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Blistering Induced Degradation of Thermal Stability Al_2O_3 Passivation Layer in Crystal Si Solar Cells

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Abstract—**Different kinds of post-deposition annealing (PDA) by a rapid thermal process (RTP) are used to enhance the field-effect passivation of Al_2O_3 film in crystal Si solar cells. To characterize the effects of PDA on Al_2O_3 and the interface, metal-insulator semiconductor (MIS) devices were fabricated. The effects of PDA were characterized as functions of RTP temperature from 400~700 °C and RTP time from 30~120 s. A high temperature PDA can retard the passivation of thin Al_2O_3 film in c-Si solar cells. PDA by RTP at 400 °C results in better passivation than a PDA at 400 °C in forming gas (H_2 4% in N_2) for 30 minutes. A high thermal budget causes blistering on Al_2O_3 film, which degrades its thermal stability and effective lifetime. It is related to the film structure, deposition temperature, thickness of the film, and annealing temperature. RTP shows the possibility of being applied to the PDA of Al_2O_3 film. Optimal PDA conditions should be studied for specific Al_2O_3 films, considering blistering.**

Index Terms—**Solar cell, field-effect passivation, Al_2O_3, post-deposition annealing, negative fixed oxide charge, thermal stability, blistering**

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I. INTRODUCTION

Currently, the solar cell market is dominated by crystalline Si solar cells. Carrier losses induced by Schockey-Read-Hall (SRH) recombination retard the efficiency of energy conversion. Surface passivation of the carriers is an important issue for high efficiency crystalline Si solar cell applications. Al_2O_3 film grown by atomic layer deposition (ALD) has demonstrated excellent uniformity and growth control, suggesting better passivation quality [1]. Al_2O_3 synthesized by ALD provides a high quality surface because its low interface state density provides good chemical passivation and the negative fixed charges near the interface for p-type c-Si provide excellent field-effect passivation [2-6]. Al_2O_3 film also can offer excellent dielectric properties [7]. Several studies show that both chemical and field-effect passivation is enhanced by post-deposition annealing in forming gas (H_2 in N_2) at a moderate temperature for about 15~30 minutes after the deposition of Al_2O_3 film [8-10].

Obviously, this high thermal budget forming gas annealing (FGA) is neither cost- nor energy-efficient. On the other hand, rapid thermal processing (RTP) is another widely used annealing method with such advantages as a short cycle time and low thermal budget. Dong Lei *et al.* studied the relationship between only the RTP temperature and the passivation of Al_2O_3 and found the SiO_x interlayer became thicker after the RTP [5]. However, few works address RTP annealing to passivate Al_2O_3 in c-Si solar cell applications [5, 8].

In this work, we studied the relationship of the field-effect passivation and the effective carrier lifetime as a

function of the RTP time and temperature. A common FGA at 400 °C for 30 minutes was also used for comparison to ascertain whether the RTP can provide good enough field-effect passivation for Al_2O_3 on c-Si solar cells.

II. EXPERIMENTAL

To examine the electrical properties of the Al_2O_3 film, metal-insulator semiconductor (MIS) devices were fabricated. The process flow is summarized in Fig. 1. p-type silicon wafers were used. After a standard Radio Corporation of America (RCA) cleaning, a 20 nm Al_2O_3 thin film was deposited by thermal ALD at 250 °C, with trimethylaluminium ($Al(CH_3)_3$ and water (H_2O) precursors. Then samples were annealed in an RTP system with a vacuum of $1.5x10^{-5}$ Torr as a function of temperature at 400, 500, 600 and 700 °C for 30 seconds and as a function of time at 30, 60, 90, and 120 seconds at 400 °C. A reference sample and another sample annealed in a tube furnace at 400 °C for 30 minutes in forming gas ambient (H_2 4% in N_2) were also prepared for comparison. After a 100 nm thick layer of Ti was sputtered as the top metal by an RF sputter system, the samples were patterned by photolithography. Finally, 100 nm thick Al was sputtered on the backside of the samples to reduce resistance. The capacitance-voltage (C-V) measurements were performed by an HP 4284A LCR meter. Effective carrier lifetime was measured by the Quasi Steady State PhotoConductance (QSSPC) method on samples cut in 5 × 5 cm squares. Morphological stability was observed by field-emission scanning electron microscopy (FESEM). X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) were used to examine the change in the binding energy, the atomic ratio of Al to O, and the depth profile of elements before and after annealing, respectively.

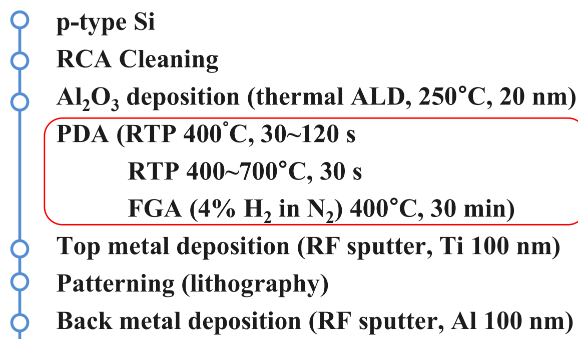
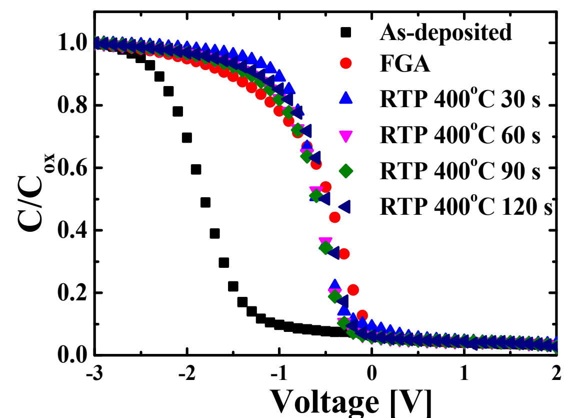


Fig. 1. Process flow for the MIS devices.

III. RESULTS AND DISCUSSIONS

The results of C-V measurements at a frequency of 1 MHz are shown in Fig. 2. After the PDA, the curves shift to the positive direction, which means that the negative fixed charges ($-Q_f$) increased. The Q_f are related to the field-effect passivation of the solar cell. The minority charge carriers are repelled from the interface by the Q_f formed electric field. Thus, fewer minority charge carriers will be lost. The fixed charge density (N_f) was calculated by $N_f = -\Delta V_{FB}$ x C_{ox}, ΔV_{FB} is the difference between the experimental flatband voltage (V_{FB}) and the



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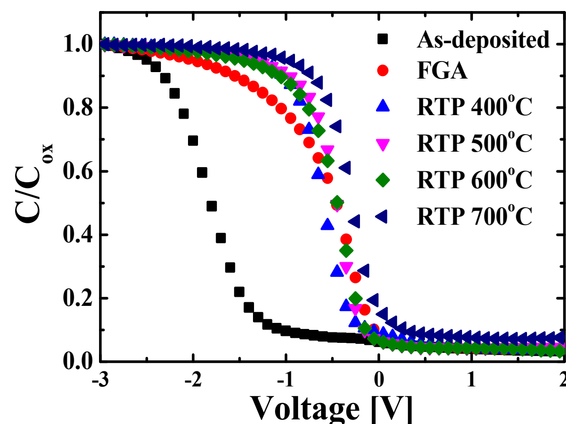


(b)

Fig. 2. The normalized C-V curves obtained at 1MHz (a) PDA at RTP 400 °C from 30 seconds to 120 seconds, (b) PDA by RTP from 400 °C to 700 °C for 30 seconds.

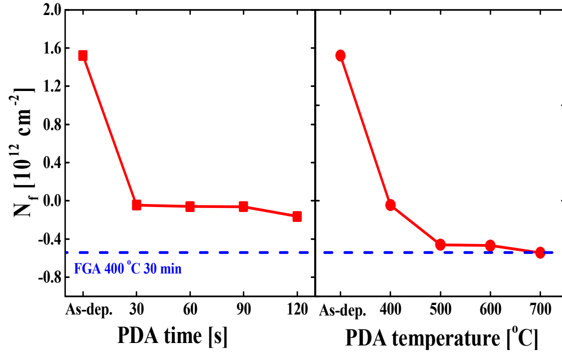


Fig. 3. Fixed oxide charge density (a) annealed at a 400 °C RTP, (b) annealed at 400~700 °C RTP for 30 s.

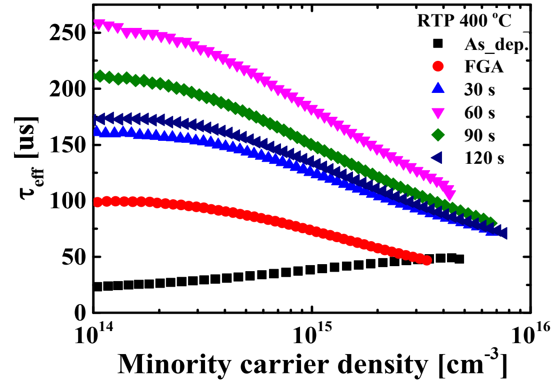
ideal V_{FB} of -0.53 V, which was calculated in our previous work by fitting the V_{FB} vs. the thickness of the Al_2O_3. C_{ox} is the maximum capacitance from the C-V curve.

In Fig. 3, the as-deposited sample shows that the sign of the positive fixed charges and the fixed charges turn to negative fixed charges after the PDA. The negative fixed charges do not significantly increase with longer process times from 30 seconds to 120 seconds at 400 °C. The better interface states help improve the slopes of the C-V curves annealed by RTP as opposed to FGA. When the temperature increases from 400 to 700 °C for 30 seconds, the sample has nearly the same negative fixed charges as the sample treated by FGA in Fig. 3(b). With a relatively high temperature anneal, an interlayer of SiO_x can be formed [5]. Tetrahedrally coordinated Si in SiO_x contributes to tetrahedrally coordinated Al at the interface, causing the negatively charged Al vacancies close to the interface [4-6, 8, 11, 12].

Effective lifetime (τ_{eff}) measured by QSSPC is shown in Fig. 4. In the QSSPC measurement, a conventional xenon photoflash generates excess carriers in the sample. A fast or slowly diminishing flash is used to measure the photoconductivity. The derived excess carrier density (Δn) and generation rate (G) vs. time give the τ_{eff} in Eq. (1).

$$\tau_{eff}(\Delta n) = \frac{\Delta n(t)}{G(t) - \frac{d\Delta n(t)}{dt}} \tag{1}$$

The sample annealed with an RTP at 400 °C for 60 s has the longest τ_{eff}, and 90 s and 120 s annealed samples show degradation in Fig. 4(a). With the increase of



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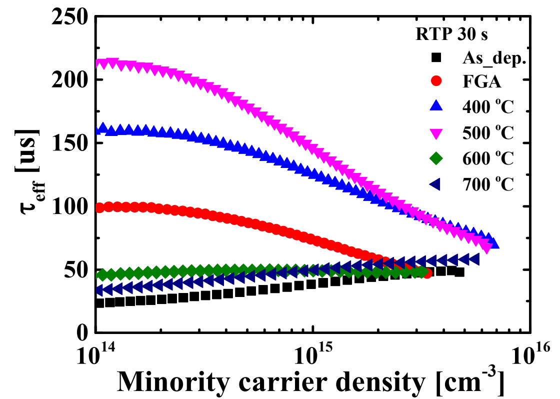


(b)

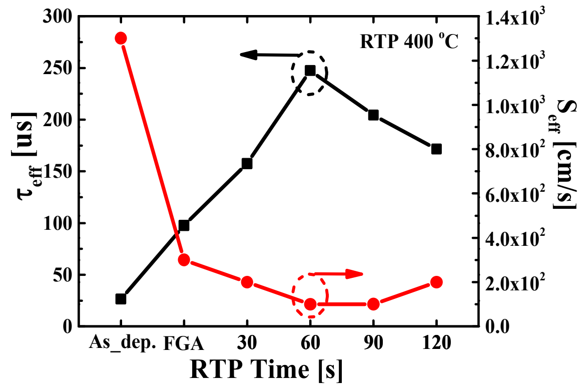
Fig. 4. Effective lifetime measured by QSSPC method (a) annealed at the RTP 400 °C, (b) annealed by the RTP 400~700 °C for 30 s.

temperature, a 500 °C RTP shows the best lifetime and above 500 °C, rapid degradation occurs in Fig. 4(b). However, even a 500 °C annealed sample shows no better τ_{eff} than a 60 s annealed sample at RTP 400 °C.

At an injection level of 2×10^{14} cm^{-3}, τ_{eff} and surface recombination velocity (S_{eff}) were extracted (shown in Fig. 5. S_{eff} was extracted from Eq. (2),

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2S_{eff}}{W}, \tag{2}$$

where W is the effective wafer thickness (carrier profile thickness) and τ_{bulk} is the bulk minority carrier lifetime that is assumed to be infinite [15, 16]. In Fig. 5(a), the increased RTP time at 400 °C, 60 s, shows the highest τ_{eff} and lowest S_{eff}. In Fig. 5(b), the RTP temperature of 500 °C shows the highest τ_{eff} and lowest S_{eff}. However, it is not as good as the 60 s RTP at 400 °C. The degradation at high temperature may be explained by the formation of



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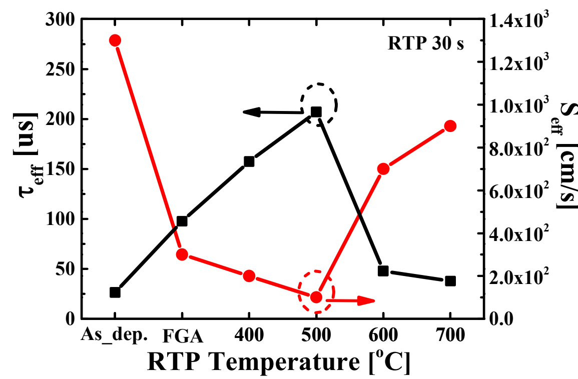

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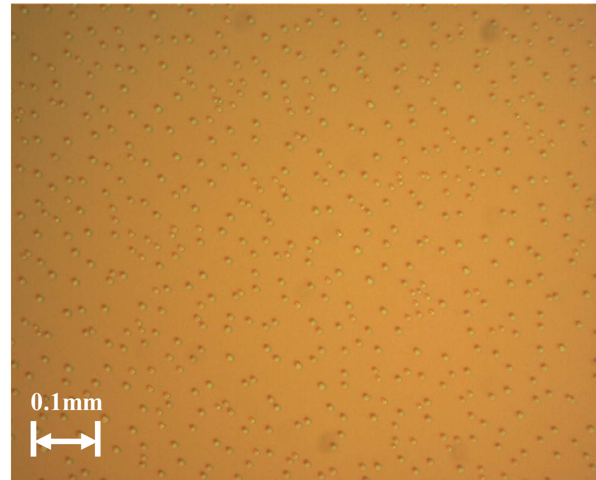
Fig. 5. Effective lifetime and surface recombination velocity at 2×10^{14} cm^{-3} (a) annealed at RTP 400 °C, (b) annealed at RTP 400~700 °C for 30 s.



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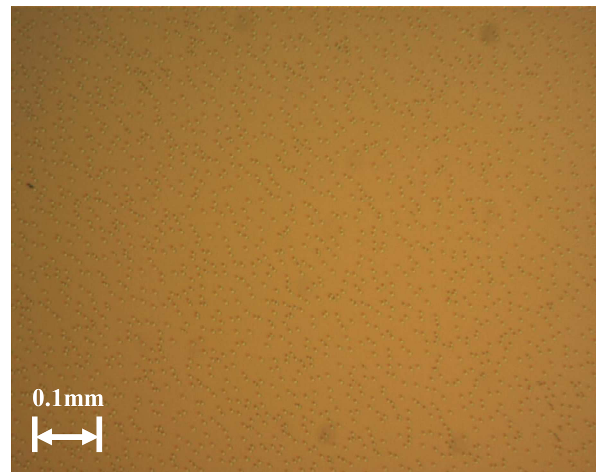


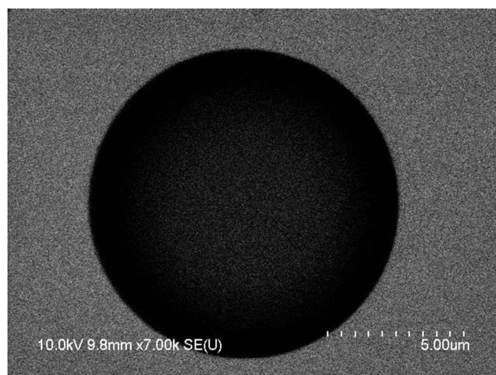
(b)

Fig. 6. Blisters observed by optical microscopy (a) PDA by RTP 600 °C for 30 s, (b) PDA by RTP 700 °C for 30 s.

silicate under high temperature annealing [5]. Nevertheless, annealing Al_2O_3 at a high temperature may be risky because it may induce blistering. D. Schuldis *et al.* reported in detail the blistering mechanism of Al_2O_3, which is related to the film structure, deposition temperature, thickness of the film, and the annealing temperature and time. It is thought that the diffusion barrier properties of Al_2O_3 and the outdiffusion of H-containing species during annealing are the reasons for the happening of blister [13], which degrade τ_{eff} and thermal stability. Although the sample treated by FGA has more negative fixed charges, poor interface states are shown and blistering may initiate this. Fig. 6 shows the blisters observed by optical microscopy. A lower process temperature (Fig. 6(a)) causes larger but fewer blisters and a higher process temperature (Fig. 6(b)) results in smaller but more blisters.

Fig. 7 shows an overview and side view of blisters observed after RTP at 600 °C (Fig. 7(a)) and 700 °C (Fig. 7(b)). The blister looks like a hillock, which degrades the thermal stability in the firing process. Thus the annealing time should be chosen carefully. Increasing it to over 400 °C is probably not wise for a thin Al_2O_3 film.

Without considering high temperature annealing, the FGA at 400 °C for 30 minutes apparently has the greatest thermal budget; therefore, it was selected to examine by XPS and SIMS the trend of the changes in the Al_2O_3 film after PDA. Fig. 8 shows the curve-fitting results of the O 1*s* from XPS. After FGA at 400 °C for 30 min, the Al_2O_3 peak becomes higher than the peak of the adsorbed water. The atomic ratio of Al to O is 1:2.4 as-deposited and becomes 1:2.6 after the FGA. This means the surface of the sample becomes relatively O-rich. Moreover, the metallic Al atoms decrease and turn to Al_2O_3 or atoms of



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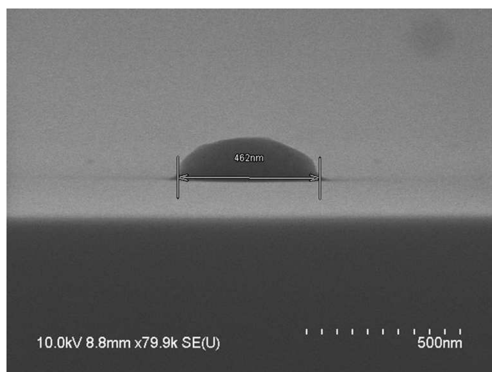

(b)

Fig. 7. Morphological analysis of annealed samples by FESEM (a) The overlook of blister after RTP 600 °C, (b) The side view of blister after RTP 700 °C

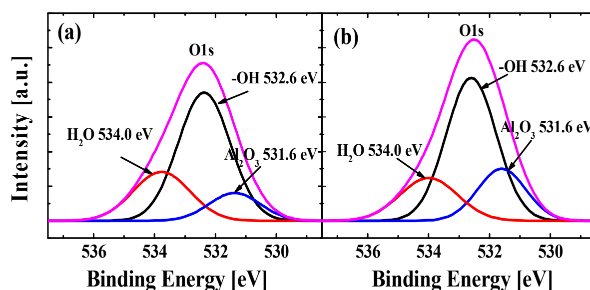

Fig. 8. O 1s photoelectron spectra of Al_2O_3 films recorded by XPS (a) the sample of as-deposited, (b) the sample after FGA at 400 °C, 30 minutes.

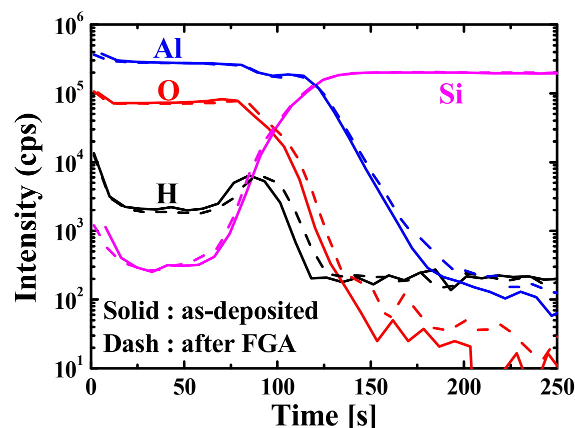

Fig. 9. Depth profile of Al, O, H and Si elements by SIMS. The sample of as-deposited in solid line, and the sample after FGA treatment in dash line.

other compositions and bonding structures. Byungha Shin *et al.* reported that ALD Al_2O_3 films are O-rich near the interface and become progressively more Al-rich further away from the interface. Additionally, the sign of the fixed charge is correlated with the local stoichiometry of the films, such that a negative fixed charge exists within the O-rich regions near the interface and a positive fixed charge is within Al-rich regions away from the interface [14]. The ratio of O to Al increases after annealing, indicating more O-related interstitials or fewer Al-related vacancies, which may be responsible for the change in the fixed charge density.

In Fig. 9, SIMS shows the depth profile before and after FGA. It can be see that H and O diffuse at the interface to the substrate of Si, which can explain the chemical passivation of the dangling bonds at the interface by forming –OH. The O element diffuses to the interface and makes a more O-rich interface, which is the source of field passivation by the negative fixed charges.

IV. CONCLUSIONS

We have found that a PDA using RTP at 400 °C can better passivate 20 nm thick Al_2O_3 than FGA at 400 °C for 30 minutes, indicating the potential of PDA for passivating Al_2O_3 on c-Si by RTP. A high thermal budget treatment, especially a high temperature treatment, must be used carefully with Al_2O_3 films because of the blistering. The outdiffusion of H-containing species is believed to be the reason for the formation of blisters. The blistering degrades thermal stability and effective lifetime. An optimal annealing time and temperature that avoids the formation of blisters should be studied for different kinds of Al_2O_3 in the passivation of solar cell applications. The diffusion of O and H elements to the interface are believed to improve the passivation of the interface.

ACKNOWLEDGMENTS

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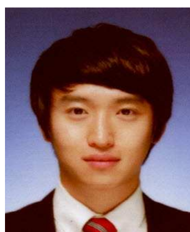

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