GOOD SURFACE PASSIVATION OF C-SI BY HIGH RATE PLASMA DEPOSITED SILICON OXIDE

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ABSTRACT

Silicon dioxide films were deposited by the (industrially applied) expanding thermal plasma technique using a gas mixture of argon-oxygen-octamethylcyclotetrasiloxane (OMCTS) and at deposition rates in the range of 5-23 nm/s. The films composition was investigated by means of spectroscopic ellipsometry, Fourier transform infrared spectroscopy and Rutherford backscattering. The composition was close to that of thermal oxide, with only a small residual hydrogen content of 2 at.%. The surface passivation of the silicon dioxide films was tested on 1.3 Ω cm *n*-type FZ crystalline silicon wafers. A good level of surface passivation of 54 cm/s was reached after a 15 minute forming gas anneal at 600°C.

INTRODUCTION

Silicon dioxide is the superior material to fulfill the requirements when decreasing the solar cell wafer thickness and maximizing solar cell efficiency. However, the growth of these oxides generally implies long processing times and temperatures that can deteriorate the wafer bulk quality. Recently these problems were partly solved by using a wet oxidation at 800 °C resulting in a record multi-crystalline silicon solar cell [1]. However, the processing times were still in the order of hours due to the requirement of a rather thick SiO_2 film of ~100 nm for optimal optical performance at the back of the solar cell. The application of a plasma-deposited silicon dioxide film, obtained in a low temperature process and with a good level of surface passivation, might form a preferred alternative to reduce the processing time needed.

Plasma enhanced chemical vapor deposition (PECVD) deposited silicon dioxide films are already widely used for various technological applications, for example as dielectric in CMOS devices [2]. In the field of microelectronics a lot of effort was put in the development of PECVD silicon dioxide with a low interface defect density. Chen et al. [3] developed a plasma deposited silicon dioxide film with a interface defect density comparable to thermal oxide on nearly intrinsic (> 500 Ω cm) c-Si. The level of surface passivation on low resistivity *p*-type silicon was, however, only modest with a surface recombination velocity of 700 cm/s [4]. Also Leguit et al. [5] achieved a good level of surface passivation on high resistivity *p*- and *n*-type c-Si. However, on low resistivity c-Si the level of surface passivation was again moderate with surface recombination velocities in the range of 300-400 cm/s. The best results reported in the literature are obtained by silicon dioxide films deposited from O_2 (or N_2O)-SiH_4 mixtures. However, also organosilicons such as tetraethoxysiloxane (TEOS), hexamethyldisiloxane (HMDSO) or octamethylcyclotetrasiloxane (OMCTS) can be used for the deposition of silicon dioxide films. Organosilicons are relatively inexpensive, non-flamable and have a low toxicity rating. Hence, no special safety installation is required as in the case of SiH_4.

In this study we will use OMCTS as the silicon containing precursor. OMCTS consists of 4 cyclic Si-O groups and 8 methyl groups. From an extensive material characterization we will make sure that high-quality silicon dioxide films are deposited at a high rate using OMCTS with the ETP technique. Finally, we will show that these silicon dioxide films exhibit a good level of surface passivation on low resistivity *n*-type silicon after a post-thermal treatment.

EXPERIMENT

The silicon dioxide films were deposited in a lab scale reactor employing the expanding thermal plasma (ETP) technique (see e.g. van Hest et al. [6]), as shown in Fig. 1. In the ETP source an Ar plasma is created at sub-atmospheric pressures (typically 0.5 bar) and then expands supersonically into a low pressure reactor vessel (typically 0.2-0.5 mbar). In the nozzle O_2 is injected into the expanding plasma (typically 200 sccm). Finally, an Ar-OMCTS mixture is fed into the plasma by an injection ring positioned ~5 cm from the plasma source.

The OMCTS flow rate (4-200 g/h) is set by means of a Bronkhorst liquiflow meter and is thereafter evaporated in and mixed with Ar in a controlled evaporator module (CEM, Bronkhorst W-202A). The Ar-OMCTS mixture is transported to the reactor vessel in a heated line (~120 °C) to prevent condensation.

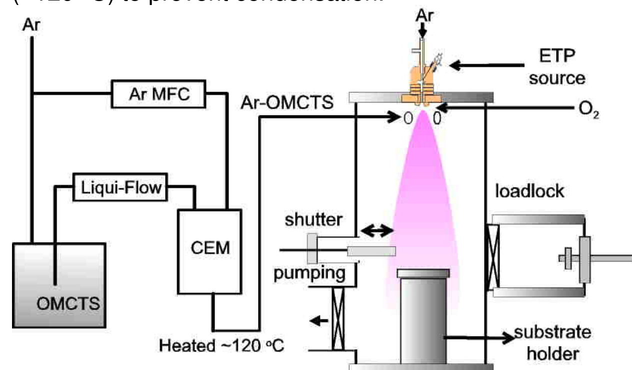

Fig 1. Schematic representation of the lab-scale setup employing the expanding thermal plasma technique used for the deposition of silicon dioxide film.

For the material characterization, silicon dioxide films were deposited on 10-20 Ω cm *p*-type Cz wafers. These samples where extensively studied by means of spectroscopic ellipsometry, Fourier transform infrared (FTIR) spectroscopy, Rutherford backscattering (RBS), elastic recoil decay (ERD) and secondary ion mass spectrometry (SIMS).

The level of surface passivation of the silicon dioxide films was investigated on 380 µm 1.3 Ω cm *n*-type c-Si. The silicon substrates were cleaned using conventional RCA1 & RCA2 cleaning with a final HF dip (5 %). A silicon dioxide like film was deposited at both sides of the substrate and the carrier lifetime was measured by the photoconductance decay method, both in quasi-steady-state and transient mode (Sinton WCT-100 [7]). The lifetime samples received a forming gas anneal (10 % H_2 in N_2) after deposition in a rapid thermal anneal oven at the temperatures indicated.

RESULTS

Material properties

The silicon dioxide films were deposited using the operating conditions summarized in Table 1. The OMCTS flow rate was varied in the range of 6-28 sccm and the refractive index and deposition rate was determined by means of spectroscopic ellipsometry and are shown in Fig. 2.

Table 1: Operating conditions used for silicon dioxide deposition.

Ar flow rate	2000 sccm
O_2 flow rate	200 sccm
OMCTS flow	6-28 sccm
Deposition temperature	400 °C
Arc current	75 A
Reactor pressure	0.41-0.49 mbar
Deposition time	12 s

From Fig. 1(a) we can see that the refractive index for a OMCTS flow rate < 13 sccm is constant at ~1.47. This is close to the refractive index reported for thermal oxide. From RBS and ERD measurements we determined that the oxygen to silicon ration was 65:32 for these films, indicating that indeed stoichiometric silicon dioxide films were deposited for OMCTS flows below 13 sccm using the process conditions summarized in Table 1. From ERD and SIMS analysis we obtained that there was a residual hydrogen content of 2 at.% in the films, however, no residual carbon could be detected above the detection limit of SIMS (0.03 at.%) indicating that carbon-free films were deposited at OMCTS flows below 13 sccm. The high fluxes from the ETP plasma source enables us to deposited these low impurity silicon dioxide films at ultra-high deposition rates in the range of 5-23 nm/s.

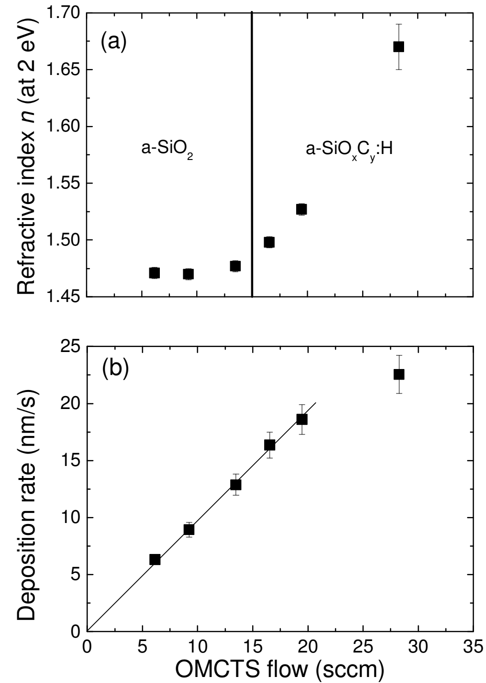

Fig. 2: (a) Refractive index (at 2 eV) and (b) deposition rate as a function of the OMCTS flow for films deposited using the process conditions summarized in Table 1.

For OMCTS flows higher than 13 sccm the refractive index increases, as shown in Fig. 1(a). From RBS analysis it was confirmed that this was mainly caused by a reduction of the oxygen to silicon ratio below 2. In addition there is a relative small amount of carbon built into the film. For the highest OMCTS flow (28 sccm) used in this study, approximately 4 at.% of carbon was detected by RBS. The hydrogen content of the films also significantly increases up to ~18 at.% for the film deposited with a OMCTS flow of 28 sccm. In this case we will refer to the films as silicon dioxide-like films, to account for the high impurity content present in these films.

In Fig. 3 the infrared transmission spectra of the silicon dioxide films for two OMCTS flows is shown. All the characteristic Si-O-Si absorption modes are visible in the infrared transmission spectra [8]. For OMCTS flow rates of 28 sccm, also hydrogen and carbon related absorption peaks are visible in the infrared transmission spectrum. For the silicon dioxide films deposited with a low OMCTS flows, we detected that the hydrogen was mainly bound to oxygen [9]. For the silicon dioxide-like films deposited with high OMCTS flows a significant absorption by Si-H groups was observed. This means that the hydrogen was mainly bound to silicon, instead of oxygen or carbon. This is remarkable, because the precursor molecule does not contain Si-H bonds.

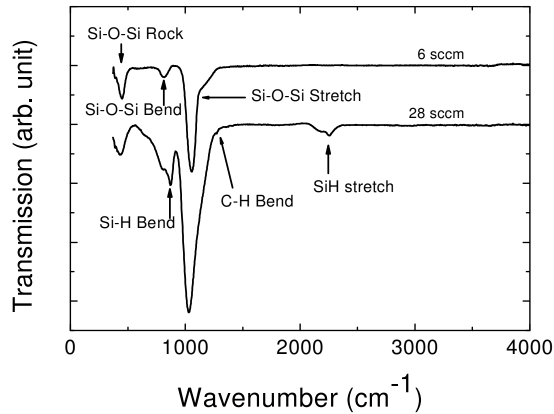

Fig. 3: Infrared transmission spectra for films deposited for two OMCTS flows (as indicated). The spectra are offset vertically for clarity.

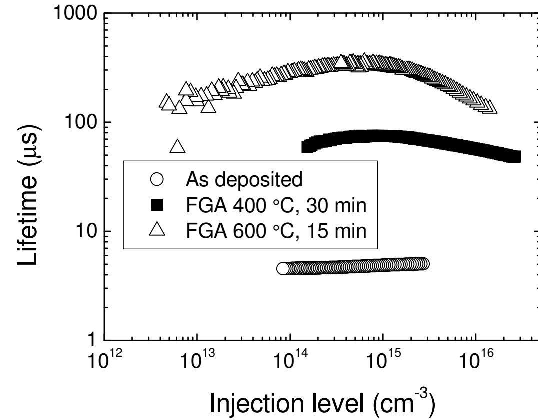

Fig. 4: Effective carrier lifetime of 380 μm 1.3 Ω cm *n*-type crystalline silicon substrates passivated by PECVD silicon dioxide film. The post-thermal treatment of the films is indicated in the figure.

Surface passivation

Silicon dioxide films deposited with an OMCTS flow of 9 sccm were chosen to test the surface passivation on low resistivity *n*-type crystalline silicon. The effective carrier lifetime of the lifetime samples was measured prior to and after a post thermal treatment, as indicated in Fig. 4. The lifetime of the lifetime sample with as-deposited silicon dioxide was rather poor, with effective carrier lifetimes of 5-10 μs. This is comparable to results reported for silicon dioxide grown by wet oxidation [1], but lower compared to values obtained for thermal oxide [10]. However, a 30 minute conventional forming gas anneal at 400 °C already improves the effective carrier lifetime up to 90 μs, similar as reported on low resistivity *p*-type silicon for silicon dioxide grown by wet oxidation [1]. By increasing the annealing temperature we observed that the carrier lifetime also increased. Finally the best results were obtained for a 15 minute forming gas anneal at 600 °C, where an effective carrier lifetime of 350 μs was obtained corresponding to an effective surface recombination velocity of 54 cm/s assuming an infinite bulk lifetime. Increasing the annealing temperature even further did not yield a further improvement of the effective lifetime. The effective lifetime of the lifetime samples was tested to remain constant over a period more than half a year.

The level of surface passivation reached in the present study is significantly higher compared to the results reported previously. The best values reported so far for PECVD silicon dioxide on low resistivity *n*-type silicon were in the 100-400 cm/s range for slightly higher resistivity *n*-type wafers (3-6 Ω cm) [5, 11]. And generally the level of surface passivation decreases when lower resistivity wafers are used. The improvement of the level of surface passivation by increasing the annealing temperature up to 600 °C is differing from the results published by Chen et al. [3], where an optimal annealing temperature of 350 °C was found and the level of surface passivation was reported to deteriorate when the annealing temperature was increased.

The impact of the post-deposition anneal was investigated in more detail. It was shown that the presence of H_2 during the anneal was essential to obtain a good level of surface passivation. No significant improvement in effective lifetime was observed when the lifetime sample was annealed in N_2. From FTIR and ERD we could also see that the hydrogen content in the silicon dioxide film decreases during the FGA. However, it is plausible that hydrogen redistributes in the film and passivates defects at the interface between silicon dioxide and c-Si. From FTIR we could also observe an increase in the number and absorption peak position of Si-O bonds, this indicates that the silicon dioxide film reconstructs and densifies during the anneal [9].

CONCLUSIONS

In this paper we have shown that silicon dioxide films with a low impurity content and good level of surface passivation can be deposited at high rate employing the ETP technique using OMCTS as the growth precursor. The level of surface passivation of the PECVD silicon dioxide like films is significantly improved by a post-deposition forming gas anneal and the best results are obtained for a 15 minute forming gas anneal at 600 °C where an effective surface recombination velocity of 54 cm/s is obtained on low resistivity *n*-type silicon.

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