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Silicon Surface Passivation by Al_2O_3 film using Atomic Layer Deposition

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***Abstract*—Silicon surface passivation is studied using Al_2O_3 thin film deposited by thermal process using atomic layer deposition (ALD) method. Minority carrier lifetime measurements showed that the film passivate the silicon surface effectively. Capacitance-voltage measurement confirms the activation of negative fixed charges after sintering at 400ºC.**

***Index Terms*—Passivation, Al_2O_3, ALD.**

I. INTRODUCTION

In recent years, passivation of crystalline silicon (c-Si) surface is a subject of renewed interest to reduce surface recombination losses and their application in silicon based devices particularly thinner bulk silicon solar cells. The passivation reduces surface recombination losses by two ways, (i) chemical passivation (reduction of the density of electronic surface states) and (ii) field effect passivation (due to presence of fixed charges in the oxide layer). Aluminum oxide (Al_2O_3) is a versatile dielectric that has excellent surface passivation properties on c-Si [1-2]. Atomic Layer deposition (ALD) has been proven a valuable tool for the growth of Al_2O_3 thin films for the application in solar cells. However, the passivation mechanism of Al_2O_3 is not yet fully understood.

In this paper, we have studied the surface passivation of silicon by Al_2O_3 film. Minority carrier lifetime and capacitance-Voltage measurements (CV) are performed on as deposited and sintered film to understand the passivation quality and mechanism.

II. EXPERIMENTAL DETAILS

Al_2O_3 thin films were grown in a thermal ALD reactor (M/s Picosun, Oy, Finland, Model: R-200) using trimethylaluminum [TMA, $Al(CH_3)_3$)] and H_2O as the precursors for aluminum and oxygen. One deposition cycle consists of two half cycles; one TMA pulse and one H_2O pulse and each step is followed by nitrogen purge. The surface chemistry during the first and second half cycle of thermal ALD can be described by eq. (1) and (2) respectively [3-4].

$$Al - OH^{*} + Al(CH_3)_3 \rightarrow AlO - Al(CH_3)_2^{*} + CH_4 \tag{1}$$

$$AlO - AlCH_3^{*} + H_2O \rightarrow AlOAl - OH^{*} + CH_4 \tag{2}$$

(Asterisks denote the surface species)

The films were grown on CMP p-type silicon wafer (FZ, <100> orientation, 325µm thickness) at a substrate temperature of 300ºC for 300 cycles. Prior to the Al_2O_3 film deposition, the wafers were cleaned by piranha solution [H_2SO_4:H_2O_2 :: 4:1] for 15 min followed by HF (5%) dip.

The film thickness was measured by spectroscopic ellipsometer (J.A. Wollam Co. Inc). Minority carrier lifetime was measured using photoconductance decay method (M/s Sinton Instruments, USA; Model: WCT-120) and microwave photoconductive decay technique (µ-PCD; Semilab Model WT-2000 system). Atomic force microscopy (M/s Veeco Instruments, Multimode V) was used for surface morphology information. Metal-insulator-semiconductor (MIS) structure was fabricated by depositing aluminum using e-beam evaporation system for capacitance-voltage (C-V) measurements which was done with the help of an impedance/gain phase analyzer (M/s Solartron, Model: 1260).

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III. RESULTS & DISCUSSIONS

Fig. 1 shows the thickness distribution of Al_2O_3 film (300 cycles) on 100 mm diameter wafer. Thickness was found to be ~ 30 nm as measured by spectroscopic ellipsometer. Film thickness variation across the wafer from edge to center is less than ±1% which indicates the good uniformity of the film across the wafer. The growth rate was ~0.1 nm/cycle.

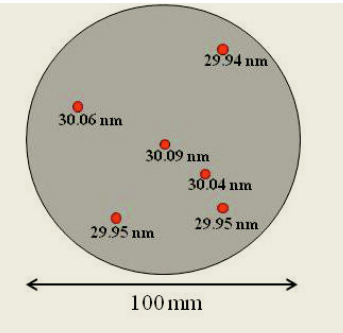


FIG. 1. Thickness distribution of Al_2O_3 film on 100 mm diameter silicon wafer.

Fig. 2 shows the AFM image of as deposited film in tapping mode at a scan area of 3µm x 3µm. The image showed uniform surface morphology with rms roughness ~1-2 nm, a value same as obtained on bare silicon. Silmilar results are also confirmed by SEM images (Not shown here).

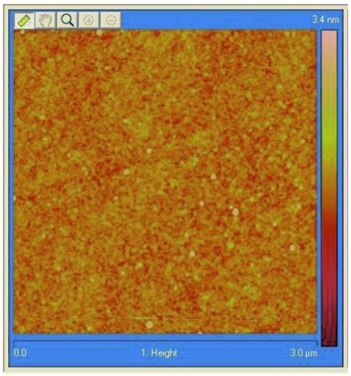


FIG. 2. AFM image of Al_2O_3 film (scan size = 3µm x 3µm)

Fig. 3 shows effective minority carrier lifetime (τ_{eff}) as a function of injection level (Δn) measured on bare silicon wafer and a wafer with Al_2O_3 film. These two samples were part of the same wafer. The measured τ_{eff} in bare silicon was 1.5 µs at an injection level of $1x10^{14}$ cm^{-3} whereas the value after Al_2O_3 was 430 µs at an injection level of $1x10^{15}$ cm^{-3}. This is a clear indication of good passivation by Al_2O_3.

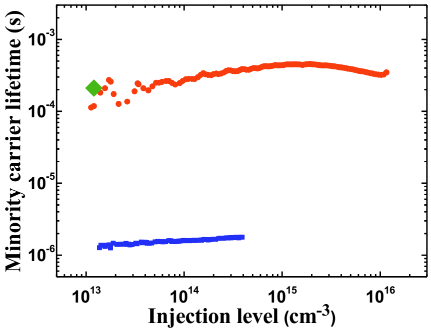
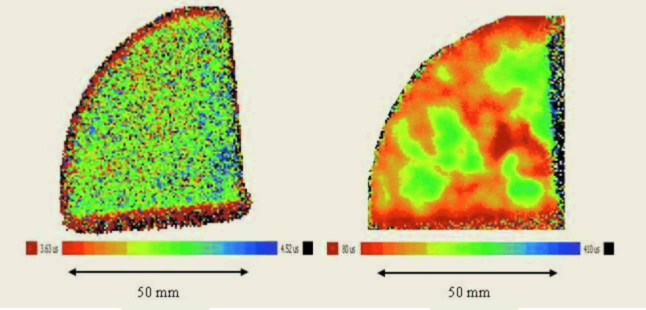


FIG. 3. Effective minority carrier lifetime as a function of injection level measured using Sinton's method. Bare (Blue curve) and passivated (Red Curve). The green symbol shows measured τ_{eff} using µ-PCD.

Surface recombination velocity (SRV) is a quantitative measure of passivation quality. The SRV (S_{eff}) can be calculated from τ_{eff} using the eq.(3).

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2S_{eff}}{d} \qquad (3)$$

where, τ_{bulk} is the bulk lifetime and d is the wafer thickness. The S_{eff} was increased to 38 cm/s (Δn = $1x10^{15}$ cm^{-3}) for the passivated wafer by Al_2O_3 thin layer compared to bare silicon value (10800 cm/s).



(a) (b)

FIG. 4. Minority carrier lifetime map for (a) bare and (b) as deposited Al_2O_3 film measured by µ-PCD.

the value obtained by Sinton lifetime tester if the injection levels are taken in consideration (Table-1). Similar observation has been made in [5]. A typical lifetime map of bare and Al_2O_3 passivated silicon wafer is shown in Fig. 4.

TABLE 1. Effective lifetime data of bare & passivated silicon

	Sinton Lifetime	μ-PCD Lifetime
Bare Silicon	1.5 μs (Δn=1x10^{14} cm^{-3})	4.1 μs (Δn=1.2x10^{13} cm^{-3})
Al_2O_3 film	430 μs (Δn=1x10^{15} cm^{-3})	210 μs (Δn=1.2x10^{13} cm^{-3})

C-V measurements were performed on Al /Al_2O_3/Si MIS structure fabricated on as deposited film and on the sample sintered at 400°C in nitrogen ambient for 10 min. Fig. 5 shows normalized C-V curves of an as deposited and sintered Al_2O_3 films at 1 MHz. The voltage was swept from inversion to accumulation regions (+ve to –ve voltage) and then back to inversion state. Hysteresis has been obtained in C-V data which may be due to the presence of interface states/traps. The observed hysteresis may have contribution from the charging of neutral traps in the dielectric layer during inversion to accumulation transformation and in reversal of the process which generally gives an equidistant shift towards negative voltages [6].

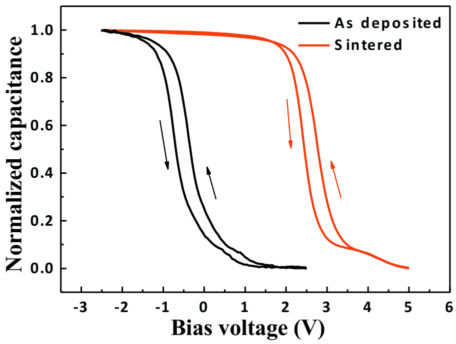


FIG. 5. Normalized C-V curves for as deposited (black) and the film sintered at 400°C (red) at 1MHz.

The transition from accumulation to inversion is not sharp which is indicative of high density of interface states in the structure. It can be noted that hysteresis is not reduced after sintering. The negative fixed charge density Q_f is calculated. We found a negative fixed charge density Q_f of ~3x10^{9} cm^{-2} in as-deposited film. A positive shift in C-V curve was observed with sintering, which corresponds to increase in negative fixed charge density Q_f (=~6x10^{10} cm^{-2}). It confirms that sintering activates the negative fixed charges in the oxide [2,7,8]. It is known that Al vacancies and O interstitials exhibit a negative charge and Al interstitials and O vacancies exhibit a positive charge [9]. The interface between Al_2O_3 and Si also play an important role in determination of nature and the density of fixed charges. It has been reported that a thin SiOx layer exists at the interface [10]. The increase in thickness of this interface layer decreases the negative fixed charge density in the Al_2O_3 films. It has also been reported that chemical passivation is dominant mechanism for surface passivation realized by Al_2O_3 layer grown by thermal process whereas field effect passivation plays an important role in the films made by plasma ALD [11]. A detailed investigation about the role of interface is in progress and will be reported elsewhere.

IV. CONCLUSIONS

An Al_2O_3 layer (30 nm) was grown by thermal ALD system. The lifetime measurements showed good surface passivation with Al_2O_3 film. C-V measurements confirm the negative fixed charges which get activated after sintering.

V. ACKNOWLEDGEMENTS

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