

Relation of lifetime to surface passivation for atomic-layer-deposited Al₂O₃ on crystalline silicon solar cell



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ABSTRACT

We investigated the relation of potassium contamination on a crystalline silicon (c-Si) surface after potassium hydroxide (KOH) etching to the lifetime of the c-Si solar cell. Alkaline solution was employed for saw damage removal (SDR), texturing, and planarization of a textured c-Si solar wafer prior to atomic layer deposition (ALD) Al₂O₃ growth. In the solar-cell manufacturing process, ALD Al₂O₃ passivation is utilized to obtain higher conversion efficiency. ALD Al₂O₃ shows excellent surface passivation, though minority carrier lifetime varies with cleaning conditions. In the present study, we investigated the relation of potassium contamination to lifetime in solar-cell processing. The results showed that the potassium-contaminated samples, due to incomplete cleaning of KOH, had a short lifetime, thus establishing that residual potassium can degrade Al₂O₃ surface passivation.

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1. Introduction

One of the most important means of improving the efficiency of crystalline silicon (c-Si) solar cells is to decrease the recombination velocity by removing contamination and enhancing passivation effectiveness [1]. Surface passivation is carried out in order to stop electrons and holes generated by incident photons from recombining with other electrons and holes before reaching the electrodes [2–6]. For the purposes of silicon substrate passivation-quality enhancement, many thin films such as amorphous Si (a-Si), SiO₂, and Al₂O₃ have been studied [7–12]. It has been reported that Al₂O₃ is one of the prime candidates for Si substrate passivation [13]. Recently, atomic layer deposition (ALD) Al₂O₃ has frequently been employed to improve surface passivation. Surface passivation mechanism of Al₂O₃ film consists of the contribution of chemical passivation and field effect passivation. The field effect passivation and the chemical passivation are represented by the negative fixed charge and the interface trap density, respectively [6,14]. Al₂O₃ has a characteristic high-negative fixed-charge density (~10¹¹ elementary charges per cm²), which negative charges repel the minority

carrier electrons in the p+ emitter from the surface, thus decreasing the surface recombination rate [3]. Additionally, Al₂O₃ provides a good level of chemical passivation owing to its relatively low interfacial defect density of ~10¹¹ eV⁻¹ cm⁻² [11].

The lifetime of ALD Al₂O₃ can be influenced by surface conditioning [15,16]. For texturing, alkaline solutions such as potassium hydroxide (KOH) and tetramethylammonium hydroxide (TMAH) generally are used. TMAH is an aqueous solution but is very expensive, and neither can it be adopted for low-cost solar-cell production. In any case, contamination caused by alkaline- or acid-solution residue should be removed by post cleaning and rinsing [17].

In the present study, in order to determine the cause of lifetime variation, we investigated the relation of ALD Al₂O₃ passivation to the potassium contamination that remains after saw damage removal (SDR) and alkaline (KOH)-solution texturing [18]. That potassium residue could contaminate Si solar cells after KOH etching has been well established; however, there has been no relevant reported data on potassium-residue-contaminated Si-wafer surfaces. Ciraci et al. reported that under monolayer coverage, the charge from the adsorbed potassium atoms is transferred into the empty, anti-bonding dangling-bond surface states, resulting in the metallization of the Si (001) substrate surface [19]. Furthermore, whereas the performance of solar cells passivated by ALD Al₂O₃ varies by the wet-solution cleaning conditions, the reason for this

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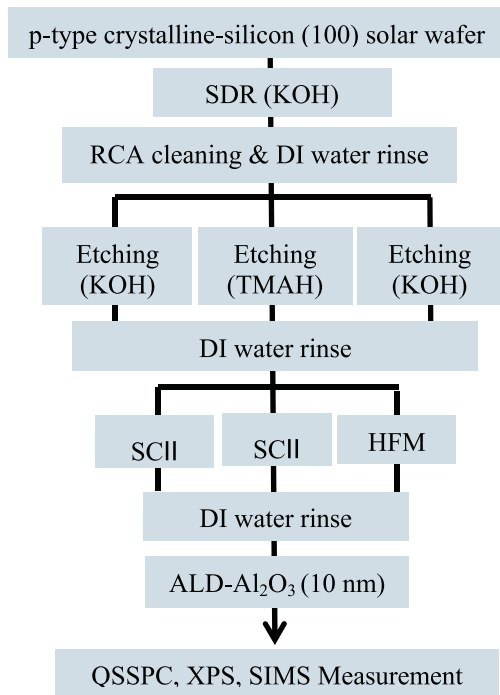


Fig. 1. Process-flow schematics from SDR to data measurement.

is not known. Therefore, we undertook to study them, and the associated mechanism of Si solar-cell lifetime, by secondary ion mass spectroscopy (SIMS).

To determine the effects of potassium residue on the lifetime of a solar cell, we measured the minority carrier lifetime with Sinton WCT-120 in the quasi-steady-state photoconductance (QSSPC) mode and investigated, by SIMS, the remnant potassium quantity after KOH SDR and planarization. Al_2O_3 thickness was measured by ellipsometry, and the interfacial states between the Al_2O_3 layer and the Si substrate was analyzed by X-ray photoelectron spectroscopy (XPS). In the results, the lifetime measured after ALD Al_2O_3 growth varied significantly as a function of the Radio Corporation of America (RCA) cleaning conditions.

2. Materials and methods

We used p-type crystalline Czochralski (Cz)-Si (100) wafers of 3–6 Ω cm resistivity, 200 ± 20 μm thickness and 156 mm \times 156 mm area as samples. Fig. 1 shows the process-flow schematics of the experimental procedure, from SDR etching to data measurement. The crystalline Si (100) solar wafers were initially etched in 8.5% KOH solution at 80 $^\circ\text{C}$ for 5 min to remove saw damage, followed by RCA cleaning and deionized water (DIW) rinsing for about 30 min. Aqueous 8.5% KOH solution was prepared with solid pallets. To determine the effect of the alkaline solutions used in texturing, the first sample was dipped into KOH solution under the same conditions as previously described, and then DIW rinsed. Subsequently it was cleaned with standard clean-2 (SC-2) solution at 80 $^\circ\text{C}$ for 15 min to remove the alkaline ion and metallic contamination. The second sample was etched by TMAH [(CH_3)₄NOH] at 80 $^\circ\text{C}$ for 5 min, followed by DIW rinsing. Then, the wafer, like the first sample, was cleaned with SC-2 solution at 80 $^\circ\text{C}$ for 15 min. As regard the third sample, it was dipped into KOH solution under the same conditions as the first sample, and then cleaned with hydrochloric and hydrofluoric mixture (HFM). HFM, consisting of hydrofluoric acid (HF), hydrochloric acid (HCl) and DIW (HF: HCl: DIW = 10% (w/w): 2% (w/w): 88%) (produced by OCI Company Ltd.), neutralizes a sample by fluorine. After KOH etching and DI water rinsing, all the

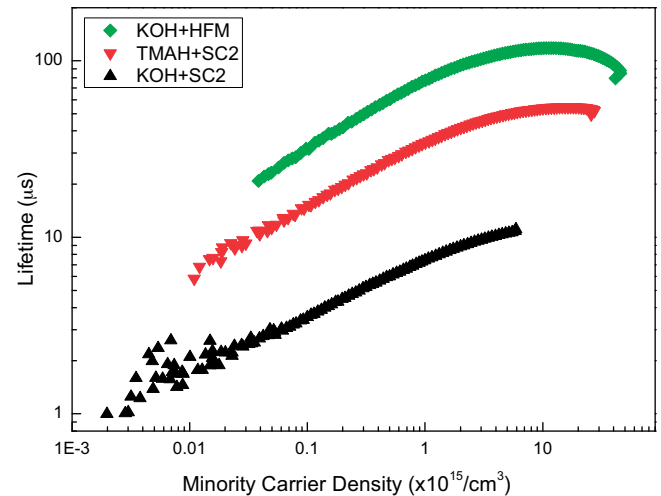


Fig. 2. Lifetime measurements for KOH etching+SC-2, TMAH etching+SC-2, and KOH etching+HFM cleaning by QSSPC mode. At $1 \times 10^{15} \text{ cm}^{-3}$ minority carrier density, the lifetimes are 7 μs , 34 μs , and 77 μs , respectively.

samples were loaded into the ALD chamber, and an Al_2O_3 layer was grown over the entire surfaces of all three Si (100) samples at the same time. Using H_2O as an oxidant, this Al_2O_3 layer was grown at 250 $^\circ\text{C}$ to a thickness of approximately 10 nm and the same SDR process formed similar morphologies for all of the samples. SIMS was employed to investigate the depth profile of the remnant surface potassium, and the lifetime was measured in the QSSPC mode (Sinton WCT-120).

3. Results

Fig. 2 plots the lifetimes for the KOH etching+SC-2, TMAH etching+SC-2, and KOH etching+HFM cleaning samples, respectively, as measured by Sinton WCT-120 in the QSSPC mode. At an injection level of $1 \times 10^{15} \text{ cm}^{-3}$, the lifetimes were 7 μs , 34 μs , and 77 μs for KOH etching+SC-2, TMAH etching+SC-2, and KOH etching+HFM cleaning, respectively. As was evident, the lifetime varied significantly as a function of cleaning process. In solar-cell production, because the DIW rinsing time is shorter than in the present experiment, K^+ ions can remain on the Si surface. The lifetime of the SDR sample was not measured, due to its many defects. Regardless, the morphologies of the samples showed no differences in this respect, owing to the same SDR process having been followed in each case [20]. The SIMS depth profiles for Al, O, and Si in our samples were almost identical, the SIMS data confirming the uniformity of Al_2O_3 . Additionally, we found, based on the lifetime improvement, that the Al_2O_3 had covered the entire Si (001) surface uniformly.

Fig. 3 plots the SIMS depth profile for Al_2O_3 (10 nm)/Si after KOH etching+SC-2 cleaning (a), along with the potassium depth profiles of the three samples (b). Potassium present on the Si surface after KOH etching was not easily removed by DI water rinsing. Fig. 3(a) shows the potassium of the sample as subjected to KOH etching and DI water rinsing, much of it having been measured at the interface of the Al_2O_3 and Si substrate. Fig. 3(b) indicates that the quantity of the potassium decreased after TMAH etching+SC-2 cleaning, and was scarcely evident at the interface after KOH etching+HFM cleaning. Although in the case of TMAH etching+SC-2 cleaning, the quantity of potassium at the interface decreased, potassium was remained detectable on the surface after ALD Al_2O_3 growth; in KOH etching+HFM cleaning by contrast, the potassium content decreased dramatically both on the surface and at the interface. Considering the SIMS and QSSPC data synthetically, it was posited that potassium had diffused from the Si surface during ALD Al_2O_3

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