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Film properties of alumina passivation layer for silicon solar cells prepared by spin-coating method

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ABSTRACT

We prepared alumina passivation films deposited by a sol-gel wet process for silicon substrates. Aluminum acetylacetonate was used as a precursor, and the solution was spin-coated onto silicon substrates. Calcination temperature dependence of the passivation quality of the films was evaluated mainly by measuring effective lifetime using a photo conductance decay technique and capacitance–voltage measurements. Also, X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy were carried out to evaluate film properties. A large amount of negative fixed charge density ($Q_f = -3.1 \times 10^{12}$ cm^{-2}) exists in the films calcined at 300 °C. On the other hand, a long effective lifetime of 400 μs was obtained for the sample calcined at 600 °C, and the passivation films had a large amount of positive fixed charge density ($Q_f = 3.6 \times 10^{12}$ cm^{-2}) with a low interface state density.

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1. Introduction

A high quality of surface passivation is a key factor for improving solar cell technologies. As wafer thickness decreases below 100 μm, surface recombination of the cells affects cell efficiency more. To improve the cell efficiency of silicon solar cells, many passivation technologies have been introduced to the cells.

For the last few decades, various types of passivation films such as a-SiN_x:H [1,2] and thermally grown SiO_2 have been applied [3–5] for silicon solar cells. The passivation mechanism depends on film materials.

SiO_2 deposited on the silicon wafers by thermal oxidization is widely used, because a high quality of chemical passivation can be achieved by decreasing the interface defect density of the silicon surface [6]. However, the method commonly requires a high temperature oxidization process around 800 °C to 1000 °C, which unfavorably affects solar cell efficiency.

Another material, a-SiN_x:H films, shows a good chemical passivation property. In addition, the films have a large amount of positive fixed charge to achieve field effect passivation [7]. This material has been widely accepted for industrial solar cells, because properties of the films, such as the refractive index and the amount of positive fixed charge, can be easily modified by changing the composition of the films [7]. The a-SiN_x:H passivation films are effective for n-type silicon wafers and emitters; however, for p-type wafers, field effect passivation is reduced by the parasitic shunting effect [8].

To overcome the parasitic shunting effect for p-type wafers and emitters, using passivation films with negative fixed charge is adequate [9]. In 2006, Hoex et al. and Agostinelli et al. reported that alumina films can be used as high quality surface passivation films with a large amount of negative fixed charge [10,11]. Before these reports, in 1989, Hezel and Jaeger reported the alumina passivation films deposited by a pyrolysis method [12]. However, the report did not attract much attention at that time.

The passivation properties of alumina films for silicon solar cells have been widely investigated since 2006. Brilliant surface passivation quality of alumina films results from both the strong field effect passivation and the high quality of chemical passivation [13,14]. In this passivation technology, a wide variety of methods has been applied to deposit alumina films on the wafers. Alumina films, prepared by thermal [11] and plasma-enhanced [10] atomic layer deposition (ALD) techniques, suggested high passivation property for both p-type and n-type silicon wafers [15,16]. However, for the ALD process, the film deposition rate is too low for applying an industrial process.

Other methods, such as plasma-enhanced chemical vapor deposition (PECVD) [17,18] and the rf sputtering method [19] have also been demonstrated, and PECVD deposited alumina film exhibited especially good passivation quality comparable to that of ALD deposited films [18,20]. However, the method requires expensive equipment that uses a high vacuum system.

A wet process such as a sol-gel method is one candidate for preparing the alumina passivation films inexpensively and easily. Many types of wet processes have been introduced to deposit alumina films such as pyrolysis [12,21,22] and spin coating [23].

In this study, we used a wet solution consisting of aluminum acetylacetonate ($Al(acac)_3$) for a spin-coating process to prepare the alumina passivation films. We investigated the properties of the films, which were prepared at various temperatures, by lifetime measurements,

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capacitance–voltage (C–V) measurements, X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR).

2. Experimental procedure

We prepared the alumina passivation films by a wet process with a spin-coating method. In the experiment, we used (100) oriented p-type single crystalline silicon wafers with a thickness of 625 ± 25 μm and a resistivity of 12–18 Ω cm for lifetime and FTIR measurements. Other types of wafers with a resistivity of 0.11 Ω cm and 0.5–1 Ω cm were used for C–V and XPS measurements, respectively. The substrates were cleaned by acetone and methanol in an ultrasonic condition for 3 min, followed by deionized water (DIW) for 3 min. The substrates were then chemically cleaned with a hot alkaline solution (NH_4OH:H_2O_2:H_2O = 1:1:6) at 80 °C for 15 min., rinsed with DIW, dipped into a diluted HF solution, and rinsed again with DIW.

For a precursor of the alumina passivation films, we prepared a solution that consists of 0.4 g of $Al(acac)_3$ (Sigma Aldrich Co. LLC) dissolved in 20 ml of 2-methoxyethanol, where the solution was sonicated for 10 min. The solution was spin-coated on the silicon substrates at 3000 rpm for 25 s. The coated films were calcined between 300 °C and 700 °C for 1 h in a muffle furnace in air. In our experiment, $Al(acac)_3$ was expected to be decomposed at the calcination temperatures [24, 25]. $Al(acac)_3$ is a stable material in powder form at room temperature [24]. We also checked the stability of the solution by leaving it for one week. No reformation occurred.

We measured the effective lifetime of the alumina-deposited samples by using photo conductance decay equipment, which was a hand-made contactless system based on that of Yablonovitch and Gmitter [26]. In this system, impedance change due to photo-induced electrons and holes is measured by using a 100 MHz incident radio frequency wave. Intensity of the radio wave reflected from the wafer is proportional to the amount of excited electrons in the wafer; therefore, we can evaluate the effective lifetime by measuring the intensity of a time-resolved reflected radio wave. The incident light source was a xenon flash lamp (L2437, Hamamatsu Photonics Co. Ltd.), and the emission decay time of the lump was set to 1 μs in our measurement.

X-ray photoelectron spectroscopies were performed using a XPS system, a 1-255GAR precision electron energy analyzer (Perkin-Elmer Inc.) with a Mg Kα (1253.6 eV) X-ray source. Pass energy in the XPS measurements was set to 60 eV, and the energy resolution of the spectra was 0.1 eV. Generated photoelectrons were detected from a direction normal to the sample surface, and additional angle-resolved XPS measurements were also performed. In addition, a FTIR transmission measurement (FT/IR-460 Plus, Jasco Co. Ltd.) was performed to investigate the bonding state in the passivation films.

Using a Hioki 3532 LCR meter, we prepared metal–insulator–semiconductor structure samples for high frequency (1 MHz) C–V measurements to evaluate the amount of fixed charge in the alumina films and interface states. The samples consist of an alumina passivation layer on one side of the silicon substrate, and aluminum electrodes for both sides prepared by vacuum evaporation. The aluminum electrode on top of the alumina passivation films was 5.3×10^{-4} cm^2. The Terman method was used to evaluate the amount of fixed charge and interface state density in the films. Flat band voltage of the samples is fixed to −0.92 V in our condition (derived from the different work functions of the aluminum electrode and p-type silicon substrates with a resistivity of 0.11 Ω cm) [27].

3. Results and discussions

3.1. Lifetime measurements

We investigated the calcination temperature dependence of effective lifetime of the silicon substrates that were covered with sol-gel deposited passivation films. Measured effective lifetime vs. calcination temperature is shown in Fig. 1. The figure shows that passivation effects arise above 400 °C and that maximum effective lifetime appears around 600 °C in the calcination condition. On the other hand, the samples calcined at 300 °C had no lifetime enhancement. Above 700 °C, the passivation effect decreases, which may be due to desorption of hydrogen atoms from the Si/alumina interface [28,29].

Several papers have pointed out that the temperature of alumina layer deposition or post-deposition annealing affects the passivation quality of the layers that were deposited by the ALD or PECVD method [10,30–32]. Post-annealing above 400 °C is preferable to activate the passivation effect of the alumina passivation films, and our results are consistent with the past reports although the deposition method is different. The activation mechanism of the alumina passivation films is not yet fully understood and needs to be clarified in the future.

3.2. XPS and FTIR measurements

XPS measurements were performed to analyze the calcination temperature dependence of the composition in the films. Measured Al 2p, O 1s, Si 2p, and C 1s photoelectron spectra are shown in Fig. 2(a), (b), (c), and (d), respectively.

Fig. 2(a) shows that the passivation films mainly consist of Al_2O_3 for the samples that were calcined at 300 °C and 600 °C, respectively. For the sample calcined at 600 °C, a signal at 76.2 eV, which we supposed was aluminosilicate, increases, and we considered that aluminum and silicon atoms at the boundary reacted to form an aluminosilicate interlayer [33]. Next, Fig. 2(b) shows the calcination temperature dependence of Si signals. For the sample calcined at 300 °C, a strong Si signal from 99.2 eV is found. This suggests that the thicknesses of the deposited films are thin (below 10 nm). Thus the signal from the silicon substrate can be detected. Also, several signals are found between 101.6 eV and 103.3 eV, assigned to silicon suboxides and dioxide. On the other hand, the Si signal from the sample calcined at 600 °C is lower than that from the sample at 300 °C. Additionally, the peak that is assigned to SiO_2 and/or aluminosilicate around 103.4 eV is enhanced. From Fig. 2(c), an Al_2O_3 signal at 530.7 eV and a weak SiO_2 signal at 532.9 eV are found for the sample calcined at 300 °C. Meanwhile, for the sample calcined at 600 °C, a signal is found that consists of a mixture of Al_2O_3, aluminosilicate, and SiO_2. The aluminosilicate signal in particular is enhanced strongly. In Fig. 2(d), the C signal is weak for the sample calcined at 600 °C, and the film contains fewer carbons. On the other hand, a relatively large C signal is found for the sample calcined at 300 °C and is maybe derived from organic residues in the film.

We tried to estimate the layer structure of sol-gel deposited passivation films by analyzing the XPS spectra. At first, we evaluated the thickness of the silicon oxide layer using the below equation that compares

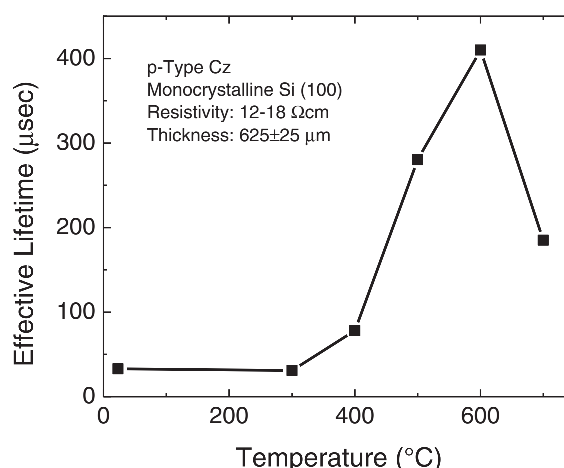

Fig. 1. Measured effective lifetime vs. calcination temperature.

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