F-10-02 Extended Abstracts of the 2020 International Conference on Solid State Devices and Materials, VIRTUAL conference, 2020, pp399-400

Passivation Mechanism of the High-performance Titanium Oxide Passivating Contacts on Crystalline Silicon Studied by Spectroscopic Ellipsometry

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Abstract

Spectroscopic ellipsometry (SE) analysis is performed to study the impact of post-deposition annealing on the passivation performance of the TiO_x/SiO_x on crystalline silicon (c-Si) prepared by atomic layer deposition (ALD) for development of the high performance ALD-TiO_x/SiO_x/c-Si heterocontacts. The effective carrier lifetime tends to increase with increasing annealing temperature (T_{anneal}) up to 275 °C and decrease from T_{anneal} = 320 °C. The highest lifetime of 2.0 ms is obtained after forming gas annealing at 275 °C for 3 min. With increasing T_{anneal}, the TiO_x layers become thicker. At T_{anneal} = 275 °C, the mixed oxide layers consisting of Si, Ti and O atoms is formed at apposite position, which is responsible for the improvement of effective carrier lifetime after post-deposition annealing.

1. Introduction

Recently, transition metal oxide has attracted much attention as novel carrier-selective contacts (CSC) for use in silicon heterojuction (SHJ) solar cells. Titanium oxides prepared by atomic layer deposition (ALD) is regarded as a promising CSC material, since the ALD-TiO_x provides high effective carrier lifetime (τ_{eff}) after post-deposition annealing [1,2]. Recently, Yang et al. demonstrated high conversion efficiency by the SHJ solar cells using ALD-TiO_x heterocontacts [3].

It is considered that the passivation mechanism of ALD-TiO_x/SiO_x/c-Si is caused by diffusion of Ti and O atoms into the SiO_x interlayer [2]. Recently, the high τ_{eff} of 1.7 ms has been demonstrated after post-deposition annealing by employing the SiO_x interlayer prepared by mixture of hydrochloric acid, hydrogen peroxide and deionized water, often called standard clean 2 (SC2). Since the SiO_x layer prepared by the SC2 solution is the lowest film density, diffusion of Ti and O atoms is enhanced around the TiO_x/SiO_x heterointerfaces [4]. Although comprehension of passivation mechanism of the ALD-TiO_x/SiO_x/c-Si heterocontacts is significantly important for further sophistication of SHJ solar cells, the diffusion of Ti and O atoms is not fully unveiled.

In this paper, we studied the change in layer thickness of the ALD-TiO_x/SiO_x/c-Si heterocontacts by spectroscopic ellipsometry (SE) so as to investigate diffusion of Ti and O atoms into the SiO_x interlayers after post-deposition annealing. Since the optical constant and layer thickness of very thin films can be nondestructively investigated by SE, SE is adequate to study the local diffusion at the TiO_x/SiO_x heterointerfaces.

2. Experiments

Floating zone grown, double side mirror-polished c-Si(100) wafers were used as substrates. The wafer thickness and resistivity were 280 ± 20 μm and 2-4 Ω·cm, respectively. To strip off the native oxide on the c-Si substrates, the c-Si substrates were cleaned by 5% hydrofluoric acid. Following the c-Si substrates were rinsed in deionized water (DIW), they were dipped into SC2 solutions ($HCl:H_2O_2:H_2O$ = 1:1:6) for 10 min to form ultrathin SiO_x layers. After rinsing in DIW, the substrates were loaded in ALD chamber. The ~3-nm-thick TiO_x layer was deposited on both sides of the c-Si substrates by ALD (GEMStar-6, Arradiance Inc.). In the ALD process, the Ti precursor, oxidizer and purge gas were tetrakis-dimethyl-amido titanium (TDMAT), water vapor and nitrogen (99.999%), respectively. The bottle for TDMAT was heated at 60 °C during ALD process. The deposition temperatures (T_{depo}) were 125, 150, and 175 °C. After depositing TiO_x, forming gas annealing (FGA) was carried out in the mixture gas of 97% Ar and 3% H_2 in order to improve passivation effect. The annealing temperature (T_{anneal}) was varied from 150 to 350 °C and the annealing duration was 3 min.

The injection-dependent τ_{eff} of the TiO_x/SiO_x/c-Si heterocontacts before and after FGA was measured by a lifetime tester (WCT-120TS, Sinton Instrument) at room temperature to investigate surface passivation performance. The layer thickness were characterized by variable-angle SE (M-2000DI, J. A. Woollam).

3. Results and discussion

Figure 1 (a) shows the τ_{eff} of the TiO_x/SiO_x/c-Si heterocontacts grown at 125, 150 and 175 °C as a function of minority carrier density. The τ_{eff} are improved after FGA at 275 °C for 3 min. Figure 1 (b) shows the impact of T_{anneal} on τ_{eff} of the TiO_x/SiO_x/c-Si heterocontacts at minority carrier density of 1×10^{15} cm^{-3}. For the as-deposited samples, the τ_{eff} increased with increasing T_{depo}. The τ_{eff} tends to increase with increasing T_{anneal} from 150 to 275 °C, while the decrease in the τ_{eff} is observed from T_{anneal} = 320 °C. The highest lifetime of 2.0 ms was realized for the TiO_x/SiO_x/c-Si heterocontacts grown at 175 °C after FGA at 275 °C for 3 min.

Figure 2 shows the influence of T_{anneal} on (a) total layer thickness of the TiO_x/SiO_x/c-Si heterocontacts (t_{total}), (b) ratio of layer thickness of the ALD-TiO_x layers (t_{TiOx}) to t_{total} and (c) ratio of layer thickness of the SiO_x interlayers (t_{SiOx}) to t_{total}. The t_{total} increases after annealing at T_{anneal} = 150 °C and the t_{total} gradually decreases with increasing T_{anneal}. The increased t_{total} after annealing is presumably due to enhanced oxidation

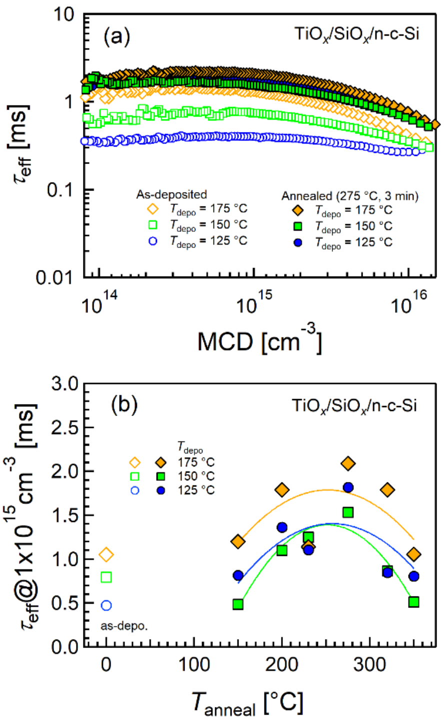

Fig. 1 (a) Effective carrier lifetime of the as-deposited and annealed TiO_x/SiO_x/c-Si heterocontacts as a function of minority carrier density (MCD). The annealing temperature and duration were 275 °C and 3 min, respectively. (b) The effect of annealing temperature on effective carrier lifetime of the TiO_x/SiO_x/c-Si heterocontacts at minority carrier density of 1×10^{15} cm^{-3}.

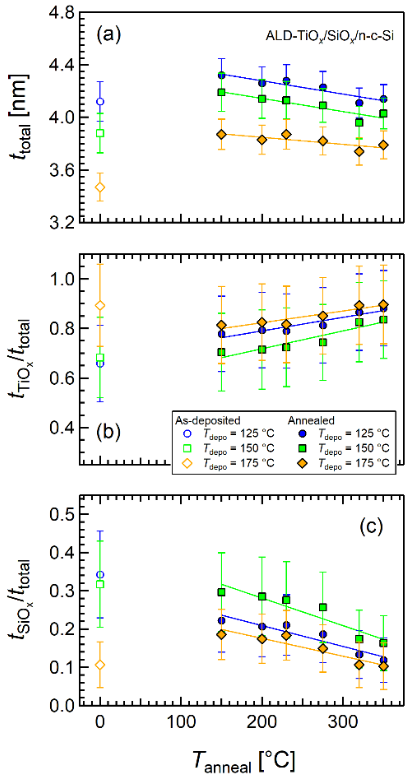

Fig. 2 (a) Total layer thickness of the TiO_x/SiO_x heterocontacts (t_{total}), (b) ratio of layer thickness of the ALD-TiO_x layers (t_{TiOx}) to t_{total} and (c) ratio of layer thickness of the SiO_x interlayers (t_{SiOx}) to t_{total} as a function of annealing temperature.

around SiO_x/c-Si interfaces, however we are not sure at the moment. Furthermore, the decrease in t_{total} by annealing can be explained by densification of the TiO_x/SiO_x/c-Si heterocontacts. The t_{TiOx}/t_{total} increase, whereas the t_{SiOx}/t_{total} decrease as T_{anneal} increase, indicating that the TiO_x layers in the TiO_x/SiO_x/c-Si heterocontacts became dominant. The behavior suggests that Ti atoms diffused into SiO_x interlayers. At present it is hard to discuss the effect of T_{depo} on the t_{TiOx}/t_{total} and t_{SiOx}/t_{total}, since the deviation of t_{TiOx}/t_{total} and t_{SiOx}/t_{total} is relatively large and significantly overlapped.

From these results, passivation performance of the TiO_x/SiO_x/c-Si heterocontacts would depend on the change of layer thickness. As mentioned above, the TiO_x layers became dominant with increase in T_{anneal}. The improved τ_{eff} at T_{anneal} up to 275 °C may be attributed to the enhanced diffusion of Ti atoms and formation of the mixed oxide consisting of Si, Ti, O atoms. The degradation of the passivation performance can be caused by crystallization of the TiO_x thin films and excessive diffusion of Ti atoms near the c-Si surface. The crystallization of the TiO_x is induced by high temperature annealing, which results in degradation of passivation performance [5]. Furthermore, it is well known that metal contaminations on c-Si surface damage severely electrical properties of Si based devices [6].

4. Summary

The effect of FGA temperature on the passivation performance were studied from the perspective of Ti diffusion from TiO_x to SiO_x by SE. The τ_{eff} was dependent on T_{anneal} and showed the highest value of 2.0 ms at T_{anneal} = 275 °C. From SE analyses, the layer thickness of the TiO_x became larger with increasing T_{anneal}. We conclude that passivation performance of the TiO_x/SiO_x/c-Si heterocontacts is influenced by Ti diffusion. The superior passivation performance can be obtained due to enough Ti diffusion and formation of mixed oxide consisting of Ti, Si and O atoms at appropriate position.

Acknowledgements

This work is supported by New Energy and Industrial Technology Development Organization (NEDO).

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