Local Structure of High Performance TiO_x Passivating Layer Revealed by Electron Energy Loss Spectroscopy

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Abstract — We investigated the local structure at the interface between titanium oxide (TiO_x) and crystalline Si with silicon oxide (SiO_x) interlayers by employing the electron energy loss (EEL) spectroscopy combined with a scanning transmission electron microscope to clarify the origin of the high performance TiO_x passivating layer deposited by atomic layer deposition. The best passivation performance was achieved by the SiO_x interlayer formed by nitric acid at room temperature. EEL spectra revealed that more stoichiometric SiO_x including a few oxygen vacancies and Ti-O-Si bonding would be formed after forming gas annealing, resulting in the enhancement of passivation performance.

I. INTRODUCTION

Carrier-selective contacts (CSCs) with low minority carrier recombination and efficient transport of one type carrier are mandatory for further increase in the power conversion efficiency (PCE). Recently, the high PCE exceeding 26% has been achieved in the crystalline silicon (c-Si) heterojunction solar cells utilizing CSCs of hydrogenated amorphous silicon (a-Si:H) [1]. However, it has been reported that the bandgap of a-Si:H is 1.7 eV, resulting in significant parasitic photon absorption, which would be regarded as an obstacle for further improvement.

Titanium oxide (TiO_x) thin layer has been intensely investigated since it shows good optical and electrical properties on c-Si due to following reasons. Firstly, the parasitic photon absorption is quite low since TiO_x has wider band gap of ~ 3.3 eV. In addition, TiO_x layer could act as an electron-selective contact thanks to the small conduction-band offset and large valence-band offset at the TiOx/c-Si heterojunction. Therefore, electrons can pass through TiO_x layer whereas holes are repelled off from the heterojunction [2]. By inserting a tunnel SiO_x at the interface between the c-Si and TiO_x thin layer, a relatively high PCE of 22.1 % was achieved due to the high surface passivation performance of amorphous TiO_x/SiO_x stack [3]. However, the passivation mechanism of TiO_x is not completely comprehended. It is reported that the passivation performance of TiO_x thin layer might be attributed to the field effect passivation caused by negative fixed charge in TiO_x [4] and the chemical passivation originating from the formation of Si-O-Ti bonding at the interface [5]. Moreover, we have recently demonstrated that the improvement of passivation performance is caused by the formation of Si-O bonding, contributing to the chemical passivation [6]. Electron energy loss (EEL) spectroscopy combined with a scanning transmission electron microscope (STEM) is a powerful tool to characterize the interface of very thin layer due to its extremely high spatial resolution. In this study, we investigated the impact of the different SiO_x interlayers on the surface passivation performance of ALD-TiO_x thin layer. From TEM images and EEL spectra, we clarified the local structure of $TiO_x/SiO_x/c-Si$ showing high passivation performance.

II. EXPERIMENT

All experiments were carried out on double-side mirrorpolished float-zone (Fz) grown p-type c-Si(100) substrates. The resistivity and thickness were 2.0-5.0 Ω ·cm and about 280 μ m, respectively. Prior to the deposition of TiO_x thin layer, c-Si wafers were cleaned by Semicoclean-23 (Furuuchi Chemicals) for 6 min in an ultra-sonic bath and dipped into 2.5% hydrofluoric acid for 1 min to remove a native silicon oxide. Five kinds of TiO_x/c-Si structures were fabricated: (A) without SiO_x interlayer, with the SiO_x interlayer prepared by (B) ozonized, deionized water (DI-O₃), (C) hydrogen peroxide (H₂O₂) and nitric acid (HNO₃) at (D) 110°C and (E) room temperature, respectively. To prepare SiO_x interlayer, c-Si substrates were dipped into each solution for 10 min. Subsequently, TiO_x layers were deposited at 150°C by a thermal atomic layer deposition (ALD) (GEMStar-6, Arradiance). The layer thickness was measured by an ellipsometry and total thickness was set to 4 nm. After the deposition of ALD-TiO_x, the forming gas annealing (FGA) at 350°C for 3 min were carried out in a mixed gas (3% H₂ and 97% Ar) to activate the surface passivation performance. The effective minority carrier lifetime (τ_{eff}) of the samples before and after FGA was measured by a WCT-120 lifetime tester (Sinton Instruments). EEL spectra were obtained using an EEL spectrometer attached to a Cs-corrected STEM (JEM-ARM200FC, JEOL Ltd.), which was operated at 200 kV.

III. RESULTS AND DISCUSSION

Figure 1 shows the τ_{eff} at the excess minority carrier density of 1.0 × 10¹⁵ cm⁻³ for the samples with different SiO_x interlayers between TiO_x and c-Si before and after FGA. By inserting SiO_x interlayer, the τ_{eff} was increased after FGA. In addition, an increase degree of passivation performance significantly depended on the treatment for forming SiO_x interlayers. Hence, the enhanced surface passivation performance is subjected to the feature of the SiO_x interlayer. The highest τ_{eff} average value of 1280 µs was obtained for the samples (E) which employed HNO₃ treatment at room temperature to form the SiO_x interlayer. Figure 2 shows the τ_{eff} as a function of excess minority carrier density (MCD) for the sample (A) and (E) before and after FGA with the calculated upper limit of the effective surface recombination velocity (S_{eff}). The S_{eff} value was given by following equation,

$$1/\tau_{eff} = 1/\tau_{bulk} + 2S_{eff}/W \qquad (1)$$

where τ_{bulk} is the effective carrier lifetime of the sample, τ_{bulk} is the carrier lifetime in the bulk c-Si wafer, and *W* is the wafer thickness of 280 µm. Here τ_{bulk} can be set to infinity since we used high quality Fz grown c-Si. For sample (E), the *S*_{eff} reduced from 24.6 cm/s to 9.5 cm/s by FGA.



 1.0×10^{15} cm⁻³ of the samples with different SiO_x interlayers between TiO_x and c-Si before and after FGA.



for the sample (A) and (E) after and before FGA.



Fig. 3 Cross sectional HRTEM image of sample (E) after FGA.

Figure 3 shows the high-resolution transmission electron microscopy (HRTEM) image of sample (E) after FGA. As can be seen, TiO_x and SiO_x thin layers were amorphous.

In order to investigate the underlying mechanisms for the origin of enhanced surface passivation of sample (E) by FGA, the EEL spectra of Si-L_{2,3} edge, Ti-L_{2,3} edge and O-K edge were acquired from some points indicated by the white circles at the Fig. 3. Figure 4 shows the EEL spectra of Si-L_{2.3} edge, Ti-L_{2.3} edge and O-K edge, respectively. In the point-I, the Si-L_{2.3} edge exhibits two peaks located at around 103 and 109 eV, associated with the Si²⁺ and Si⁴⁺ species [8], respectively. The O-K edge obtained from point-I shows weaker peak at around 539 eV. Furthermore, no sounds peaks in points-I were observed in the Ti-L_{2.3} edge. These results indicate a presence of sub-stoichiometric SiO_x in the point-I probably due to transition layer between SiO_x and c-Si. In the point-II, the Si-L_{2.3} edge exhibits two peaks located at around 107 and 109 eV, which originate from the only Si⁴⁺ species [7]. The O-K edge obtained from point-II indicates stronger peak at around 539 eV than that from point-I. The O-K edge peak of 539 eV is associated with SiO_2 [9]. Hence, more stoichiometric SiO_x is present in point-II. In addition, the Ti-L_{2,3} edge in point-II gives faint and broad two peaks, which indicates the presence of Ti atoms. In the point-III, the broader peaks of Si-L_{2.3} edge and O-K edge were observed in Fig. 4 (a) and (c). In addition, the Ti-L_{2.3} edge exhibits clearer two peaks, which indicates that Si, Ti, and O atoms coexist. Therefore, the thickness of SiO_x formed by HNO₃ was around 2 nm, which was two times thicker than the reported value of less than 1 nm [8]. These results suggest SiO_x layer became thicker by FGA. In the point-IV, Ti-L_{2,3} edge exhibits much pronounced peaks in comparison with other points. The fine structure of O-K edge drastically shifted from about 539 eV to around 533 eV, indicating structural change from SiO₂ to TiO₂. However, no sub-bands of t_{2g} and eg in Ti-L_{2,3} edge were observed, which means the weaker Ti-O bonding force [9]. In the point-V, O-K edge exhibits broader peak than that obtained from point-IV, which represents more oxygen vacancies are present in point-V.

We conclude that the enhanced passivation effect of $TiO_x/SiO_x/c$ -Si after FGA is caused by more stoichiometric SiO_x . Probably, sub-stoichiometric SiO_x is formed by HNO₃ at room temperature. After FGA, more stoichiometric SiO_x including few deficiencies of oxygen and Ti-O-Si bonding would be formed by the diffusion of O atoms in TiO_x , leading to the increase in surface passivation performance.



Fig. 4 (a) EEL spectra of (a) Si-L_{2,3} edge, (b) Ti-L_{2,3} edge and (c) O-K edge of sample (E) after FGA acquired from some points.

IV. SUMMARY

We have demonstrated that the TiO_x thin layer deposited by thermal ALD can provide excellent surface passivation performance by inserting the SiO_x interlayer layer prepared by HNO₃ at room temperature. The measured lowest S_{eff} was 9.5 cm/s on p-type c-Si. Cross sectional HRTEM image confirmed that TiO_x and SiO_x layer were amorphous and the thickness of both layer changed by FGA. EEL spectra clarified that the bonding state of Si and Ti atoms varied in the direction to outplane of TiO_x/SiO_x stack. The increase in τ_{eff} for the sample with SiO_x interlayer prepared by HNO₃ at room temperature was probably caused by the formation of more stoichiometric SiO_x, leading to termination of Si dangling bonds.

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