It shows as well that the electrical field formed by these charges, which repels the electrons from the interface, does not decrease with the layer thickness. Therefore the field-effect passivation cannot explain the loss of passivation decreasing the layer thickness. However the interface defect density is observed to increase when the aluminium oxide thickness is lower than 20 nm. The equations of Shockley and Read [4] predict a linear increase of the *SRV* with the *D<sub>it</sub>*. Therefore the decrease of the carrier lifetime with the layer thickness can be explained by the increase of the interface defects.

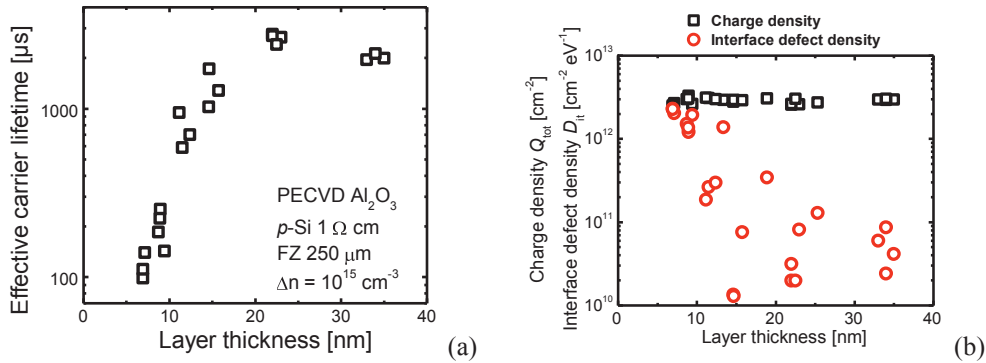


Fig 1: (a) Effective carriers’ lifetime after annealing (450°C for 10min) as a function of the layer thickness. (b) Interface state density (midgap) and charge density (negative charge density) as a function of the layer thickness. For PECVD Al<sub>2</sub>O<sub>3</sub> layers deposited on FZ *p*-type 1 Ω cm Si wafers.

2.4. Theoretical relation between the recombination and the interface trap density

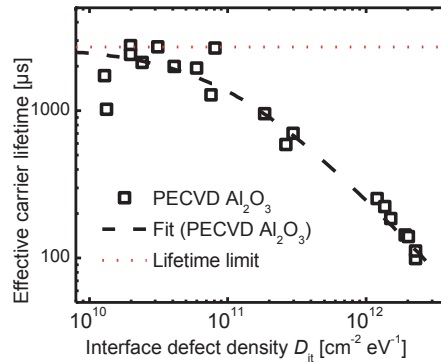


Fig 2: Effective carrier lifetime as a function of the interface state density. A fit taking in account a direct linearity between *SRV* and *D<sub>it</sub>*, and a lifetime limit (of Auger and radiative recombination) is also plotted.

In figure 2, the effective carrier lifetime  $\tau_{eff}$  as a function of the middle band gap *D<sub>it</sub>* is plotted, the fit is based on a direct linearity between *SRV* and *D<sub>it</sub>*. The formula used for the fit is

$$\tau_{eff}^{-1} = \tau_{lim}^{-1} + 2 \alpha D_{it} / W \tag{2}$$

where  $\alpha$  is the proportionality factor between the  $D_{it}$  and the  $SRV$ . The value of  $\alpha$  was determined to be  $5 \cdot 10^{-11} \text{ cm}^3 \text{ eV s}^{-1}$ .

The charge density measured shows that we are in accumulation condition, therefore from Sze [5] a simple relation, valid in low injection, exists between the surface barrier ( $V_{sb}$ ) which is the potential formed by the electrostatic field at the silicon surface and  $Q_{tot}$  the charge in the dielectric

$$Q_{tot}^2 = 2 q \epsilon_s N_A V_{th} \exp(-V_{sb}/V_{th}) \quad (3)$$

where  $q$  is the elementary charge,  $\epsilon_s$  the permittivity of silicon,  $N_A$  the doping concentration and  $V_{th}$  the thermal voltage. We introduce a new value  $c_s$  which is the ratio between the carrier concentration in the bulk and at the surface  $c_s = p_s / p_0 = n_0 / n_s$ , where  $p_0$ ,  $p_s$ ,  $n_0$  and  $n_s$  are the concentration of the hole in the bulk and at the surface, and the concentration of the electron in the bulk and at the surface respectively. After calculation we obtain  $c_s = \exp(-V_{sb}/V_{th}) \sim 1700$ , meaning that at the surface the hole concentration is 50 times larger as in the bulk and the electron concentration is 1700 times smaller to the bulk. For the following, we suppose that the surface recombination can be modeled only considering the middle band gap traps. Considering the same injection condition as in the experiment ( $N_A = 1.5 \cdot 10^{16} \text{ cm}^{-3}$ ,  $\Delta n = 1 \cdot 10^{15} \text{ cm}^{-3}$ ), we have  $p_s \gg n_i$  and  $n_s \gg n_i$ . This gives already a simplified formula the SRV,

$$S_{eff} = D_{it} N_A v_{th} (\Delta n / (\sigma_p c_s) + (c_s N_A) / \sigma_n)^{-1}. \quad (4)$$

Finally we still need to suppose that the ratio of the capture cross section  $\sigma_n / \sigma_p$  is very inferior to  $N_A c_s^2 / \Delta n$  ( $\sim 3.7 \cdot 10^4$ ). In order to further simplify the SRV expression,

$$S_{eff} = D_{it} v_{th} \sigma_n / c_s = \alpha D_{it}. \quad (5)$$

where  $v_{th}$  is the thermal velocity. Finally, we can estimate  $\sigma_n$  to be around  $1.7 \cdot 10^{-15} \text{ cm}^2$ , this value is very close to the one measured for  $\text{SiO}_2$ . Indeed an interfacial  $\text{SiO}_2$  is often observed between  $\text{Al}_2\text{O}_3$  and c-Si. In the next section we will verify this value using deep-level transient spectroscopy (DLTS).

### 3. Measurement of the capture cross section by DLTS

#### 3.1. Experimental and characterization

The wafers used are float zone (FZ) grown, crystal orientation (100),  $p$ -type and  $n$ -type doped. The specific resistivity is  $10 \Omega \text{ cm}$ , and the thickness is  $250 \mu\text{m}$ . The surfaces were shiny etched.

The cleaning and the aluminum oxide deposition were carried out in the same condition as described in section 2.1. We deposited  $20 \text{ nm}$  of  $\text{Al}_2\text{O}_3$  on one side of the sample; this side is designated as front side.

The rear contact was performed using Al evaporated by electron gun (e-gun) evaporation. After the metallization of the rear an annealing at  $425^\circ\text{C}$  for  $25 \text{ min}$  in forming gas atmosphere was carried out. Finally metal dots were evaporated on the front side using thermal evaporation. We use  $1 \text{ mm}$  diameter dots for the DLTS measurement.

We use a DLTS instrument from Sula technology. The frequency for the capacitance measurement is  $1 \text{ MHz}$ . We use small feed-in pulses of  $100 \text{ mV}$ , performing the technique know as small pulses DLTS[6]. During the pulses the band bending at the interface only change from a few  $\text{meV}$ , just sufficient

to charge/discharge enough traps for the measurement, however the position of the Fermi energy at the surface can be consider like constant. The energy level of the traps and their capture cross sections were calculated using Arrhenius plots, the sweep in energy was done using a bias voltage. An example of the DLTS measurement and the corresponding Arrhenius plot is presented Figure 3.

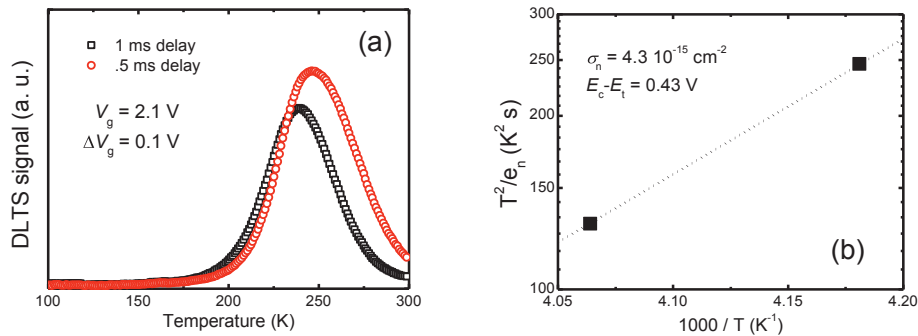


Fig 3 (a) DLTS signal as a function of the temperature on *n*-type silicon, for two different delay time, (b) corresponding Arrhenius plot, capture cross section ( $\sigma_n$ ) and trap energy ( $E_t$ ).

3.2. Capture cross section : results and discussion

In figure 4 we plot the capture cross section as a function of trap energy, for PECVD aluminium oxide compared with measurements performed on high-quality silicon dioxide by Glunz [7] and Aberle et al. [8]. More measurement points in the range of the maxima of the capture cross section would be desirable to properly compare these results. However we can determine with certainty that the ratio between the electron and hole capture cross sections obtained for aluminium oxide ( $\sigma_n / \sigma_p = 100-1000$ ) is very similar to the one of silicon dioxide [7]. The measured electron capture cross section is a factor of 10 smaller than the value estimated in section 2.4, but still consistent with it, considering that one order of magnitude is commonly admitted as the uncertainty of this type of DLTS measurements.

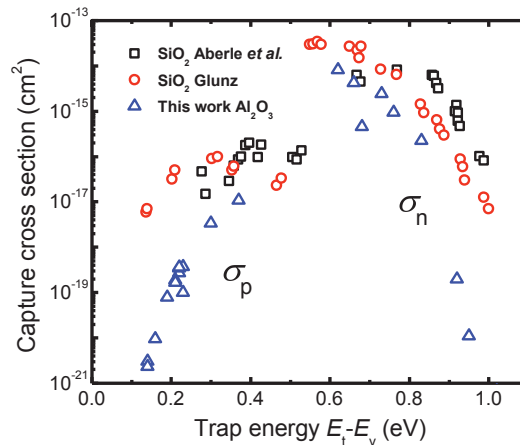


Fig 4: Capture cross sections of electrons and holes as a function of trap energy for PECVD  $Al_2O_3$  and thermally grown  $SiO_2$  from Glunz[7] at 950°C and Aberle et al[8] at 1050°C.

The values of the capture cross sections are generally lower than the one for SiO<sub>2</sub>, however considering the measurement uncertainties (one order of magnitude), these values are very similar to SiO<sub>2</sub>. This shows that the electrical signature of the main aluminum oxide interface defect level with crystalline silicon is very close to the one of silicon dioxide. The observation of an interstitial silicon dioxide layer at the interface between Al<sub>2</sub>O<sub>3</sub> and c-Si [9] consolidates the hypothesis that the chemical passivation of crystalline silicon by Al<sub>2</sub>O<sub>3</sub> is performed by the interfacial SiO<sub>2</sub> layer. It results that the electrical activity of these defects is the same and therefore the passivation of a silicon surface by aluminum oxide can be electrically modeled like the passivation of a charged silicon dioxide layer. Additionally we can also expect the same chemical activity of the interface, for example concerning the saturation of the dangling bonds by hydrogenation of the interface. However these similarities should be limited to the interface, the bulk of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> being completely different (e.g., concerning H concentration, H diffusivity, built-in charges, mechanical stress, ...).

#### 4. Conclusion

We measured the effective carrier lifetimes for *p*-type silicon wafers passivated by PECVD Al<sub>2</sub>O<sub>3</sub> layers, with varying thicknesses between 5 and 35 nm. For the deposition and annealing process presented here, it seems that a minimal thickness of 15 nm is necessary in order to benefit from the fully of the passivation quality of such a layer. For lower layer thicknesses, the cause for the passivation quality deterioration has been determined to be an increase of the  $D_{it}$ . The other important parameter, the negative charge density, remains independent of the thickness ( $Q_{tot} = -3 \cdot 10^{12} \text{ cm}^{-2}$ ). A linear relation between surface recombination velocity and  $D_{it}$  was established. This, together with a simplified Shockley and Read's [4] expression of the SRV was simplified for *p*-Si surfaces under accumulation and low carrier injection. The last enabled us to estimate  $\sigma_n$  to be around  $1.7 \cdot 10^{-15} \text{ cm}^{-2}$ .

In a second approach we measured the capture cross sections of holes and electrons using the DLTS technique. The results were found to be very similar to reported values for silicon dioxide. This consolidates the hypothesis that the chemical passivation of crystalline silicon by Al<sub>2</sub>O<sub>3</sub> is performed by the interfacial SiO<sub>2</sub> layer.

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