Journal of Ceramic Processing Research. Vol. 15, No. 3, pp. 193~196 (2014)

J O U R N A L O F
Ceramic Processing Research

Formation of anti-reflection films and p-n junction by sol-gel process for one step process

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This study examined a method to form simultaneously SiO_2/SiN anti-reflection coating (ARC) films and p-n junction using a sol-gel method and heat treatment under nitridation environment for multi-crystalline silicon solar cells. Three processes such as p-n junction formation, ARC could be reduced into one step process. Chemical analysis of films after a nitridation treatment indicated a high Si-O and Si-N peak intensity. The SiO_2/SiN films made from nitridation treatment at 1000 °C showed 13% reflectance at 550 nm. Also, the formation of a p-n junction was confirmed by I-V test.

Key words: Anti-reflection, P-n junction, Sol-gel, Silicon nitride, Solar cell.

Introduction

Solar cells have attracted considerable attention as a green energy source. Among the different types of solar cells, silicon based-solar cells have attracted more attention because of their superior light-to-electricity conversion efficiency [1]. However, there is great demand to improve their light-to-electricity efficiency to reduce the production cost of solar cells. One way of improving the light-to-electricity conversion efficiency is to reduce the optical loss. The optical loss by the light reflected at the surface can be prevented by the formation of an antireflection coating (ARC) or surface texturing. The formation of antireflection coatings on textured silicon wafers can decrease the surface reflectivity and increase the energy conversion efficiency due to an increase in the short

circuit current. ARC with a suitable refractive index (n = 2.0) and surface texturing processes have improved the efficiency of silicon solar cells [2].

Several materials can be used as antireflection coatings, such as SiO_2 (n = 1.44), SiOx (n = 1.8 ~ 1.9), Ta_2O_5 (n = 2.26), TiO_2 (n = 2.3) and SiN (n = 1.9) [3]. Recently, the adaption of silicon nitride films formed by plasma enhanced chemical vapor deposition (PECVD) in multicrystalline silicon solar cells has been studied widely [4, 5]. Silicon nitride films act as antireflection coatings that reduce considerably the optical losses and passivate the Si dangling bonds at the substrate surface [6]. Besides studies on the combination of SiO_2/TiO_2 or SiO_2/SiN double ARC layer deposited by PECVD and RF magnetron sputter suggested that the reflectance might be reduced below 10% [7-9]. But, PECVD and RF magnetron sputter usually results in a higher production cost because of expensive vacuum equipments for the processes. Furthermore, the fabrication of silicon based-solar cell using PEVCD and RF magnetron sputter involves a number of processing steps. Those are mostly surface texturing, p-n junction formation, ARC and electrode printing both on the front and back side. Research into a simple and inexpensive process for silicon solar cell fabrication is an essential demand for reducing the large number of process steps. A study on a simple sol-gel process, which formed SiO_2 ARC and p-n junction on mono-crystalline silicon solar cell at the same time, may suggest a solution [10].

This study examined a method to form simultaneously SiO_2/SiN ARC films and p-n junction using a sol-gel method and heat treatment under nitridation environment for multi-crystalline silicon solar cells. Compared to the conventional fabrication process of silicon-based solar cells, three processes such as p-n junction formation, ARC, Edge isolation can be reduced into one step process. This result may provide a lower manufacturing cost and a significant impact on the silicon-based solar cell industry.

Experimental Details

Tetraethyl orthosilicate reagent grade, $Si(OC_2H_5)_4$, (TEOS), diphenyl phosphoryl chloride, $(C_6H_5O)_2POCl$, ammonium hydroxide, NH_4OH, anhydrous ethanol, C_2H_5OH (EtOH) and deionized water were used in the sol-gel method. A solution of TEOS in EtOH in the presence of NH_4OH and deionized water was prepared and hydrolyzed. The molar ratio (TEOS: EtOH: NH_4OH: H_2O) was 1 : 4 : 0.01 : 2. A solution of $(C_6H_5O)_2POCl$ in EtOH (1 : 6) was added to the mixture and stirred for 90 min at room temperature. SiO_2 films containing

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phosphorous were spin-coated on multi-crystalline silicon substrates at 5000 ~ 8000 rpm for 30 s. The spin coated films were pre-baked at 130 on a hot plate for 10 min. The nitridation treatment of SiO_2 films was carried out at 1000 ~ 1300 for 1 h under an ammonia atmosphere in an alumina tube furnace to diffuse phosphorus into silicon wafers and decompose ammonia gas. The chemical state and composition of the films were measured by X-ray photoelectron spectroscopy (XPS). The reflectance spectra were measured in the wavelength range of 400 ~ 1200 nm using an ultra violet-visible spectrophotometer. The current-voltage (I-V) characteristics were examined to confirm the formation of the p-n junction.

Results and Discussion

Fig. 1 shows the XPS analysis that was carried out to obtain the composition and binding type of the atoms on the sample surface. Fig. 1(a) shows the O 1*s* spectra of the SiN/SiO_2 films at different nitridation treatment temperatures along with that of a spin coated SiO_2 film for comparison. The SiO_2 peak in Fig. 1 corresponds to the Si-O bonds found at a binding energy of 533 eV [11]. The SiN/SiO_2 films at 1000 and 1300 °C showed peaks for the Si-O bond located at a binding energy of 532.8 and 532.4 eV, respectively [12, 13]. The peak positions were shifted to a lower binding energy with increasing nitridation treatment temperature but the peaks for Si-O on the surfaces were present before and after the nitridation treatment. Fig. 1(b) shows the peaks for N 1*s* at different nitridation treatment temperatures. Two peaks were identified at a binding energy of 397.4 and 398 eV, which were assigned to Si_3N_4 [14, 15]. The peak positions shifted to lower binding energy when the temperatures were over 1200 °C . Fig. 1(c) obtained by the spin coated silicon dioxide film corresponded to the Si-O bonds located at the binding energy 103.3 eV [16] and the nitrided silicon dioxide films after nitridation treatment have the peaks of the Si_2N_2O and Si_3N_4 located at the binding energy around 101.7 and 102.1 eV respectively [17].

Table 1 shows the ratios of elemental O, N and Si on the spin coated SiO_2 films before and after the nitridation treatment. The ratio of oxygen and nitrogen after the nitridation treatment decreased with increasing temperature. A comparison of the SiO_2/SiN films at 1000 and 1300 °C revealed a 4.1% decrease in the concentration of oxygen, whereas the nitrogen level increased by 2.5%. These results show that the oxygen containing groups were broken and the ratio of the newly nitrogen containing groups were generated under a nitridation treatment. The peak shift to a lower binding energy was due to the difference in electronegativity of O (3.5) and N (3.0) [16].

The enhanced light absorption and forming p-n junction depend on the silicon dioxide shape, coating uniformity and heat-treatment temperature. In order to minimize the reflectance of the spherical shape SiO_2 sol-gel coated mc-wafer, the formation of uniform spherical SiO_2 layer was necessary [18]. Fig. 2 shows the Fe-SEM image of non-treated and one step processed multi-crystalline silicon wafer. Fig. 2(a) indicates that

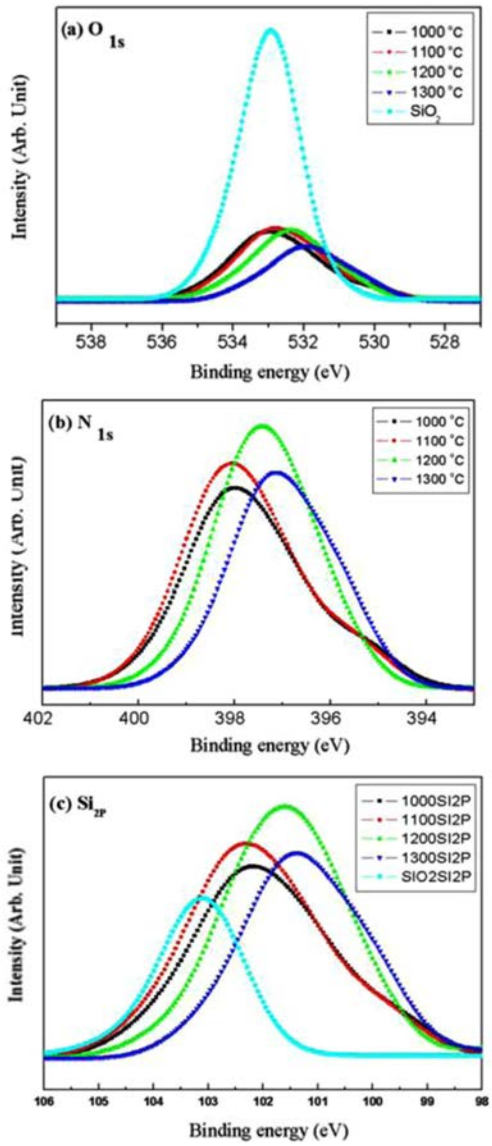

Fig. 1. XPS O 1*s* (a), N 1*s* (b) spectra of SiN/SiO_2 films at different nitridation treatment temperatures.

Table 1. Ratios of XPS (a) O1*s*, (b) N 1*s*, and (c) Si 2*p* of SiN/SiO_2 films at different nitridation treatment temperatures.

	Elemental ratio (%)		
	O_{1s}	N_{1s}	Si_{2P}
SiO_2 film	69.149	–	30.85
1000 °C	18.595	38.012	43.03
1100 °C	16.745	38.938	44.31
1200 °C	14.582	39.652	45.76
1300 °C	14.490	40.537	44.93

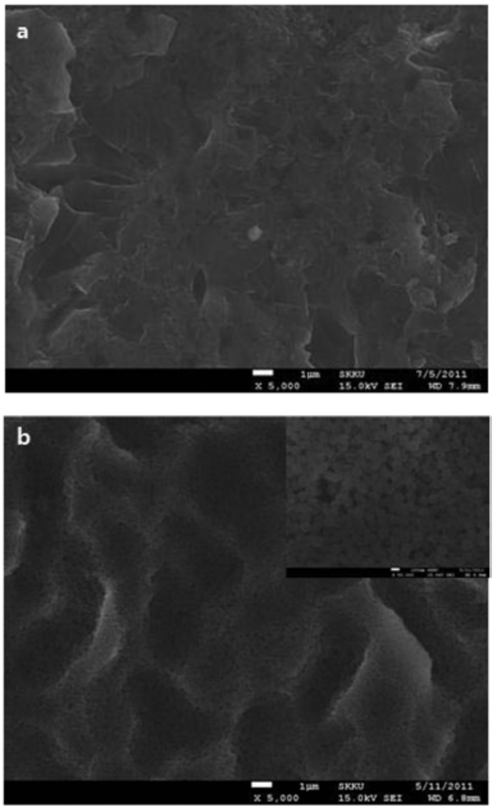

Fig. 2. FE-SEM surface images: (a) the surface image of the non textured multi-crystalline silicon wafer, (b) the surface image of the phosphorous-doped spherical shape silicon dioxide film heat treatment at 1000 °C for 1 h.

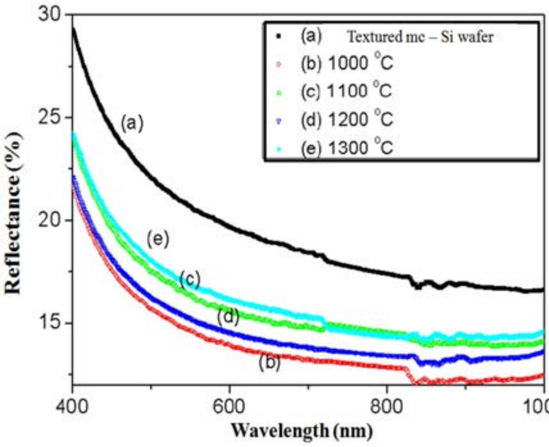

Fig. 3. UV visible reflectance spectra of the SiN/SiO_2 films at different nitridation treatment temperatures.

the surface image of the non-textured multi-crystalline silicon wafer. Fig. 2(b) shows the surface image of the one step processed multi-crystalline silicon wafer at 1000 °C for 1 h. As shown in Fig. 2(b), the size of SiO_2 particles in approximately are 100 nm. The shape and the uniformity of particles are also good. So the shape of SiO_2 nano-particles shows the perfect spherical shape. The shape and coating uniformity are very important factor for ARC. These factors can be controlled heat treatment temperature at nitridation step.

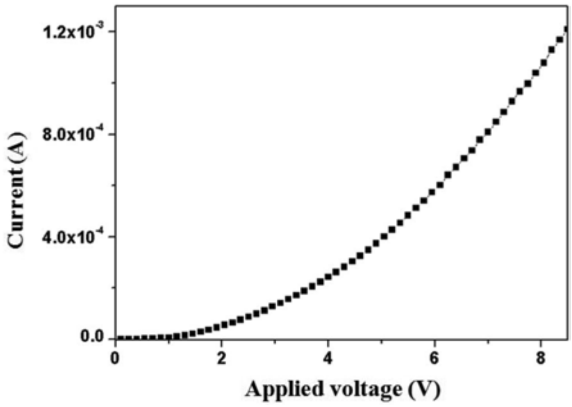

Fig. 4. Current-voltage characteristics of the SiN/SiO_2 films at 1000 °C.

Fig. 3 shows the UV-visible spectra of the SiO_2/SiN films. Fig. 3(a) shows the reflectance spectrum of a textured multi-crystalline silicon wafer without an antireflection coating. The reflectance spectra of $SiO_2/$ SiN films as antireflection coatings at different nitridation treatment temperatures are also shown. As shown in Fig. 3(b ~ e), the reflectance of the SiO_2 film with antireflection coatings from the nitridation treatment had decreased remarkably. The reflectance spectrum of the textured multi-crystalline silicon wafer was approximately 21% at 550 nm. The SiO_2/SiN films made at a nitridation treatment temperature 1000 °C shows 13% reflectance at 550 nm in the Fig. 3(b). The reflectance spectra generally increased with increasing nitridation treatment temperature except at 1200 °C .

The p-n junction is one among the basic technology for the application of solar cell. The I-V measurement was conducted to confirm the success of p-n junction from one step process (Fig. 4). From this measurement, it was confirmed that one step process can accomplish the p-n junction. However the research on the optimization of the process for solar cell application is a necessary for the future study.

Conclusions

The formation of SiO_2/SiN antireflection coatings and a p-n junction in a multi-crystalline silicon wafer was prepared by a sol-gel spin coating and a nitridation treatment. Chemical analysis of the films after the nitridation treatment indicated the presence of Si-O and Si-N bond density. The ratio of nitrogen containing groups increased with increasing nitridation treatment temperature. The SiO_2/SiN films at 1000 °C showed the lowest reflectance in the wavelength range examined with the concurrent formation of a p-n junction. The sol-gel process of SiO_2/SiN antireflection coatings may provide a great potential for the mass production of silicon solar cells with a lower cost.

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