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Antireflection coating of a SiO/SiN double layer on silicon fabricated by magnetron sputtering

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Silicon nitride and oxide double layers for anti-reflection coatings on silicon were made via RF magnetron sputtering using a silicon nitride target and then studied. The silicon nitride and oxide films were obtained at sputtering conditions of 340 W RF power, 5 mtorr (0.667 Pa) Ar, a 100 °C substrate temperature both in the presense and absence of oxygen, respectively. The films showed an average 3% reflectivity between a 400 and 1100 nm wavelength. The nitride had a refractive index of 2.36 and an absorption coefficient of 0.21 with a thickness of 85 nm, which was 26% thicker than the ideal thickness for an antireflection coating. The oxide had a refractive index of 1.48 and an absorption coefficient of 0 with an ideal thickness of 1075 nm. The surface morphology consisted of a smooth and dense film with good adhesion to the silicon surface.

Key words: antireflection coating, solar cell, silicon nitride, silicon oxide, double layer.

Introduction

Antireflection coating(ARC)s to reduce the surface reflection in c-Si solar cells are a key technology, not only in optical terms, but in bulk passivation which largely influences the final efficiency [1-3]. Over the past decade, silicon nitrides have typically been used for this purpose due to their capability to reduce the recombination of minority carriers at the surface and in the near emitter region. The suggested mechanism for passivation is the diffusion of hydrogen atoms to dangling bonds which can act as recombination sites for free carriers during the heat-treatment of the front electrodes [1-3].

Double layer ARCs can further reduce the reflectance of c-Si. An adequate ratio of refractive indexes within each layer, with an uniform thickness and optical properties, as well as a low surface roughness, are needed to maximize the beneficial effects. An MgF_2 and SiN double layer on silicon is known to reduce the reflection quite effectively [4]. The most common method to deposit the silicon nitride on a c-Si cell is plasma-assisted CVD (PECVD) [1, 3] while MgF_2 can be sputtered or sublimated if using an MgF_2 target [5]. Therefore, in this case, the in-line deposition of this ARC can not be made.

In this study, silicon oxide and silicon nitride double layers were made via sputtering using a silicon nitride target. The optical properties of the films were compared with respect to the deposition conditions and the optimum ratios of the thicknesses are discussed.

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Experimental

An RF magnetron sputtering system equipped with 4-inch (101.6 mm) stainless-steel-molded heaters and a 6-inch (152.4 mm) gun was hand-made by Ultech Co., Ltd. (Korea) [6]. The heart-shaped magnetron array was rotated eccentrically at 20 rpm. A 6-inch (152.4 mm) silicon nitride (99.99%) target was provided by High Purity Chemicals Co. (Japan). The silicon nitride was deposited on silicon substrates that were maintained at 100 °C at an RF power of 340 W under 5 mtorr (0.667 Pa) Ar. The silicon oxide was also deposited in the same manner except there was a 10% oxygen addition. A step profilometer (Kosaka Co., Ltd., ET-5000) and an UV-vis spectrometer (OPTIZEN-2120UV) were used to measure the thickness and reflectivity, respectively. The microstucture was observed with an FE-SEM (JEOL Co., Ltd., JSF-6700F) and the optical properties were analysed with a spectroscopic ellipsometer (UVISEL ER AGAS, Horiba Jovin Yvon, France).

Results and Discussion

The deposition rate of the silicon nitride film deposited under the 5 mTorr (0.667 Pa) mixed gas atmosphere and an RF power of 340 W did not change with a hydrogren concentration of 0 vol% (10.4 nm/minute) or 20 vol% (10.1 nm/minute) but it did slow at a 40 vol% concentration (8.8 nm/minute). This is partly due to the hydrogen etching effect but primarily due to the Ar concentration change in the mixed gas. Heavier Ar ions that caused sputtering decreased with the hydrogen addition but this effect was compensated for by the mean free path increment of Ar ions due to the small collision cross-section of hydrogen molecules up to 20 vol% hydrogen. Additional increases in the hydrogen concentration above 20 vol% resulted in a sputtering rate decrease. The deposition rate of silicon nitride is two times or more faster than reported previously [7, 8]. This is thought to be a result of an improved gun structure.

For an evaluation of the film uniformity, the thickness and optical properties of 13 positions on a 4 inch (101.4 mm) wafer were compared as shown in Fig. 1(a). The average of thickness, refractive index, and extinction coefficient were 54.86 ± 0.14 nm, 2.357 ± 0.008 and 0.2153 ± 0.0008, respectively. The difference of the thickness between the center and edge was 1.83 nm (3.3%). The variation of the refractive index and extinction coefficient was 2% and 0.9%, respectively. These results showed that the film uniformity was acceptable as an ARC.

UV-vis spectra for the samples obtained at 50, 100, 150 and 200 °C under 5 mtorr (0.667 Pa) Ar atmosphere at 340 W RF power showed a reflectivity minimum around 60 nm. The thickness of each film decreased slightly with the substrate temperature were 67.8, 66.6, 61.7, and 59.5 nm. The reflectivity of the 100 °C sample showed a local minimum of 7.8% which was the lowest among the four samples. The sample surface and cross-section were observed with an AFM and a FESEM, respectively. Fig. 1(b) shows a smooth surface structure and a dense and tight interface between the film and the substrate. The RMS roughness of the surface was 1.87 nm which is sufficiently small enough to allow the diffuse surface reflection to be neglected.

The dependence of refractive indices (n) and extinction coefficients (k) on substrate temperature with variations of hydrogen content are shown in Fig. 2(a). The refractive index slightly increased with substrate temperature and hydrogen content. The refractive index varied from 2.22 for 50 °C and an Ar atmosphere to 2.54 for 200 °C and a 40% H_2 atmosphere. The extinction coefficients for the samples with an Ar atmosphere showed a local minimum at 100 °C and those with a hydrogen addition showed little change. The chamber pressure also affected n and k as shown in Fig. 2(b). The refractive index decreased with the chamber pressure while the extinction coefficients showed a local minimum at 5 mtorr (0.667 Pa).

An ideal single layer ARC should satisfy the following equation in order to correctly set off the reflected waves from the front surface and back interface of the layer [9]:

$$nd = \lambda/4 \qquad \& \qquad n = \sqrt{n_{Si}} \tag{1}$$

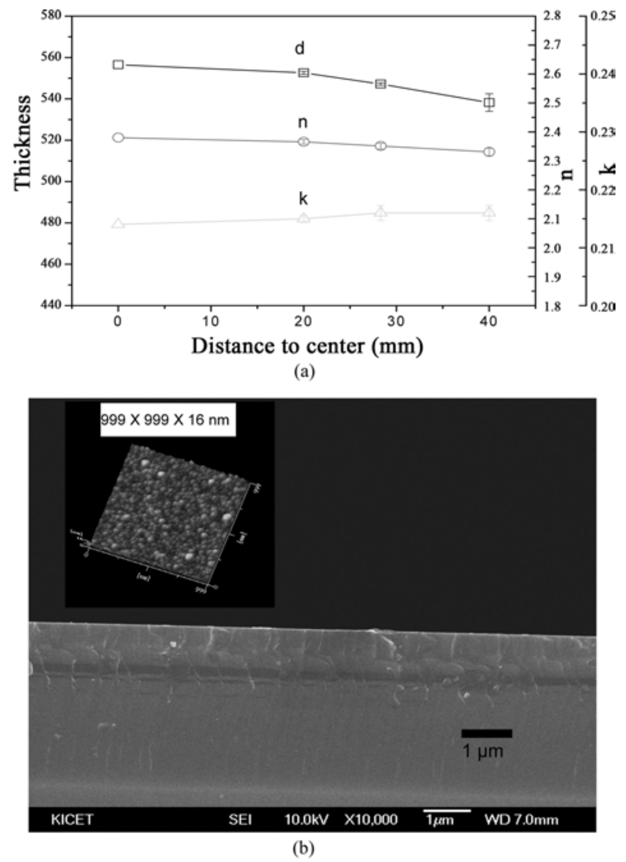

Fig. 1. Thickness(d), refractivity(n) and extinction coefficient(k) distribution on 4 inch (101.4 mm) wafer as a function of distance from the center, (a) and FESEM cross-sectional micrograph and the incerted AFM surface morphology, (b) of the SiN films deposited at 100 °C substrate temperature for 6 minutes in 5 mtorr (0.667 Pa) Ar atmosphere.

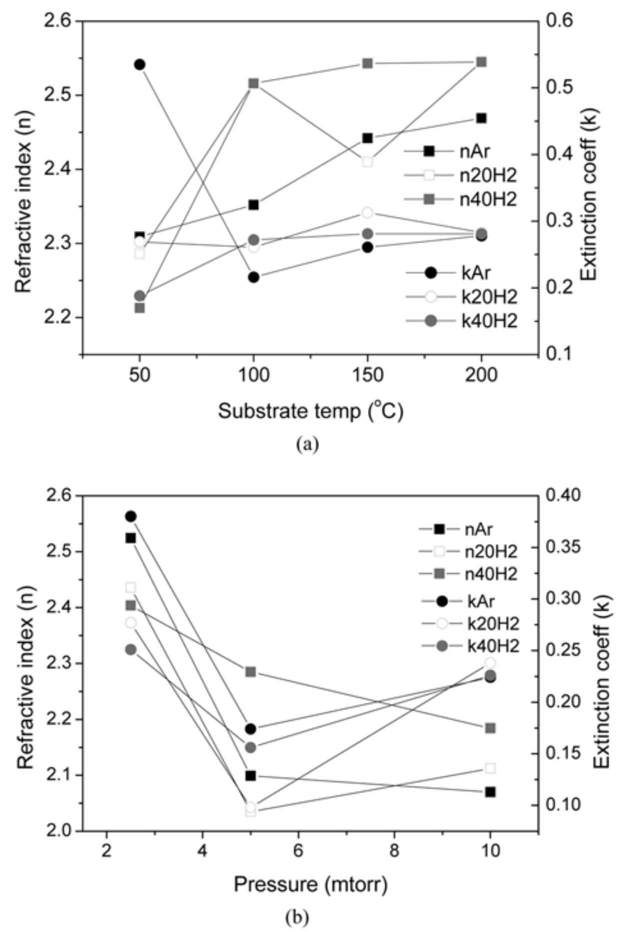

Fig. 2. Refractive indices and absorption coefficients as a function of substrate temperature (a) and sputtering pressure (b) in the given different sputtering atmosphere with a sputtering condition of 6 minutes, 5 mtorr (0.667 Pa) for (a) and 3 minutes, 50 °C for (b).

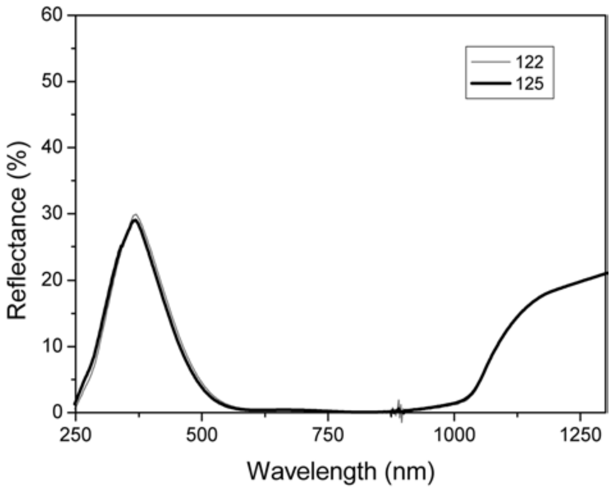

Fig. 3. UV-vis spectrum of SiO/SiN double layer having 112.7/63 nm thicknesses on an untextured Si [100] surface which shows 3.0% average reflectivity between 400 and 1100 nanometer.

where d is the thickness of the layer; λ is the wavelength of the sunlight; n and n_{Si} are the refractive indices of the layer and the silicon substrate, respectively. Therefore, if 633 nm was used for the mean wavelength of sunlight, the thickness and the refractive index for an ideal single layer ARC were 81 nm and 1.97, respectively. In the case of a film having a refractive index of 2.36 that was deposited at 100 °C under an Ar atmosphere, the thickness should be 67 nm and the calculated reflectivity shows a minimum of 3.06% [9]. This was rather lower than the measured value of 7.8%.

Double layer ARCs were acheived on a Si substrate by changing the deposition conditions. Silicon oxide could be sputtered on SiN deposited samples by a 10 vol.% oxygen addition. The oxide films showed typical optical characteristics of SiO_2. By changing the thickness ratio of SiN and SiO_2, the best results (122 and 125 in Fig. 3) that had the same deposition conditions were obtained. Two samples, 122 and 125, showed almost the same thickness and optical characteristics. The reflectivity, averaged over 400 nm and 1100 nm, was as low as 3% which was greatly improved over that of a single layer. The thickness of the SiN was 85 nm, or 26% thicker than the ideal value (67.3 nm), while that of SiO_2 was consistent with the ideal one (107 nm).

Conclusions

Double layer ARCs which consisted of silicon nitride and silicon oxide were made by the RF moving-magnetron sputtering of a silicon nitride target. The refractive index and extinction coefficient of the silicon nitride were 2.36 and 0.21 under the deposition conditions of a 5 mtorr (0.667 Pa) Ar atmosphere, 100 °C substrate temperature, and 340 W gun power, while those of the oxides were 1.48 and 0 under an O_2/[Ar + O_2] ratio of 20%, respectively. The SiN films obtained had a surface roughness (RMS) of 1.67 nm and 3.3% thickness variation on a 4-inch (101.4 mm) Si wafer. The best results with a reflectance of less than 3% over the wavelength range of 400 to 1100 Å were achieved.

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