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Effective surface passivation of crystalline silicon by rf sputtered aluminum oxide

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In recent years, excellent surface passivation has been achieved on both p-type and n-type surfaces of silicon wafers and solar cells using aluminum oxide deposited by plasma-assisted atomic layer deposition. However, alternative deposition methods may offer practical advantages for large-scale manufacturing of solar cells. In this letter we show that radio-frequency magnetron sputtering is capable of depositing negatively-charged aluminum oxide and achieving good surface passivation both on p-type and n-type silicon wafers. We thus establish that sputtered aluminum oxide is a very promising method for the surface passivation of high efficiency solar cells.

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1 Introduction For high efficiency industrial solar cells, surface passivation continues to be one of the major issues limiting their performance. The dominant technology used at present is hydrogenated amorphous silicon nitride (a-SiN_x:H) deposited by plasma-enhanced chemical vapor deposition (PECVD), which acts as an antireflection coating while providing good surface passivation [1]. Being a positively-charged dielectric, a-SiN_x:H is well adapted to passivate n-type surfaces, but has limitations on providing good surface passivation of p-type surfaces, particularly if they are highly doped (diffused) [2, 3].

Recently, aluminum oxide deposited by plasma-assisted atomic layer deposition (PA-ALD) has been investigated as an alternative to a-SiN_x:H in some applications. Being a strongly negatively-charged dielectric [4], it has provided excellent surface passivation of p-type surfaces and on lowly doped n-type surfaces [5, 6]. It has also been successfully applied to laboratory solar cells [7], achieving record efficiencies [8]. However, ALD methods are not easily adaptable to manufacturing [9, 10]. As a result, it has not been possible to apply the excellent surface passivation qualities of aluminum oxide to industrial solar cells.

Nonetheless, aluminum oxide can be deposited by a variety of methods [4]. Of these, PECVD [11] is the only method at present that is both suitable for manufacturing and capable of achieving good surface passivation, while the results from the atmospheric pressure chemical vapor deposition (APCVD) [12] and sol–gel [13] methods are encouraging. Alternatively, we put forward that sputtering can meet both requirements. Sputtering is a method quite suitable for manufacturing [14], and while decent surface passivation was not achieved in previous attempts [9, 13], in this letter we will show that aluminum oxide deposited by radio-frequency (rf) magnetron sputtering is capable of providing good surface passivation.

2 Experimental Several batches of 0.8 Ω cm, (100), float zoned p-type silicon wafers and 1 Ω cm, (100), Czochralski n-type silicon wafers were saw-damage etched and RCA cleaned. The aluminum oxide was deposited using rf magnetron sputtering; an aluminum target was reactively sputtered with 9% O_2 in Ar at a pressure of 3 mTorr. The rf power was 300 W in all cases, with intrinsic bias voltages of around 120 V. The samples were deposited at room temperature; the annealing was done in a quartz tube furnace at the temperatures of 400 °C or 500 °C in either a N_2 ambient or a forming gas (FG) ambient (~5% H_2).

To enable carrier lifetime testing, 30 nm of aluminum oxide was deposited on both sides of a wafer to create a

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symmetrical structure. These were then characterized using transient photoconductance [15] and the effective surface recombination velocity (S_{eff}) was calculated from the measured effective lifetime (τ_{eff}) [16].

Capacitance–voltage (C–V) measurements were also performed to deduce the fixed charge. Unannealed and annealed samples with aluminum oxide on one side were contacted with aluminum. They were then characterized and compared using high-frequency C–V techniques using a 4284A Precision LCR meter at 1 MHz.

Rutherford backscattering (RBS) spectroscopy and transmission electron microscopy (TEM) measurements were made on several samples to estimate the thickness and stoichiometry for the range of aluminum oxide depositions.

3 Results Figure 1 shows the measured and ideal C–V curves for a 0.8 Ω cm, p-type sample passivated with 30 nm of aluminum oxide and annealed at 500 °C in N_2. For this sample, it was deduced that the negative fixed charge (Q_f) of the aluminum oxide changed from -8.6×10^{11} cm^{-2} to -3.4×10^{12} cm^{-2} after 30 min of annealing. When the thickness of the aluminum oxide was varied between 15 nm and 150 nm, both positive and negative charges were measured before annealing. After annealing, however, all of the samples showed a shift to negative charges in the range of -3×10^{12} cm^{-2}, with the Terman density of states (D_{it}) at midgap in the range of 4×10^{12} cm^{-2} eV^{-1}.

The dependence of the effective lifetime on the injection level of several samples is shown in Fig. 2. No significant surface passivation was observed when the aluminum oxide was initially deposited, but decent surface passivation is achieved as quickly as five minutes after annealing.

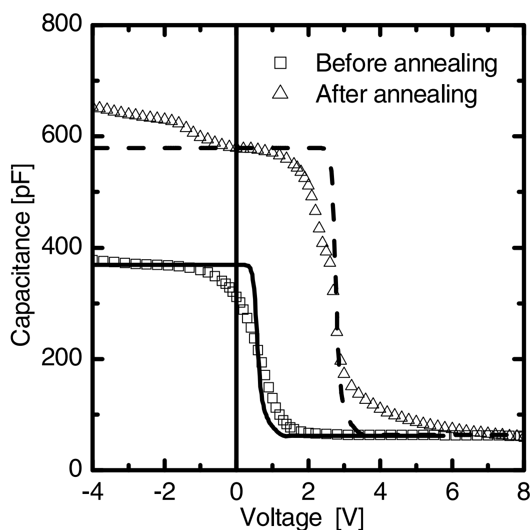

Figure 1 C–V curves of a p-type sample passivated with 30 nm of rf sputtered aluminum oxide before and after N_2 annealing at 500 °C. The lines show the ideal C–V curves used for the analyses.

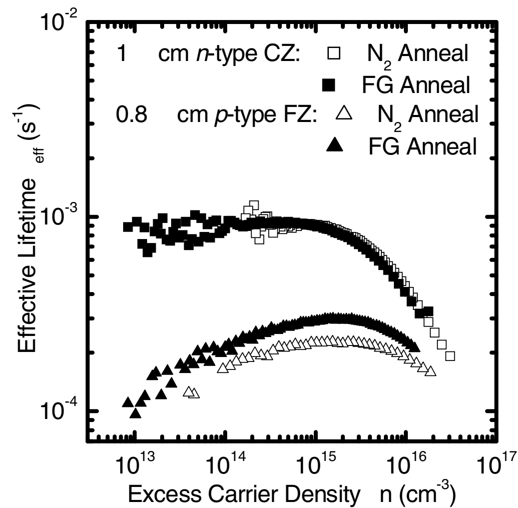

Figure 2 Effective lifetime as a function of the excess carrier density for samples passivated with 30 nm of rf sputtered aluminum oxide after 60 min of annealing at 400 °C in FG or N_2.

Further annealing improves the surface passivation, typically reaching the maximum after an hour of annealing. The measured lifetimes of the samples annealed in a N_2 ambient were always lower but comparable to those annealed in a FG ambient.

For the best results on the 0.8 Ω cm p-type samples, the τ_{eff} (at $\Delta n = 10^{15}$ cm^{-3}) and the calculated S_{eff} were in the range of 200 µs and 74 cm/s, respectively, when annealed in the N_2 ambient, and in the range of 290 µs and 55 cm/s when annealed in the FG ambient. On the 1 Ω cm n-type samples, the τ_{eff} and the calculated S_{eff} were in the range of 800 µs and 16 cm/s, respectively, when annealed in the N_2 ambient, and in the range of 900 µs and 14 cm/s when annealed in the FG ambient.

RBS measurements show that the samples are slightly oxygen-rich, showing a ratio of 2:3.55 on average. The densities of the films were evaluated to be between 2.8 g/cm^3 and 3 g/cm^3.

4 Discussion The results demonstrate that aluminum oxide deposited by rf sputtering is capable of forming negative charges, which is desirable for the surface passivation of p-type surfaces. The negative charge of about -3×10^{12} cm^{-2} is similar to what has been achieved previously by sputtering [17] and APCVD [12]. It is slightly more than the -1.6×10^{12} cm^{-2} achieved with PECVD [11] or sol–gel [13], but is still three times lower than the magnitude of negative charge of -1×10^{13} cm^{-2} achieved by PA-ALD [4].

This strong negative charge of PA-ALD aluminum oxide has contributed to achieving S_{eff} of 13 cm/s and 2 cm/s on 2 Ω cm p- and 1.9 Ω cm n-type wafers, respectively [5]. Similarly, the stronger charge of the sputtered aluminum oxide of this work would explain why it has better surface passivation than that from APCVD, which achieves S_{eff} of

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~210 cm/s on 2 Ω cm p-type wafers, or that from sol–gel, which achieves S_{eff} of ~100 cm/s on 1 Ω cm p-type wafers. However, despite a stronger negative charge compared to PECVD, the latter achieves better surface passivation with S_{eff} of ~10 cm/s on 8.5–12 Ω cm p-type wafers. This is because the Q_f and D_{it} are of the same magnitude in the rf sputtered aluminum oxide; despite the magnitude of Q_f the passivation effect of the negative charges is being limited by the D_{it} [4]. Thus, improving the surface passivation from rf sputtered aluminum oxide will require both the reduction of the D_{it} and the increase in the magnitude of Q_f.

Both the former and the latter are likely to be achieved with further optimization of the deposition and annealing conditions. A reduction in the plasma power, for example, can reduce the surface damage from high-energy ions during deposition, and subsequently reduce the D_{it}. Meanwhile, the deposition of a stoichiometric (2:3) film could lead to both an increase in the magnitude of the negative charge and a reduction of the D_{it}.

No contamination from other elements was detected in the RBS measurements, except for minute traces of argon. Due to the nature of the measurement method, the presence of hydrogen could not be evaluated. With the sputter deposition at room temperature, it is likely that a non-negligible amount of hydrogen (similar to the results of van Hemmen et al. [18]) is present prior to annealing and would contribute to the surface passivation after annealing; this effect would be enhanced with the use of FG ambients during both sputtering and annealing.

The levels of surface passivation achieved in this work are consistent with the possibility of achieving open-circuit voltages (V_{oc}) [19] of up to 695 mV for both the 1 Ω cm n-type and the 0.8 Ω cm p-type wafers. Note that the respective dopant concentrations are $N_D = 5 \times 10^{15}$ cm^{-3} and $N_A = 1.9 \times 10^{16}$ cm^{-3}, which explains why a different value for S_{eff} can result in a very similar value for the implied V_{oc}. It is therefore fair to say that these levels of surface passivation are already acceptable for high efficiency solar cells.

The rf sputter deposition of 30 nm of aluminum oxide requires seven minutes in the current laboratory system; in an industrial setup this deposition can be even faster and over large areas. The required thickness and annealing conditions of the sputtered aluminum oxide appear similar to those of its PA-ALD counterpart; the incorporation of the annealing step into the formation of the contacts [7, 8] should be possible. If all the above can be realized, sputtering will be a quick and effective solution for depositing negatively-charged aluminum oxide on high-efficiency industrial solar cells.

5 Conclusion The experimental results presented here demonstrate that rf magnetron sputtered aluminum oxide can provide good surface passivation of both p- and n-type silicon wafers. $C-V$ measurements have confirmed the presence of negative charges after annealing, which opens the way for effectively passivating highly doped p-type surfaces, such as those resulting from a boron diffusion. While the magnitude of the negative charge and the achieved surface passivation is not yet as good as what can be achieved through PA-ALD, there is scope for further improvement. The use of rf magnetron sputtering should greatly facilitate the introduction of aluminum oxide passivation in the manufacturing of high efficiency industrial solar cells.

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