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Silicon Surface Passivation by Al_2O_3: Effect of ALD Reactants

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Abstract

We have studied the surface passivation of p- and n-type silicon by thermal atomic layer deposited (ALD) Al_2O_3. The main emphasis is on different ALD reactant combinations and especially on using ozone as an oxidant. Thermal stability of Al_2O_3 will also be briefly addressed. Our results show that in p-type CZ-Si Al_2O_3 leads to much higher passivation than thermal oxidation, independent of the reactants. The best minority carrier lifetimes are measured when a combination of Al_2O_3 and TiO_2 is used. In n-type CZ-Si similar results are obtained except the choice of reactants seems to be more crucial. However, the combination of Al_2O_3 and TiO_2 results again in the best passivation with measured lifetimes well above 10 ms corresponding surface recombination velocities of ~2 cm/s. Finally, we demonstrate that Al_2O_3 passivation is also applicable in high resistivity n-type FZ-Si and in ~1 Ωcm p-type multicrystalline Si.

Keywords: Al_2O_3 ; Silicon ; Passivation ; ALD ; Reactant ; Ozone

1. Introduction

Al_2O_3 grown by atomic layer deposition (ALD) has been shown to provide a good surface passivation for lightly and highly doped p-type silicon and for lightly doped n-type silicon [1]. The high level of surface passivation is reached by the combination of chemical and field-effect passivation induced by the fixed negative charge close to the c-Si/Al_2O_3 interface [2].

ALD can be divided into thermal and plasma-enhanced processes. There are many studies where Al_2O_3 deposited by these two processes are compared [1-4]. On the other hand, not so much information is available on how different reactants affect the surface passivation properties of Al_2O_3. Thermal ALD can be implemented by using either H_2O or O_3 as an oxidant. H_2O is more widely studied and only recently O_3 as an oxidant in Al_2O_3 surface passivation has been addressed [5].

In this paper, we compare three different reactant combinations in thermal ALD process using O_3 as the primary oxidant. We also study if the reactants behave differently depending on the wafer type and resistivity. Therefore, we include in our study low-resistivity CZ wafers (both p- and n-type) as well as high resistivity n-type FZ and p-type (~1 Ωcm) multicrystalline wafers.

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2. Experiments

Three different reactant combinations were chosen for the thermal ALD. These processes were named as ALD1, ALD2 and ALD3 as shown in Table 1. TMA (trimethylaluminum) was used as aluminum source in all cases. In ALD1 mere ozone was used as an oxidant whereas in ALD2 and ALD3 also H_2O was added. In ALD3 Ti was doped into the film using $TiCl_4$ (titanium tetrachloride) as the Ti source. This resembles the $(Al_2O_3)_x(TiO_2)_{1-x}$ pseudobinary alloys that are known to passivate p-type Si surfaces [6].

Table 1. ALD processes and the corresponding reactants.

Abbreviation	Reactants
ALD1	TMA + O_3
ALD2	TMA + H_2O + O_3
ALD3	TMA + O_3 + $TiCl_4$ + H_2O

The following wafer types were used as the substrate material for the experiments: p-type CZ-Si (2-5 Ωcm), n-type CZ-Si (2.2 Ωcm), high-resistivity (>10 kΩcm) n-type FZ-Si and p-type mc-Si (~1 Ωcm). All the samples received a basic RCA cleaning followed by a HF (1:50) dip for 30 s to etch the native oxide. Two identical p- and n-type CZ wafers received Al_2O_3 depositions on both sides at 200 °C. ALD processes were followed by annealing for 30 minutes at 450 °C in N_2. The resulting Al_2O_3 film thickness was ~40 nm. After the annealing, a firing step for ~3 s in a peak temperature of 800 °C was done for one of the p-type CZ and one of the n-type CZ wafers with Al_2O_3 deposited by using ALD1 reactants. For FZ and mc-Si wafers, ALD1 process was chosen. Al_2O_3 deposition on both sides at 200 °C was followed by a 30 min anneal at 430 °C in N_2. In these samples, the resulting film thickness was ~23 nm. ALD2 reactant set was also tested for mc-Si wafers. Subsequent to the deposition of ~23 nm thick Al_2O_3 at 200 °C annealing at 450 °C in N_2 for 30 minutes was done. Summary of the experiments is shown in Table 2.

Table 2. Wafers and processes used in this study.

Wafer type	Resistivity (Ωcm)	Thickness (μm)	Size	ALD process	Al_2O_3 thickness (nm)	Post-deposition anneal
p-type CZ	2-5	525	dia. 100 mm	ALD1 - ALD3	~40	450 °C, 30 min, N_2
n-type CZ	2.2	400	dia. 100 mm	ALD1 - ALD3	~40	450 °C, 30 min, N_2
n-type FZ	>10 000	525	dia. 100 mm	ALD1	~23	430 °C, 30 min, N_2
p-type mc-Si	~1	200	62 mm × 125 mm	ALD1, ALD2	~23	430-450 °C, 30 min, N_2

As a reference for the surface passivation quality, thermal oxidation (SiO_2) was carried out for each wafer type, excluding the mc-Si samples. Oxidation was done at 900 °C for 40 minutes followed by a 20 minute N_2 anneal at 900 °C which resulted in 15 nm thick oxides. The surface passivation of such films enhanced by external corona charging is well known to yield low surface recombination velocities ($S_{eff} < 1$ cm/s at a wafer doping $4.2 \cdot 10^{16}$ cm^{-3}) [7]. The samples were measured both by quasi-steady-state photoconductance (QSSPC) and microwave photoconductance (µ-PCD) techniques.

3. Results

3.1. p- and n-type CZ wafers

Let us first study the surface passivation in p-type CZ wafers. Fig. 1a shows the effect of different ALD reactants on minority carrier lifetimes as a function of injection level. Wafers were kept in the dark between processing and measurements to minimize the effect of light induced degradation. With all injection levels Al_2O_3 seems to provide a better surface passivation than the oxidized reference independent of the ALD reactants. At higher injection levels Auger recombination limits the lifetime values. When we compare the ALD reactants, ALD3 (with Ti addition) yields the best passivation within the whole injection range. ALD2 and ALD3 seem to be comparable, yet better than oxide, which indicates that water as an ALD reactant does not make a huge difference to pure ozone case. Lifetimes measured with µ-PCD at an injection level of about $3 \cdot 10^{14}$ cm^{-3} are also included in the same figure and they can be seen to be in agreement with the QSSPC results. µ-PCD maps also confirmed that the passivation by Al_2O_3 was laterally homogeneous.

Next we compare the same set of ALD reactants in n-type CZ wafers. The corresponding minority carrier lifetimes measured with QSSPC are shown in Fig. 1b. Again, the Auger limit at higher injection levels is seen. In n-type samples there is no clear injection level dependence at low injection levels. The results are somewhat similar to p-type wafers but some differences exist. First of all, the measured lifetimes are much higher in general (in ms range). Secondly, ALD1 (only TMA and O_3 as reactants) results in much lower passivation than ALD2 and ALD3, even lower than the reference oxidation. In Fig. 1b ALD2 and ALD3 can be seen comparable and lifetimes as high as 8-11 ms are obtained. This corresponds to surface recombination velocities of $S_{eff} = 1.8$-2.5 cm/s if an infinite bulk lifetime is assumed. µ-PCD measurements lead to similar results.

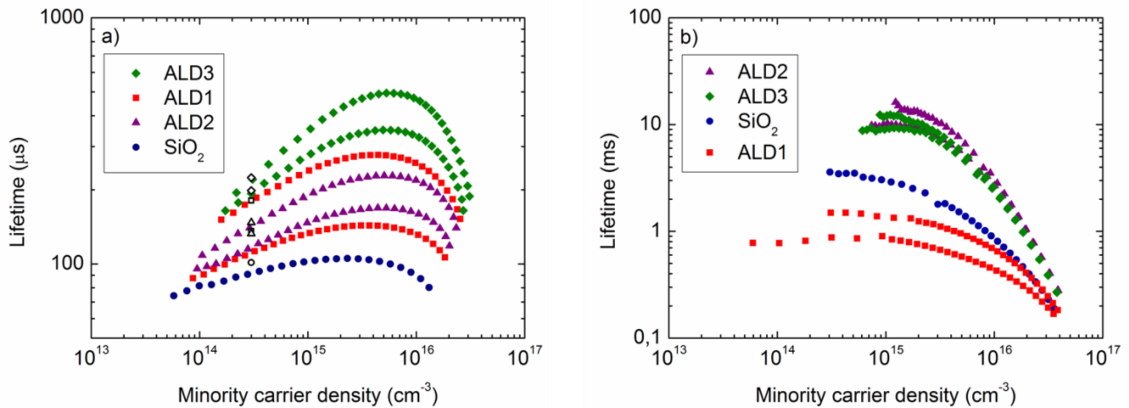

Fig. 1. Carrier lifetimes as a function of minority carrier density measured with QSSPC in (a) p-type CZ (2-5 Ωcm) and in (b) n-type CZ (2.2 Ωcm) wafers. Al_2O_3 was deposited with three different reactant combinations (ALD1, ALD2 and ALD3) in the thickness of ~40 nm. Post-deposition anneal was done at 450 °C in N_2 for 30 minutes.

3.2. High resistivity n-type FZ wafers

We studied Al_2O_3 passivation in high resistivity n-type FZ-Si. It is well known that this material has extremely long bulk lifetime which makes it ideal for surface passivation studies [1]. Here in this study we report the Al_2O_3 results made with ALD1 process (TMA + O_3). The QSSPC measurement results of these wafers are shown in Fig. 2. As can be seen both the oxidized and the Al_2O_3 passivated wafer yields rather high lifetimes (~40 ms corresponding to $S_{eff} \approx 0.66$ cm/s). These results indicate that Al_2O_3 could be used as an effective surface passivation in other photonic applications as well, e.g. in radiation detectors where surface passivation of high resistivity wafers is essential. Equipment limitations prevent measurements at lower injection levels ($< 1\cdot10^{14}$ cm^{-3}). The RF sensor of the QSSPC measurement equipment (WCT-120 Photoconductance lifetime tester) was calibrated for high-resistivity wafer with a series of calibration wafers of known conductance. The point is to use "extra" silicon wafer on measurement stage below the wafer to be measured during RF sensor calibration and high-resistivity wafer measurement.

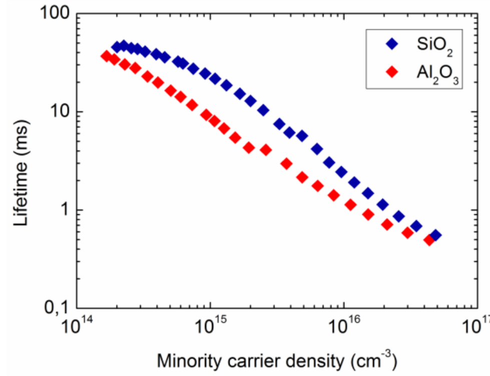

Fig. 2. Carrier lifetimes of high-resistivity n-type FZ wafers as a function of minority carrier density measured with QSSPC. Al_2O_3 was deposited on both sides of the wafer in a thickness of ~23 nm by using ALD1 reactant set. Post-deposition anneal was carried out at 430 °C in N_2 for 30 minutes.

3.3. mc-Si wafers

We also studied the surface passivation quality of Al_2O_3 on multicrystalline p-type silicon. This is a very common solar cell material and Al_2O_3 could be used for the rear surface passivation of such solar cells [8]. Lifetime maps of the mc-Si wafers measured with µ-PCD are shown in Fig. 3. The figure shows that Al_2O_3 deposited both with ALD1 (Fig. 3a) and ALD2 (Fig. 3b) reactants can passivate very well also the mc-Si wafers, since more than 50 % of the wafer area has lifetime over 30 µs. In the red areas lifetime is most likely limited by bulk defects so that surface passivation has no effect on the measured lifetime in these locations.

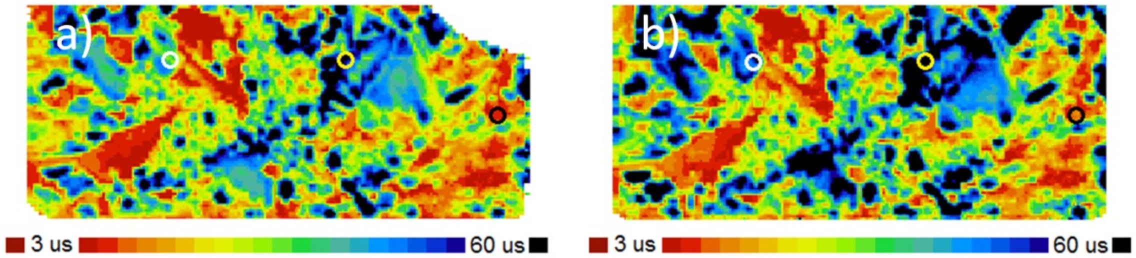

Fig. 3. Lifetime maps of Al_2O_3 passivated p-type mc-Si wafers when (a) ALD1 and (b) ALD2 reactants are used. Circles indicate the areas where lifetime averages are taken for comparison. Yellow indicates a good grain, black a poor grain and white an average grain. Al_2O_3 was deposited on both sides of the wafers in a thickness of ~23 nm. Post-deposition anneal was carried out at 430 °C in N_2 for 30 minutes with ALD1 reactants and at 450 °C in N_2 for 30 minutes with ALD2 reactants.

In Fig. 4 lifetime values of Al_2O_3 passivated wafers are shown. Three of six adjacent wafers were Al_2O_3 passivated by using ALD1 (A1-A3) reactants and three by using ALD2 (B1-B3) reactants. Areas of different quality were chosen and average lifetime values were taken from these areas that are also shown in Fig. 3 with circles. Yellow indicates a good grain, black a poor grain and white an average grain. It seems that Al_2O_3 deposited with ALD2 reactants works better on good grains whereas in poor grains there is no significant difference. This result is congruent with the measurements of n-type CZ wafers. It is also worth mentioning that there are notable differences between identical grains of adjacent wafers

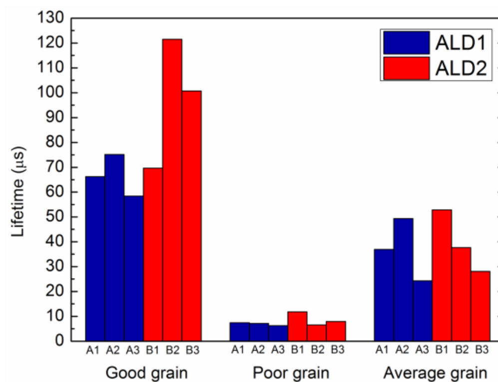

Fig. 4. Lifetime values from small areas of different quality. In the good grains a clear difference is seen whereas in the poor grains results are comparable. Three of six adjacent mc-Si wafers were Al_2O_3 passivated by using ALD1 reactant set (A1-A3) and three by using ALD2 reactant set (B1-B3).

3.4. Thermal stability

Thermal stability of Al_2O_3 passivation has been a popular topic of discussion because in industrial solar cell fabrication high temperatures are needed in the contact firing [9]. We tested the firing stability of Al_2O_3 passivation on p-type CZ (2-5 Ωm) and n-type CZ (2.2 Ωm) wafers. ALD1 reactant set (TMA + O_3) was used in the Al_2O_3 deposition. QSSPC results before and after the firing step (~3 s, 800 °C) are shown in Fig. 5. It can be seen that in p-type CZ lifetimes at lower injection levels are not affected by high temperature treatment whereas at higher injection levels a clear decrease is distinct. This was verified also by the μ-PCD results. In n-type CZ lifetime is decreased regardless of the injection level.

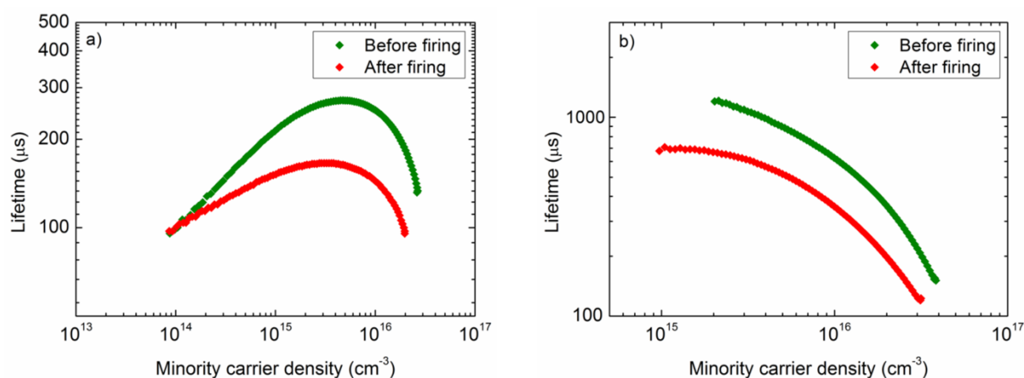

Fig. 5. Lifetime values as a function of minority carrier density before and after firing (~3 s, 800 °C) in (a) p-type CZ-Si and (b) n-type CZ-Si measured with QSSPC. ALD1 reactant set (TMA + O_3) was used in the Al_2O_3 deposition. Annealing for 30 minutes at 450 °C in N_2 was done before the firing step.

4. Conclusions

We have shown that the choice of reactants can play a major role in surface passivation quality of thermal atomic layer deposited Al_2O_3. In general, it seems that Al_2O_3 can provide similar or even better surface passivation quality than thermal oxidation. In our wafers, we obtained the best results with TMA + $TiCl_4$ + H_2O + O_3 reactant combination both in n-type and p-type CZ-Si. The lifetime variation between ALD reactant combinations are related to the differences in the interface charge and defect density. Al_2O_3 film deposited by using ALD2 reactants can contain more hydrogen than the film deposited with ALD1 reactants. In ALD2 H_2O acts as one hydrogen source whereas in ALD1 mere O_3 is used. During annealing greater hydrogen content can result in better interface quality due to hydrogen diffusion. In future studies the hydrogen content in the films and the interface charge density could be measured before and after annealing to verify this theory.

The passivation quality of Al_2O_3 deposited from TMA and O_3 was deteriorated by a high temperature treatment both on p-type and n-type CZ. This can be caused by hydrogen diffusion from the interface. Al_2O_3 was shown to passivate well also the high resistivity FZ-Si when reactant combination TMA + O_3 was used. In mc-Si Al_2O_3 passivation worked with both ALD1 and ALD2 reactants. In future studies the passivation quality of Al_2O_3 when TMA + $TiCl_4$ + H_2O + O_3 reactant set is used will be tested also on high-resistivity n-type FZ and p-type (~1 Ωcm) mc-Si wafers.

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