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Exploring the deposition of oxides on silicon for photovoltaic cells by pulsed laser deposition

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Abstract

Since most commercially available solar cells are still made from silicon, we are exploring the introduction of passivating qualities in oxides, with the potential to serve as an antireflection coating. Pulsed laser deposition (PLD) was used to deposit TiO_2 and $SrTiO_3$ coatings on silicon substrates. Introduction of passivating qualities was achieved by changing the deposition ambient and/or deposition set-up (not placing the substrate in the customary position parallel to the target surface but perpendicular to it). This change in deposition set-up resulted in a remarkable increase in passivating qualities for TiO_2 coatings. The plasma shape and place of the substrate in the plasma influenced greatly properties as smoothness, thickness distribution and passivating quality. The particle energy on arrival at the substrate and the oxygen content at the surface appeared to be key parameters in achieving surface passivation of silicon.

Keywords: Oxides; Passivation; Interface

1. Introduction

The trend towards thinner cells and the desire to produce high-efficiency solar cells make the issue of surface passivation (reduction of surface recombination losses) of greater importance. Furthermore, for improvement of light coupling into the semiconductor an antireflection coating is applied because of their high reflection coefficients. It would be desirable if the antireflective and passivating properties could be introduced in a single coating. Since most commercially available solar cells are still made from silicon, we are exploring the introduction of passivating qualities in oxides on silicon. Pulsed laser deposition is used because of its flexibility in deposition set-up and the possibility of changing the deposition parameters in a broad range.

Because a stoichiometric oxide coating (TiO_2, $SrTiO_3$, $BaTiO_3$) has barely any passivating qualities, the oxide–silicon interface characteristics have to be altered. The first approach is to change the background gas in which deposition takes place. Altering these deposition parameters changes the plasma characteristics. A study has been made on the visible changes in the plasma as function of deposition parameters and the effect on the measured surface passivation. The second approach was to change the interface species present by using different cleaning procedures and ablation of different oxide materials (TiO_2, $SrTiO_3$, SrO, $SrSiO_4$). These experiments show the importance of the oxide content at the surface. In a third approach, the deposition set-up has been changed. Wafers were

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placed in the plasma perpendicular to the target surface (''perpendicular set-up'') instead of in the customary position opposite to and facing toward the target (''parallel set-up''). To get a better understanding why coatings show surface passivation, effort is undertaken to determine the extent and content of the interface between the coating and silicon substrate.

2. Experimental set-up

The pulsed laser deposition system is equipped with a KrF excimer laser ($\lambda = 248$ nm). Single-crystalline TiO_2 and $SrTiO_3$ disks were used as targets. The base pressure in the deposition chamber was 2×10^{-5} or 2×10^{-6} mbar in the load lock system. Films have been grown on p-type (1 0 0) silicon substrates (14 mm × 14 mm, 1.5 Ω cm) and p-type (1 0 0) wafers (diameter 76.2 mm, 5–7 Ω cm). Deposition took place in different gasses (argon, oxygen, neon and water vapour) with pressures ranging from 5×10^{-3} up to 0.55 mbar. The temperature of the substrates, clamped on a thermo coax heater, was 300 °C. The wafers were coated at room temperature.

The passivating qualities of the films were quantified with the effective lifetime of the minority charge carriers τ_{eff}. Its value represents both the achieved bulk lifetime and surface lifetime.

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{1}{\tau_s} \quad (1)$$

where τ_b is the bulk lifetime and τ_s the surface lifetime. The effective lifetimes were measured with modulated free carrier absorption (MFCA). For these measurements films were deposited on both sides of float zone silicon substrates. In the MFCA set-up, excess carriers are generated by an 850 nm laser diode in the silicon substrate, which is passivated identically on both sides. The light intensity of the laser is modulated sinusoidally at a frequency ω. The generated excess carrier concentration inside the wafer is probed by a second 1550 nm laser beam. It follows the same frequency as the generation beam, though shifted by a certain phase angle (φ) because of the lifetime of the generated carriers. By measuring the modulation frequency at which a 45° phase shift occurs (ω_{45}), the effective lifetime τ_{eff} can under some conditions be determined according to: $\tau_{eff} = 1/\omega_{45}$ [1]. At this phase shift, the measurement set-up is also most sensitive to changes in the phase shift as a function of the applied frequency ω.

3. Deposition ambient and passivating quality for TiO_2 coatings

The passivating quality of a TiO_2 coating can be enhanced by introducing positive fixed charge in the coating to induce field effect passivation (band bending) [2–4]. Ablation from the stoichiometric TiO_2 target results in an oxygen deficient top layer on the target. To deposit a stoichiometric film, deposition has to take place in an oxygen containing ambient. XPS measurements showed that deposition in an oxygen ambient of 3.2×10^{-2} mbar results in stoichiometric TiO_2 films. Oxygen deficient $TiO_{2-\delta}$ films can be deposited by regulating the partial oxygen pressure. A positive value of δ would account for the presence of oxygen vacancies, hence positive charge. $TiO_{2-\delta}$ films have been deposited in vacuum, in an oxygen, argon or water vapour ambient, and in mixed gasses (argon/oxygen, argon/water vapour).

A stoichiometric TiO_2 film, deposited in an oxygen pressure of 3.2×10^{-2} mbar, shows barely any passivating qualities. One could expect an increased passivating quality for films deposited in an argon pressure of 3.2×10^{-2} mbar, which was indeed the case. However, in vacuum or low oxygen pressures (5×10^{-3} mbar), the plasma dynamics change so much that the coating actually showed no passivation. The best result was obtained in an oxygen/argon ambient. Although, the partial oxygen pressure was close to 3.2×10^{-2} mbar (2.5×10^{-2} mbar) with a total deposition pressure of 0.1 mbar, the measured effective lifetime with MFCA (Fig. 1) was three times higher than for the stoichiometric TiO_2 film. This indicates that the total effect of two partial gas pressures is not a linear system. A further increase of the effective lifetime has been achieved by deposition in a water vapour ambient. The TiO_x:H coating with, so far, the best passivating qualities has been deposited in a 0.55 mbar H_2O ambient with the substrate placed at the edge of the plasma. The maximum measured effective lifetime has been 35.15 μs for a power density of 856 mW/cm^2 of the generation laser beam on the substrate.

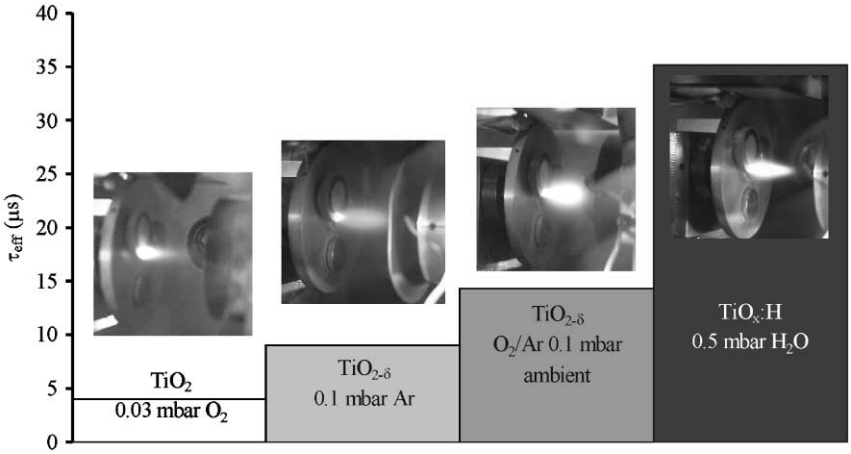

Fig. 1. The graph shows the measured effective lifetime as a function of deposition ambient for titanium dioxide coatings. The photos show the induced plasmas with a laser fluency of 1.5 J/cm^2 for each particular deposition ambient.

A change in the deposition ambient affects the plasma shape. In Fig. 1, the plasma is shown for the four different cases of the deposition ambient. It was already mentioned for TiO_2 plasmas that the total effect of two partial gas pressures is not a linear system. Since not only the kind of gas present is of importance, but also the kinetics of the arriving particles at the substrate these plasma characteristics will be of importance for the achieved surface passivation.

4. Perpendicular set-up

The customary target-substrate set-up in pulsed laser deposition is the substrate placed at the edge of the plasma opposite to and facing toward the target, here called ''parallel set-up''. We have placed wafers perpendicular to the target surface (''perpendicular set-up''), in the plasma, to get a ''cross-section'' of the ablation plume. The ablated particles flow along the substrate and nucleate instead of impinging on the substrate. Deposition of $TiO_{2-\delta}$ in an argon/oxygen ambient in this set-up resulted in much higher carrier lifetimes for the same pressure range. The perpendicular set-up is shown in Fig. 2. The resemblance in pattern between the deposited coating and the measured effective lifetime is remarkable. This resemblance cannot be explained by the thickness distribution, since the measured τ_{eff} first increases from 78.6 to 97.1 µs along the centre axis of the deposited coating, after which τ_{eff} decreases to a value of 39.3 µs, while the thickness of the deposited coating

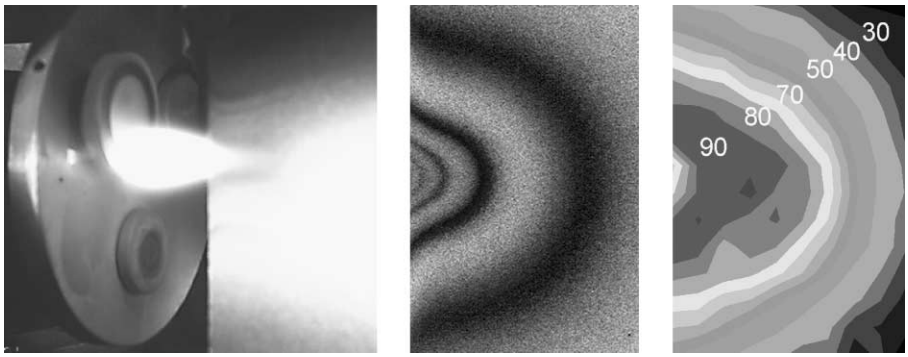

Fig. 2. Perpendicular set-up, deposited $TiO_{2-\delta}$ coating and measured effective lifetimes (µs).

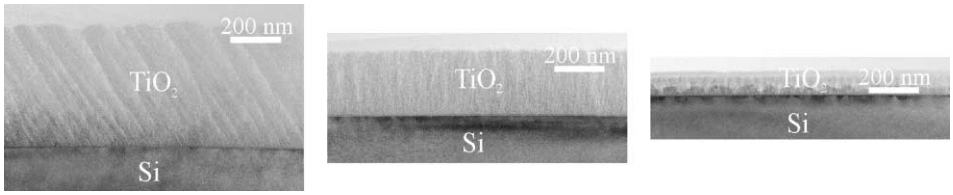

Fig. 3. TEM pictures of TiO_2 coating from perpendicular set-up at three different positions (centre position, 16 and 36 mm behind the centre point) for deposition at 1.5 J/cm^2 in $P_{oxygen} = 0.01$ mbar and $P_{argon} = 0.01$ mbar.

is a constantly decreasing function of the distance from the wafer edge.

Fig. 3 shows three TEM pictures taken at three different spots in the wafer along the centre axis: the centre point at the edge, and 16 and 36 mm behind the centre point. The measured τ_{eff} in those points were 33.8, 112.0 and 54.7 μs, respectively. As the local thickness of the coating can be seen in the TEM pictures, the corresponding measured values of τ_{eff} do indeed not correspond with this thickness distribution. The coating at the centre point shows a columnar structure, oriented with a certain angle with respect to the substrate. This columnar morphology is presumably developed because of low adatom mobility conditions, thus due to a self-shadowing mechanism under oblique incidence of ablated particles [5,6]. The columnar structure is still present in the second point, but it is now oriented perpendicular to the silicon substrate. Apparently, the ablated particle flux arrived more perpendicular to the substrate. In the third point, although columns are still visible, other less structured layers are present. The measured difference in τ_{eff} could be related to these different packing densities, but the characteristics of the interface could be more important. Further research is undertaken to determine the material content of the interface.

5. Oxygen contribution in $SrTiO_3$ coatings

$SrTiO_3$ has been proved to be an attractive material due to its various properties such as electrical transport, dielectric and optical properties. Although extensively investigated, $SrTiO_3$ is not a well-known material in photovoltaic devices. Since it has the desired optical properties to serve as an antireflection coating, we have been exploring its passivating qualities. Deposition has been done in neon and argon in the pressure range 0.01–0.15 mbar on both sides of p-type silicon substrates.

The left graph in Fig. 4 shows the dependence of τ_{eff} on deposition pressure. The first observation to be made is the large increase in measured τ_{eff} for unetched (no last HF cleaning step) Si substrates. The presence of a native/chemical oxide layer before deposition is in the whole used range of deposition parameters beneficial for the passivating quality of

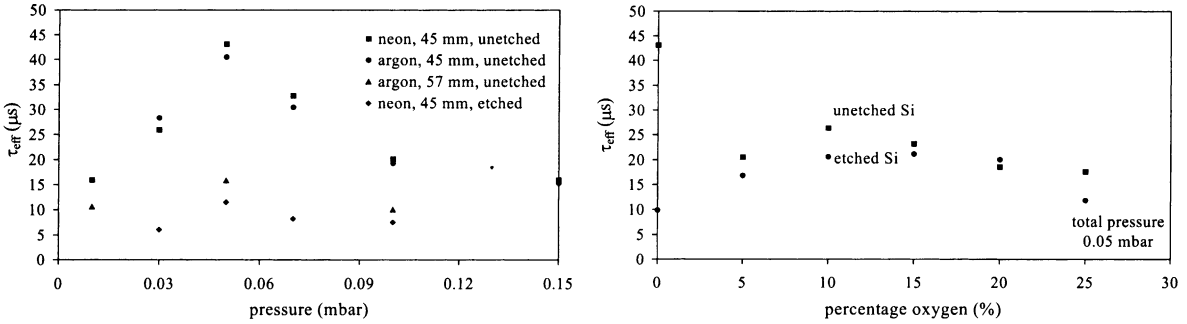

Fig. 4. Measured effective lifetime as a function of used cleaning method, deposition gas, pressure, target-substrate separation and percentage oxygen in neon ambient.

$SrTiO_3$ coatings on silicon, as opposed to TiO_2 coatings for which this is never the case. The increase in pressure could stand for two effects: lower partial oxygen pressure (oxygen supply from target) and/or lower energy of particles on arrival at the substrate. However, the maximum of τ_{eff} is both for etched and unetched substrates found at 0.05 mbar neon pressure. If the target-substrate separation is increased from 45 to 57 mm, the measured τ_{eff} decreases, but its maximum is still found at 0.05 mbar. So, the particle energy on arrival at the substrate is certainly of importance, but a second phenomenon is likely to play also a role. The role of the partial oxygen pressure is further investigated by introduction of neon/oxygen mixtures in the deposition chamber. The right graph in Fig. 4 shows the measured τ_{eff} as function of the percentage oxygen flow for a total pressure of 0.05 mbar, while the total gas flow has been held constant at 40 ml/min. For the HF-etched Si substrates an increase in oxygen flow results at first in an increased τ_{eff}, but for higher oxygen flows than 15% τ_{eff} decreases. This indicates that too low partial oxygen pressures are not beneficial for the passivating quality of $SrTiO_3$ coatings. The presence of a native/chemical oxide layer on the Si substrate can function as an oxygen source, which could explain the improved passivation for the unetched coatings. Indeed, the $SrTiO_3$ coatings deposited on the unetched Si substrates do show a decrease in τ_{eff} for increasing oxygen flow. However, τ_{eff} does not decrease continuously but shows a large decrease in the case of 5% oxygen flow after which τ_{eff} first increases to a higher value (lower than 0% oxygen flow) to decrease further with increasing oxygen flow. The change in plasma is also large for adding only a small amount of oxygen to the argon ambient. This effect is reproducible for a reduced total gas flow of 20 ml/min.

6. Conclusions

Use of the flexibility of the pulsed laser deposition set-up resulted in highest passivation levels reported for TiO_2 coatings. The partial oxygen pressure and the energy of the arriving particles on the substrate are the two most important deposition parameters in achieving surface passivation in TiO_2 and $SrTiO_3$ coatings. The importance of the interface between the oxide coating and the silicon substrate is shown by the difference in achieved surface passivation for HF-etched substrates and non-etched substrates. The influence of the interface on surface passivation will be researched further by deposition of different oxides (TiO_2, $SrTiO_3$, SrO, $SrSiO_4$).

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