Materials Science in Semiconductor Processing 83 (2018) 171–174

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Hydrogen induced interface passivation in atomic layer deposited Al_2O_3 films and Al_2O_3/SiO_2 stacks

Shizheng Li, Ning Yang, Xiao Yuan*, Cui Liu, Xiaojun Ye, Hongbo Li*

School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

ARTICLE INFO

Keywords:
Atomic Layer Deposition
Al_2O_3
Hydrogen content
Passivation performance
SiO_2 capping layer

ABSTRACT

Atomic layer deposited (ALD) Al_2O_3 films shows significant passivation effect on crystalline silicon (c-Si) wafers. We study the effect of hydrogen content in ALD Al_2O_3 films and the stacks of ALD Al_2O_3 and SiO_2 deposited by electron beam evaporation on the quality of surface passivation. Al_2O_3/SiO_2 stacks show preferable passivation performance and thermal stability to the single Al_2O_3 passivation films for the higher hydrogen content at the Al_2O_3/Si interface. Effective minority carrier lifetime (τ_{eff}) of c-Si wafer passivated by Al_2O_3/SiO_2 stacks is 3130 μs much higher than that 1886 μs in the case of using single Al_2O_3 film. Hydrogen at the interface contributes obviously to the improvement in passivation performance, and this effect is mainly affected by annealing temperature. The reduction of hydrogen content results in the increasing of interface defect density, degrading the passivation quality. SiO_2 capping layer can be considered as a resistance to reduce the escape of hydrogen. Furthermore, annealing time makes little impact on the hydrogen content at the interface as well as the surface passivation performance.

1. Introduction

Efficient surface passivation is of great importance for crystalline silicon solar cells to achieve high conversion efficiency. Due to the high level of chemical passivation and field-effect passivation caused by negative-fixed charge, atomic layer deposition (ALD) Al_2O_3 films exhibit excellent surface passivation performance [1–5]. The stacks of ALD Al_2O_3 and SiN_x by plasma-enhanced chemical vapor deposition (PECVD) are generally used to passivate the p^+ boron emitter of N-type solar cells and the rear surface of the passivated emitter and rear contact (PERC) solar cells [6–9]. For different ALD process, the hydrogen content is about 2–4 at% [10]. Dingemans et al. investigated the hydrogen induced passivation of 190 nm thermally-grown SiO_2/30 nm ALD Al_2O_3 stacks and 300 nm thermally-grown SiO_2/100 nm ALD Al_2O_3 stacks, but the films used were reversed in structure and much thicker than what used in practical production [11]. Some researchers considered that hydrogen made a contribution to surface passivation in thermal treatment of Al_2O_3/SiN_x stacks [12,13].

In this work, we studied the passivation effect induced by changing hydrogen content in ALD Al_2O_3 films and Al_2O_3/SiO_2 stacks. In order to study the release of hydrogen under actual condition, we deposited an 80 nm thickness SiO_2 layer as a capping layer by electron beam evaporation for introducing no extra hydrogen. With same thermal treatment, the sample with SiO_2 capping layer was observed to have better passivation performance with higher hydrogen content in the passivation film and the interface. The hydrogen level was more related to the annealing temperature but less to the annealing time.

2. Experimental details

In the present study, we used n-type crystalline Czochralski (CZ) Si wafers of 1–7 Ω-cm resistivity, 180 ± 20 μm thickness and 156 × 156 mm^2 overall size, because of the high bulk lifetime over 10 ms provided by the wafer supplier. First, surface damage caused during wafer sawing was removed by etching in 15% KOH solution (~ 15 μm each side). Then these wafers were cleaned by standard Radio Corporation of America (RCA) cleaning immediately prior to Al_2O_3 deposition [14]. ALD Al_2O_3 films of about 20 nm thickness were deposited at 250 °C using trimethylaluminium ($Al(CH_3)_3$, TMA, 99.9999%) and de-ionized water (H_2O, DIW) as precursors. One cycle of thermal ALD-Al_2O_3 growth consisted of a pulse of TMA, followed by a pulse of DIW carried by a flow of nitrogen and a nitrogen purge was between two pulses. To avoid the introduction of extra hydrogen, the SiO_2 films of about 80 nm thickness were deposited at 200 °C by electron beam evaporation with a high-purity silicon dioxide crystal (99.999%) as the E-Beam source for the process. The base pressure of the system was 5×10^{-4} Pa before the deposition and the deposition rate was about 0.8–1.2 Å per second. At last, annealing was performed

* Corresponding authors.
E-mail addresses: yuanxiao@ecust.edu.cn (X. Yuan), lihongbo@ecust.edu.cn (H. Li).

https://doi.org/10.1016/j.mssp.2018.04.031
Received 18 December 2017; Received in revised form 28 March 2018; Accepted 22 April 2018

in a Rapid Thermal Annealing (RTA) system with different annealing treatment (at 300, 400, 500 °C for 5 min, 800 °C for 4 s and 400 °C for 20 min under nitrogen atmosphere). All annealing processes were under nitrogen atmosphere for avoiding the influence of moisture and oxygen in the air to the interface.

The film thickness was tested by a J.A. Woollam Co., M-2000XI Spectroscopic Ellipsometry (SE) system at a wavelength of 632.8 nm. The effective minority carrier lifetime of the bifacial passivated samples were tested by a Sinton Instruments WCT-120 system in Quasi-Steady State Photoconductance (QSSPC) mode and the values were taken at an injection level of 5×10^{15} cm^{-3}. Each wafer was tested by 9 points and each point was tested by 5 times, then take the average as the sample's lifetime. The change of the film structure was analyzed with reference to X-ray photoelectron spectroscopy (XPS). Secondary ion mass spectroscopy (SIMS) was used to evaluate and compare the depth profiles of the elements before and after annealing [15]. The negative fixed charge density (Q_f) and interface defect density at midgap (D_{it}) were measured by Semilab SDI PV2000 using the Corona oxide characterization of semiconductors (COCOS) contactless measurement method [16]. Each wafer was tested by 9 points and then take the average.

3. Results and discussion

The tested effective minority carrier lifetimes of the bifi-passivated c-Si wafers with Al_2O_3 film and Al_2O_3/SiO_2 stacks are shown in Fig. 1. At the annealing temperature of 300 °C, the effective lifetime had a slight increase due to the strengthening of chemical passivation and field-effect passivation. Then it reached a maximum at 400 °C, and rapidly decreased as further increasing the annealing temperature. In all annealed samples, the effective lifetimes of the c-Si wafer with SiO_2 capping layer were almost double of the value without the SiO_2 layer. At the annealing temperature of 800 °C, the passivation performance of the c-Si wafer with single Al_2O_3 film was even worse than the as deposited state, but the c-Si wafer with Al_2O_3/SiO_2 stacks still had an effective lifetime of 660 μs, maintaining a passable passivation performance.

It is clear that anneal temperature has great effect on the effective lifetime [5]. There is a peak effective lifetime for the two different passivation films at the anneal temperature of 400 °C. The highest lifetime of the two series are 1886 μs and 3130 μs, respectively. According to reference [17], the effective surface recombination velocity (*SRV*) S_{eff} can be calculated by Eq. (1):

$$S_{eff} = \left(\frac{1}{\tau_{eff}} - \frac{1}{\tau_{bulk}}\right) \times \frac{w}{2} \quad (1)$$

where w is the wafer thickness (~ 150 μm), and τ_{bulk} is set infinity in Eq.

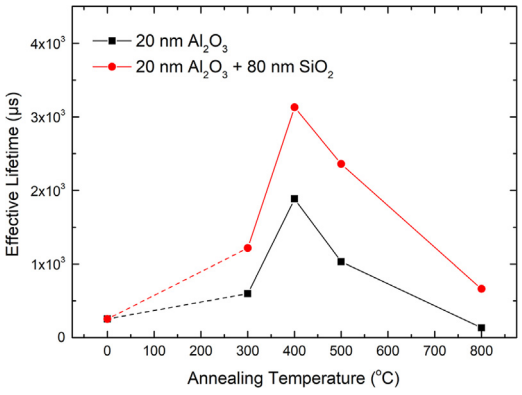

Fig. 1. The effective minority carrier lifetime for different annealing treatment (at 300, 400, 500 °C for 5 min and 800 °C for 4 s under nitrogen atmosphere) for c-Si wafers with single Al_2O_3 film and Al_2O_3/SiO_2 stacks. In which 0 °C means the as deposited state without any annealing process.

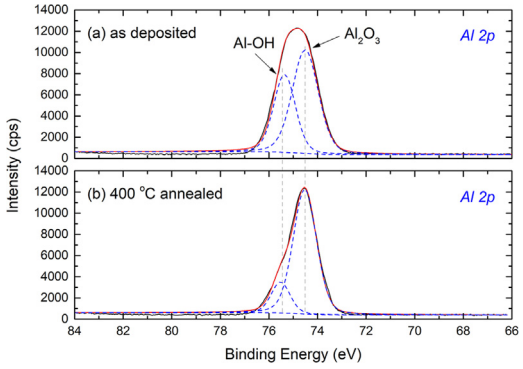

Fig. 2. X-ray photoelectron spectroscopy data for a 20 nm Al_2O_3 film (a) before and (b) after annealing (400 °C, 5 min, N_2). The black line represents the experimental data and the red line represents the fitting data.

(1) because the bulk lifetime of the c-Si wafers are more than 10 ms to calculate the upper limit of the *SRV*. From Eq. (1) S_{eff} of wafers passivated with Al_2O_3 film and Al_2O_3/SiO_2 stacks is 4 cm/s and 2.4 cm/s, respectively. According to the results, anneal process plays an important role in the passivation performance, and Al_2O_3/SiO_2 stacks have better passivation performance than single Al_2O_3 film, especially at high annealing temperature.

The changing structure of the Al_2O_3 film at the interface was the major factor to the variation of passivation performance. As shown in Fig. 2, XPS spectra were used to monitor the structure difference before and after annealing process (400 °C, 5 min, N_2). The Al 2*p* peak is sensitive to structural variation of the Al_2O_3 films, and mainly characterizes in Al_2O_3 structure (~ 74.5 eV) and Al-OH bonds (~ 75.4 eV) [18,19]. Fig. 2(a) is the XPS spectra of the as deposited Al_2O_3 film, the most prominent contributions can be assigned to the Al_2O_3 structure, but a large portion exists in the form of Al-OH bonds. Compared with the as deposited film, great change occurred in the annealed film in Fig. 2(b). The signal of the Al_2O_3 structure (~ 74.5 eV) is quite stronger but the Al-OH bonds (~ 75.5 eV) is much weaker than the as deposited state. The variation in the signal strength of Al-OH bonds indicates that large amount of hydrogen atoms was released from the Al_2O_3 film and diffused into the c-Si wafer, passivating the dangling bonds at the silicon surface.

To confirm the hydrogen depth profiles, SIMS for the Al_2O_3/SiO_2 samples were carried out. Hydrogen depth profiles of the whole passivation films with different annealing treatment were shown in Fig. 3, and the inset shows the hydrogen depth profiles from the Al_2O_3/SiO_2

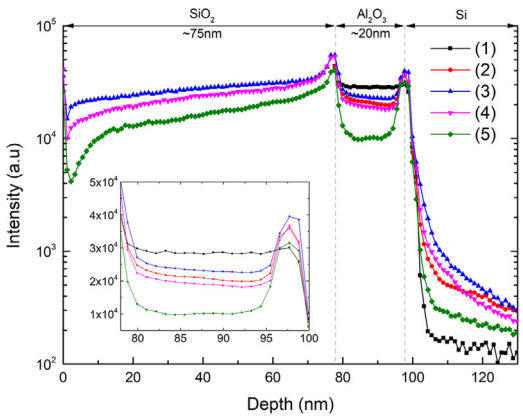

Fig. 3. Hydrogen depth profiles measured with SIMS for Al_2O_3 film before (as deposited (1)) and after annealing (400 °C, 5 min, N_2 (2)) and Al_2O_3/SiO_2 stacks after annealing (400 °C, 5 min, N_2 (3), 500 °C, 5 min, N_2 (4) and 800 °C, 4 s, N_2 (5)). The inset shows the hydrogen content in the Al_2O_3 films from the SiO_2/Al_2O_3 interface to the Al_2O_3/Si interface.