Extended Abstracts of the 2013 International Conference on Solid State Devices and Materials, Fukuoka, 2013, pp486-487

Influence of Post-Deposition Annealing on the Passivation Quality of Room Temperature Atomic Layer Deposited Aluminum Oxide

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Abstract

This work investigates the influence of post-deposition annealing treatments on the interface properties, such as fixed charge density (Q_f) and interface trap density (D_{it}), of AlO_x films deposited on single crystalline Si at room temperature by O_3-based batch atomic layer deposition technique. We found that PDA in atomic hydrogen can significantly increase negative Q_f in 10 nm-thick AlO_x films by enhancing structural and chemical reorganization in the interlayer. In addition, we also found that nitrogen ions can effectively remove or passivate dominant positive fixed charges in 10 nm-thick AlO_x films. Finally, we demonstrated that PDA in N_2 plasma is effective technique to enhance the interface properties of 30 nm-thick AlO_x films as indicated by the significantly reduced D_{it} down to 6.6×10^{11} $cm^{-2}\cdot eV^{-1}$ with negative $Q_f \geq 10^{12}$ cm^{-2}.

1. Introduction

Surface passivation of crystalline silicon (c-Si) plays an essential role in the performance of solar cells as the wafer thickness progressively decreases because of cost-driven reductions. To improve the efficiency of standard c-Si solar cells based on mature screen-printed technology, passivation by a suitable dielectric layer should be employed on the rear side of solar cells. It is reported that atomic layer deposited (ALD) aluminum oxide (AlO_x) provides an excellent surface passivation quality for both lowly and highly doped p-type Si. This feature is attributed to a high negative fixed charge density (Q_f) up to $\sim10^{13}$ cm^{-2} in the passivation film and a low interface trap density (D_{it}) of $\sim10^{11}$ $eV^{-1}cm^{-2}$ at the ALD AlO_x/c-Si interface [1].

Recently, various methods of atomic layer deposition, such as H_2O- and O_3-based batch atomic layer deposition, have been successfully used to deposit AlO_x films for c-Si surface passivation, which is promising for mass production. However, the optimal combination of the process conditions for ALD AlO_x passivation films has been set to a deposition temperature (T_{dep}) $\geq$ 200 ℃ followed by a post deposition annealing (PDA) treatment in N_2 at 400-450 ℃ for at least 10 min. This justifies the interest for a combination of a room temperature process using O_3 as an oxygen precursor and a decent PDA treatment in order to reduce a thermal budget during the preparation of AlO_x passivation films. In this contribution we investigate the influence of various PDA treatments on the interface properties, such as Q_f and D_{it}, of O_3-based batch ALD AlO_x films deposited on c-Si at room temperature (RT).

2. Experimental

About 10 and 30 nm-thick AlO_x films were deposited on both sides of a p-type (100) single c-Si substrate (MCZ, ρ = 15~30 Ω·cm, 770 μm) from TMA and O_3 by batch ALD process at RT. PDA in N_2 was performed at 400 ℃ for 30 min by a rapid thermal annealing (RTA) system. PDA in N_2 plasma with a RF power of 400 W was performed at temperatures ranging from 200 ℃ to 400 ℃ and a pressure of $2.4x10^{-3}$ Pa for 30 min. PDA in atomic hydrogen generated by a tungsten hot wire catalyst heated to 1800 ℃ was performed at a pressure of 5 Pa for 30 min. Q_f and D_{it} were extracted from capacitance-voltage (C-V) measurements. High resolution transmission electron microscopy (HRTEM) was employed to investigate AlO_x film structures and interfacial structures formed at an AlO_x/c-Si interface.

3. Results and discussion

We investigated the influence of post-deposition annealing (PDA) performed at different temperatures in N_2, N_2 plasma or atomic hydrogen on the interface properties of 10 nm-thick AlO_x samples deposited at room temperature (RT). As shown in Fig. 1 all annealed samples show significantly increased negative fixed charge density (Q_f) but only AlO_x samples annealed at 400 ℃ in atomic hydrogen and at 200 ℃ in N_2 plasma show lower interface trap density (D_{it}) compared to as-deposited AlO_x samples. Among investigated AlO_x samples, AlO_x samples annealed in atomic hydrogen show the best interface properties. The change in Q_f shows that positive fixed charges in as-deposited films decrease, or that negative fixed charges in the films increase after annealing, while excessively incorporated nitrogen at the interface region would increase D_{it}.

In Fig. 2 high resolution transmission electron microscopy (HRTEM) images reveal that the significantly enhanced Q_f of AlO_x samples annealed in atomic hydrogen is owing to the better structural and chemical reorganization of the interlayer compared to AlO_x samples annealed in N_2. We previously reported that 30 nm-thick O_3-based batch ALD AlO_x samples deposited at RT have a thick, chemi-

cally loose interlayer including aluminum silicate with showing insignificant level of surface passivation in an as-deposited state. After PDA in N_2, the thermal densification of an interlayer chemical structure and the phase transformation of aluminum silicate into mullite in the interlayer owing to diffused oxygen and hydrogen from AlO_x films activate the surface passivation of Si by AlO_x films deposited at RT [2]. From the result, the amount of oxygen and hydrogen diffused from thinner AlO_x films is insufficient to complete the densification and the phase transformation but the sufficient supply of atomic hydrogen can enhance the structural and chemical reorganization of the interlayer. In addition, atomic hydrogen and nitrogen ions are efficient at removing or passivating dominant positive fixed charges in AlO_x films [3,4]. This can also contribute to the significant increase of Q_f in AlO_x films after PDA in atomic hydrogen or N_2 plasma.

PDA in N_2 plasma has some merits compared to PDA in hot-wire atomic hydrogen: less consumption of gas and energy, and safety to be free from explosive gas. So we decided to investigate the effects of PDA in N_2 or N_2 plasma on 30 nm-thick AlO_x samples deposited at RT. As shown in Fig. 3, 30 nm-thick AlO_x samples annealed at 200 ℃ and 400 ℃ in N_2 plasma show the lowest D_{it} (= 6.6 $\times 10^{11}$ $cm^{-2}\cdot eV^{-1}$) and the highest negative Q_f (= -4.3×10^{12} cm^{-2}), respectively. AlO_x samples annealed in N_2 plasma at 400 ℃ show the enhanced interface property compared to AlO_x samples annealed in N_2 but the D_{it} (= 2.3 $\times 10^{12}$ $cm^{-2}\cdot eV^{-1}$) is of the same order as Q_f (= -4.3×10^{12} cm^{-2}). Therefore, for AlO_x on c-Si, it is not expected that the effect of this enhanced interface property can be significant because the D_{it} is typically at least one order of magnitude lower than the magnitude of the negative Q_f in the film. However, we can expect better surface passivation from AlO_x samples annealed in N_2 plasma at 200 ℃ because D_{it} (= 6.6 $\times 10^{11}$ $cm^{-2}\cdot eV^{-1}$) is about one order of magnitude lower than the magnitude of Q_f (= -2.0×10^{12} cm^{-2}). From the result, we can conclude that PDA with N_2 plasma is promising technique to enhance the passivation quality of AlO_x samples deposited at RT though we need further studies on structural and chemical changes during PDA and optimization of PDA processes.

3. Conclusions

In this study, the influence of PDA treatments on the interface properties of O_3-based batch ALD AlO_x films deposited on c-Si at RT was investigated. We found that PDA in atomic hydrogen can significantly increase negative Q_f in thin AlO_x films by enhancing structural and chemical reorganization of the interlayer. In addition, atomic hydrogen and nitrogen ions could effectively remove or passivate dominant positive fixed charges in 10 nm-thick AlO_x films. Finally, we demonstrated that PDA in N_2 plasma of 30 nm-thick AlO_x films is more effective to enhance interface properties than that of 10 nm-thick AlO_x films. From the result, PDA using N_2 plasma could be promising technique for solar cell applications.

Acknowledgements

This work was supported by the Core Research of Evolutional Science and Technology program (CREST) from the Japan Science and Technology Agency (JST).

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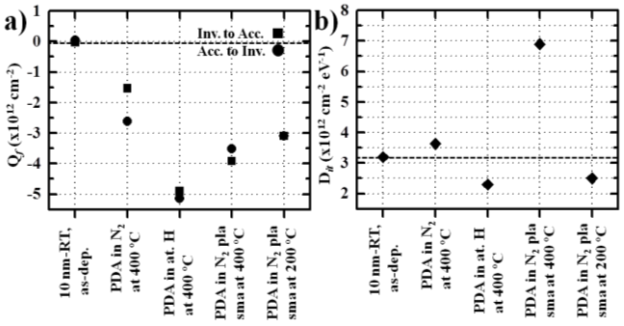

Fig.1 a) Q_f and b) D_{it} values obtained from 10 nm-thick AlO_x samples annealed in N_2, N_2 plasma or atomic H.

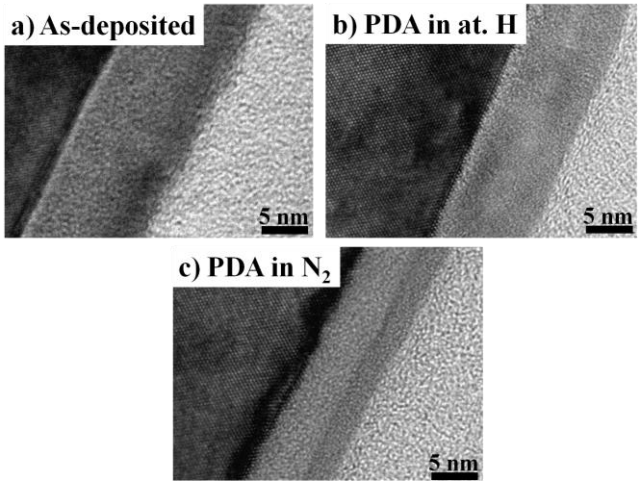

Fig.2 Cross-sectional HRTEM images of 10nm-thick AlO_x films a) as-deposited, b) annealed in atomic H and c) annealed in N_2, respectively.

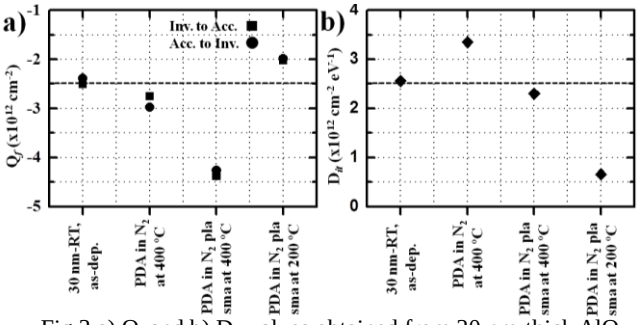

Fig.3 a) Q_f and b) D_{it} values obtained from 30 nm-thick AlO_x samples annealed in N_2 or N_2 plasma.