



# Reduction of surface recombination velocity by rapid thermal annealing of p-Si passivated by catalytic-chemical vapor deposited alumina films



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## ABSTRACT

Excellent electrical-passivation of p-type Si (p-Si) in Si solar cells has been achieved by post-deposition rapid annealing of aluminum oxide ( $\text{AlO}_x$ ) films prepared by catalytic chemical vapor deposition (Cat-CVD) using trimethyl aluminum (TMA) and  $\text{O}_2$ . Extremely small surface recombination velocity of below 0.1 cm/s has been obtained at post-deposition annealing temperatures in the range of 350–400 °C for an annealing time of 2 min. The reduction of surface recombination velocity has been attributed to band bending induced by a fixed negative charge density of  $5 \times 10^{11}$  charges/cm<sup>2</sup> and an additional small interface trapping density of around  $10^{10}$  cm<sup>-2</sup> eV<sup>-1</sup>.

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## 1. Introduction

Electrical passivation of p-Si surfaces to reduce surface recombination in crystalline Si solar cells is very important for increasing their conversion efficiency. It is becoming all the more important as solar cells are becoming thinner in order to reduce their cost [1,2]. Recently, there have been reports on Alumina ( $\text{AlO}_x$ ) film-passivation techniques which can reduce surface recombination velocity ( $S_0$ ) mainly by dint of band bending effect attributed to fixed charges induced by  $\text{AlO}_x$  films deposited on Si [3]. The creation of fixed charges is attributed to precursor gases, annealing of  $\text{AlO}_x$  films, and method depositing the films. Fixed charges have been created in  $\text{AlO}_x$  films deposited on Si using the following deposition methods at various annealing temperatures, and annealing times: remote plasma enhanced chemical vapor deposition of tri-ethylaluminum and tri-sec-butoxide (400 °C, 30 min) [4], pyrolysis of aluminum tri-isopropoxide (510 °C, 15 min) [5], atomic layer deposition (ALD) of TMA and  $\text{H}_2\text{O}$  (300 °C) [6], plasma-assisted atomic layer deposition (PA-ALD) of TMA and  $\text{O}_2$  (425 °C, 30 min) [7–9], plasma-enhanced chemical vapor deposition (PE-CVD) of TMA,  $\text{CO}_2$  and  $\text{H}_2$  (around 400 °C) [10], sputtering of an aluminum target with  $\text{O}_2$  ambient 500 °C, 30 min) [11], spatial atomic layer deposition of TMA and  $\text{H}_2\text{O}$  (350–425 °C, 15 min) [12], and Cat-CVD of TMA and  $\text{O}_2$  (from 230 °C, cooled for 300 min) [13]. The surface recombination velocity obtained has been very small in all deposition methods mentioned above. It has been reported that post-deposition annealing is very effective in reducing surface recombination velocity [14,15]. We have already obtained extremely small surface recombination velocity ( $S_0$ ) of below 0.1 cm/s in p-Si passivated by Cat-CVD deposited

alumina films which have been cooled down slowly for several hours in a vacuum [13]. The extremely small surface recombination velocity of below 0.1 cm/s in these films has been kept intact for over one year [13]. However, the duration of the thermal treatment of several hours is too long for industrial applications.

In this study, the post-deposition annealing process has been investigated to achieve a decrease of a surface recombination velocity by dint of the  $\text{AlO}_x$  film passivation. Film samples have been prepared by Cat-CVD deposition at varying annealing temperature ( $T_a$ ) and time ( $t_a$ ). The surface recombination at the interface between the  $\text{AlO}_x$  film and Si surface has been characterized by photoconductivity decay (PCD) curves and evaluated also by direct measurement of surface recombination velocities ( $S_0$ ). Furthermore, fixed charge density ( $N_f$ ) and interface trapping densities ( $D_{it}$ ) have been obtained from capacitance voltage (C–V) curves measured for metal-oxide-semiconductor (MOS) diodes fabricated using  $\text{AlO}_x$  films. The annealing temperature and time which achieve the smallest surface recombination velocity due to the  $\text{AlO}_x$  passivation films have been determined from PCD curves, measured surface recombination velocities, and fixed charge density. The mechanism for reduction of surface recombination velocity has been studied in terms of the behaviors of measured fixed charge density and interface trapping density.

## 2. Experimental

Aluminum oxide films were deposited on p-Si wafers by Cat-CVD using TMA and  $\text{O}_2$  as the precursor gas. The experimental apparatus used in this study is shown in Fig. 1. Si substrates used for the samples were Czochralski (CZ) grown crystalline p-Si (100) wafers having a resistivity of 10  $\Omega\text{cm}$  with a mirror-polished front surface and a chemically-polished back surface.  $2 \times 2$  cm<sup>2</sup> samples were scribed

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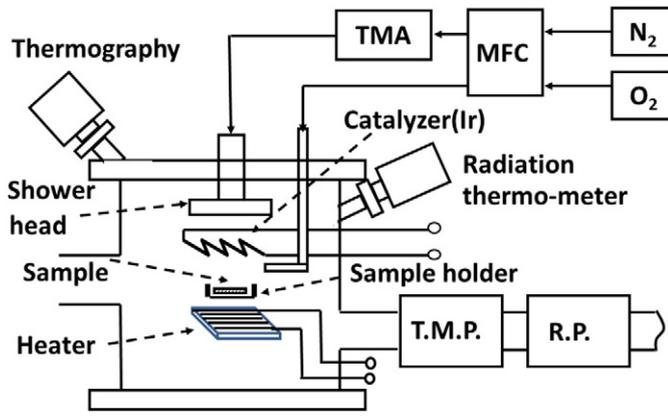


Fig. 1. Schematic illustration of apparatus used for film deposition and post-deposition rapid thermal annealing.

from the wafers. The samples were then slightly etched by a 2.5 wt.% hydrofluoric acid (HF) rinse to remove the natural oxide to obtain an H-terminated surface, and rinsed in deionized (DI) water prior to deposition. The samples were mounted on the sample holder 7 cm away from the catalyzer. The samples were heated from the back side by radiation from a Chromel alloy-wire heater mounted in a zigzag manner on a ceramic plate as shown in Fig. 1. The sample temperature ( $T_{sub}$ ) was measured by thermography. An oxidation resistant 25 cm long, a 0.2 mm diameter iridium wire was used as the catalyzer. The wire was wound around the holder in a W-shaped bend, and the catalyzer temperature ( $T_{cat}$ ) was measured by a radiation thermometer. The deposition of  $AlO_x$  films on the p-Si samples were carried out using  $N_2$  gas as a carrier gas for the TMA which was introduced through the shower head and  $O_2$  gas was independently blown around the catalyzer.

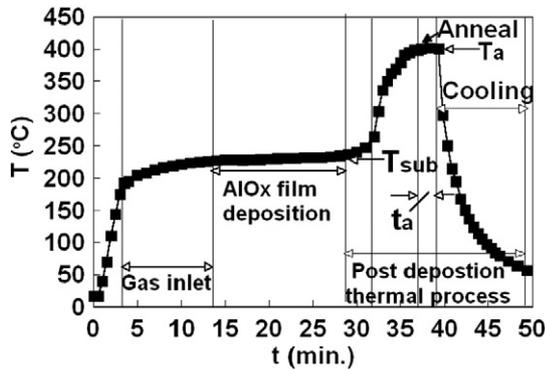


Fig. 2. Time chart used for film deposition and post-deposition thermal annealing.

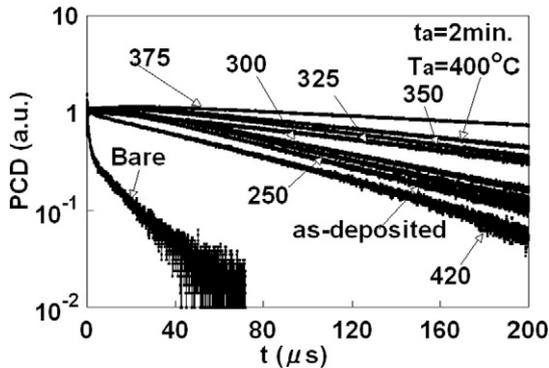


Fig. 3. Photoconductivity (PCD) curves observed by BS- $\tau$  for  $AlO_x/p$ -Si samples prepared by varying post-deposition annealing temperature, as-deposited and bare wafers (without  $AlO_x$  films).

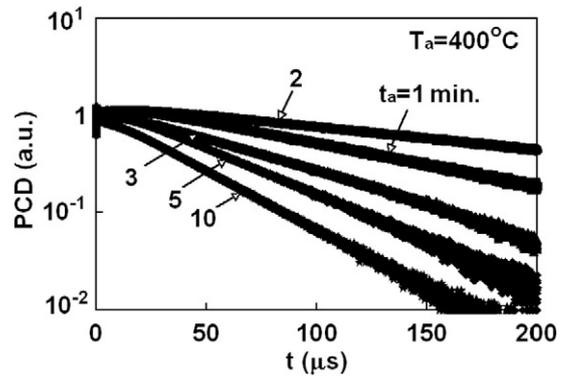


Fig. 4. PCD curves observed by BS- $\tau$  for  $AlO_x/p$ -Si samples prepared by varying post-deposition annealing time.

The films were deposited for 15 min at  $T_{sub}$  of 240 °C under  $O_2/TMA$  gas flow-rate ratio of 15 and a chamber pressure of 17 Pa. The flow rate of TMA was determined using the equivalent  $N_2$  flow rate to satisfy the vapor-pressure of TMA. Subsequent to deposition, as seen in Fig. 2, the samples were annealed by elevating the sample temperature to the maximum annealing temperature ( $T_a$ ) which was kept constant for the annealing time ( $t_a$ ) of several minutes in  $N_2$  ambient at a pressure of  $10^5$  Pa. The samples were prepared varying  $T_a$  in the range of 250–420 °C for  $t_a = 2$  min, and then varying  $t_a$  in the range of 1–10 min with  $T_a = 400$  °C. The  $AlO_x$  film thicknesses of the samples were measured to be in the range of 2.1–3.1 nm by a spectroscopic ellipsometer (ALPHA-SE, J.A. Woolam Co., Inc.) using two-layer model composed of an  $AlO_x$  layer and a  $SiO_2$  layer. The surface recombination at the interface in  $AlO_x/p$ -Si was characterized by the initial decay in photoconductivity decay curves measured and evaluated also by the surface recombination velocity ( $S_0$ ) measured using contactless techniques [16–19]. In this experiment, the photoconductivity change was detected by a reflected 500 MHz electromagnetic wave. Excess carriers were created by impulse-irradiation of 904 nm laser diode with a photon flux density of  $7.7 \times 10^{12} \text{ cm}^{-2}$ . Surface recombination velocities in the samples were directly determined by applying bi-surface photoconductivity decay (BS-PCD) method to two PCD curves measured by a BS- $\tau$  lifetime profiler equipment from Hemmi Inc. [16–19]. Fixed charge density ( $N_f$ ) was obtained from the flat-band voltage shift of C–V curves measured at 1 MHz. Interface trapping density ( $D_{it}$ ) was measured varying the signal frequency in the range of 10 Hz–1 MHz using the conductance method [20] with a signal amplitude of 20 mV for MIS diodes consisting of the  $AlO_x$  insulator film and an aluminum-gate electrode of 500  $\mu\text{m}$  in diameter.

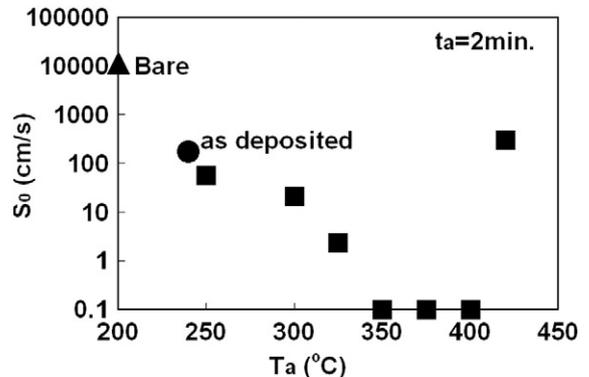


Fig. 5. Surface recombination velocity ( $S_0$ ) measured as a function of post-deposition annealing temperature ( $T_a$ ).

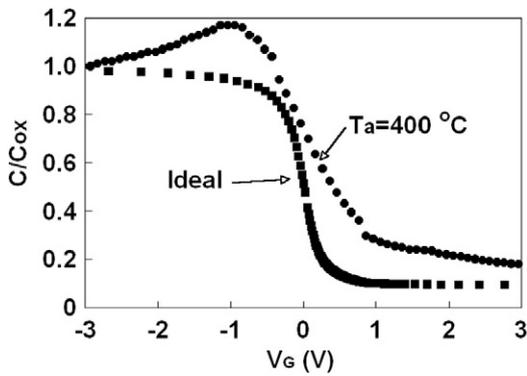


Fig. 6. One example of C–V curve shift attributed to fixed charges generated by post-deposition annealing temperatures.

### 3. Results and discussion

Fig. 3 shows PCD curves measured for the bare mirror-surface sample, the as-deposited sample, and those prepared varying  $T_a$  in the range of 250–420 °C, when the pulse laser for photo-carrier excitation was irradiated on the  $\text{AlO}_x$  film surface of samples. As seen in the figure, the curve for the as-deposited sample decays slowly compared with that for the bare samples. The curves for  $T_a$  of 350–400 °C display no-decay initially, suggesting extremely small  $S_0$  due to the band bending effect. Fig. 4 shows PCD curves for the samples prepared by varying  $t_a$  in the range of 1–10 min. As seen in the figure, the decay is sensitive to  $t_a$  and the PCD curve at  $t_a = 2$  min indicates no-decay initially, suggesting the smallest surface recombination obtained. Therefore, the PCD curves in Fig. 3 were measured under  $t_a = 2$  min.  $S_0$  measured using BS-PCD method is shown in Fig. 5 as a function of annealing temperature.  $S_0$  for the bare silicon sample prior to HF etching is very large at 11,275 cm/s and decreases to 179 cm/s for the as-deposited sample.  $S_0$  for  $T_a$  from 350–400 °C decreases below 0.1 cm/s, and  $S_0$  for the higher  $T_a$  of 420 °C increases to 300 cm/s. These behaviors are in good agreement with those seen in Fig. 3. Until now, we were able to find that the annealing temperature in the range of 350–400 °C and the annealing time of 2 min are optimum conditions in order to achieve extremely small  $S_0$  by rapid post-deposition annealing. The reduction of  $S_0$  is attributed to band bending due to fixed charges. In order to obtain a magnitude of fixed charges, C–V curves for MIS diodes fabricated using  $\text{AlO}_x$  films annealed at  $T_a$  of 250–420 °C were measured. The C–V curve measured for  $\text{AlO}_x$  annealed at  $T_a$  of 400 °C is shown in Fig. 6 along with the ideal curve as a reference. The curve for 400 °C shifts in the positive voltage direction suggesting creation of negative charges. Fig. 7 shows the fixed charge densities ( $N_f$ ) as a function of annealing temperature, where  $N_f$  is determined from the flat band voltage shift in measured C–V curves as shown in Fig. 6. As seen in the figure, large negative fixed charges of above  $3.7 \times 10^{11}$  charges/cm<sup>2</sup> are obtained at  $T_a$  of

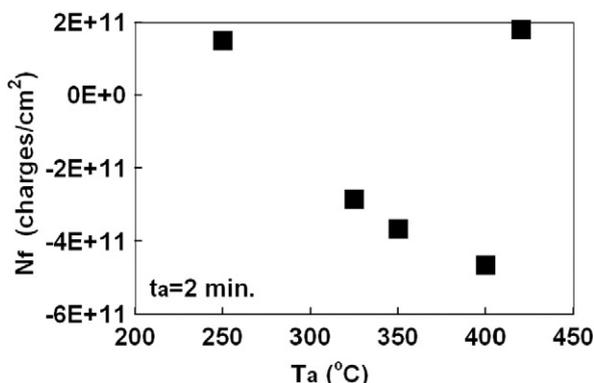


Fig. 7. Fixed charge density ( $N_f$ ) as a function of post-deposition annealing temperature.

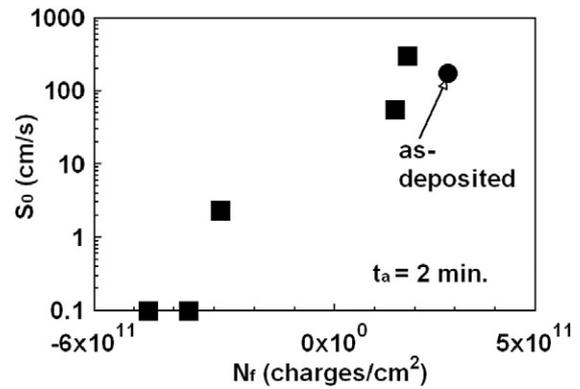


Fig. 8. Surface recombination velocity ( $S_0$ ) as a function of fixed charge density ( $N_f$ ).

350–400 °C corresponding to  $T_a$  which obtains very small  $S_0$ s. This implies that very small  $S_0$  is caused by band bending effect attributed to fixed negative charges created by post-deposition rapid thermal annealing. Fig. 8 shows  $S_0$  as a function of  $N_f$ . The  $S_0$  is strongly depended on the magnitude of  $N_f$ . Extremely small  $S_0$  data of below 0.1 cm/s is obtained by fixed negative charge density greater than  $3.7 \times 10^{11}$  charges/cm<sup>2</sup>. These extremely small two sets of  $S_0$  data correspond to  $S_0$  data obtained at annealing temperatures of 350 and 400 °C. It seems that the abrupt reduction of  $S_0$  and extremely small  $S_0$  data are obtained by dint of the fixed negative charges. Surface recombination velocity is dependent not only on band bending but also on interface trapping density ( $D_{it}$ ). Fig. 9 shows the behavior of interface trapping density taken at the mid-gap for the samples in Fig. 8 prepared by varying  $T_a$  from 250–420 °C together with  $D_{it}$  for the as-deposited sample. The interface trapping density seems to be constant around  $10^{10}$  cm<sup>-2</sup> eV<sup>-1</sup> and not dependent on the fixed charge densities of the order of  $10^{11}$  charges/cm<sup>2</sup> created by post-deposition rapid anneal process in this study. Therefore, it can be concluded that abrupt reduction to small  $S_0$  is caused by a change in band bending due to a change in fixed negative charges created corresponding to the change of anneal temperature.

### 4. Conclusion

The effects of post-deposition rapid thermal annealing on  $\text{AlO}_x$  films deposited on p-Si by Cat-CVD have been investigated in order to reduce surface recombination as the  $\text{AlO}_x$  films enable the adapting for use as passivation films of crystalline Si solar cells. Extremely small surface recombination velocity below 0.1 cm/s in p-Si with  $\text{AlO}_x$  films deposited at a substrate temperature of 240 °C has been obtained by post-deposition rapid thermal annealing at temperatures in the range of 350–400 °C for an annealing time of 2 min. It can be explained that

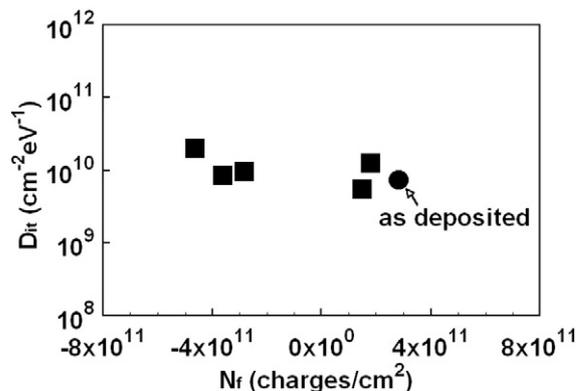


Fig. 9. Interface trapping density ( $D_{it}$ ) as a function of fixed charge density.

the extremely small  $S_0$  has been reduced below 0.1 cm/s by dint of the band bending effect attributed to negative charges greater than  $3.7 \times 10^{11}$  charges/cm<sup>2</sup> and by the small interface trapping density of around  $10^{10}$  eV<sup>-1</sup> cm<sup>-2</sup>.

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### References

- [1] M. Hofmann, S. Janz, C. Schnmidt, S. Kambor, D. Suwito, N. Koh, J. Rentsch, R. Preu, S.W. Glunz, *Sol. Energy Mater. Sol. Cells* 93 (2009) 1074.
- [2] A.G. Aberle, *Prog. Photovolt. Res. Appl.* 8 (2000) 473.
- [3] (for example). B. Hoex, J.J.M. Gielis, M.C.M. Van de Sanden, W.M.M. Kessels, *Appl. Phys. Lett.* 104 (2008) 113703.
- [4] R.S. Johnston, I. Lucovsky, *J. Vac. Sci. Technol.* A194 (2001) 1353.
- [5] R. Hezel, K. Jaeger, *J. Electrochem. Soc.* 136 (1989) 518.
- [6] G. Agostinelli, A. Delabie, P. Vitanov, Z. Alexieva, H.F.W. Dekkers, S. De Wold, G. Beaucarne, *Sol. Energy Mater. Sol. Cells* 90 (2006) 3438.
- [7] B. Hoex, S.B.S. Heil, E. Langereis, M.C.M. Van de Sanden, W.M.M. Kessels, *Appl. Phys. Lett.* 89 (2006) 042112.
- [8] B. Hoex, J. Schmidt, R. Bock, P.P.A. Altermatt, M.C.M. Van de Sanden, W.M.M. Kessels, *Appl. Phys. Lett.* 91 (2007) 112107.
- [9] B. Hoex, J. Schmidt, P. Pohl, M.C.M. Van de Sanden, W.M.M. Kessels, *J. Appl. Phys.* 104 (2008) 044903.
- [10] S. Miyajima, J. Irikawa, A. Yamada, M. Konagai, *Appl. Phys. Express* 3 (2010) 012301.
- [11] T.-T. Li, A. Cuevas, *Phys. Status Solidi* 5 (2009) 160 (RRL3).
- [12] F. Werner, B. Veith, V. Tiba, P. Poodt, F. Roozeboom, R. Brendel, J. Schmidt, *Appl. Phys. Lett.* 97 (2010) 16103.
- [13] Y. Ogita, M. Tachihara, Y. Aizawa, N. Saitoh, *Thin Solid Films* 519 (2011) 4469.
- [14] D. Lei, X. Yu, L. Song, X. Gu, G. Li, D. Yang, *Appl. Phys. Lett.* 99 (2011) 052103.
- [15] G. Dingemans, F. Einsele, W. Beyer, M.C.M. Sanden, W.M.M. Kessels, *Appl. Phys. Lett.* 111 (2012) 093713.
- [16] Y. Ogita, Y. Iwami, H. Daio, K. Yakushiji, *Proceedings of The 2nd International Symposium on Advanced Science and Technology of Silicon Materials, The Japan Society for the Promotion of Science, 1996*, p. 455.
- [17] Y. Ogita, M. Minegishi, H. Higuma, Y. Shigeto, K. Yakushiji, *Institute of Physics, Conference Series Number, 149, 1996*, p. 325.
- [18] Y. Ogita, *J. Appl. Phys.* 79 (1996) 6954.
- [19] H. Daio, Y. Uematsu, Y. Ogita, *Jpn. J. Appl. Phys.* 37 (1998) 6283.
- [20] E.M. Vogel, et al., *IEEE Trans. Electron Devices* 47 (2000) 601.