Optical Properties of Ga-Doped TiO₂ Films Prepared by Spin-Coating Method

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Ga-doped TiO₂ films were prepared by spin-coating method and optical properties of non-doped and Ga-doped TiO₂ films were investigated. In the films prepared using low concentration of Ga to Ti in the solution, few Ga₂O₃ crystals existed in the TiO₂ films. The thickness of Ga-doped TiO₂ films increased and the refractive index of the films decreased with increasing the ratio of Ga to Ti in the solution. In the reflectance measurements, there was little dependency of doping concentration as long as the concentration was not too high. The transmittance increased with increasing the ratio of Ga to Ti in the solution. The bandgap of the non-doped and Ga-doped TiO₂ films were obtained using absorption coefficients calculated with reflectance and transmittance spectra. The bandgap of the films was almost constant regardless of the ratio of Ga to Ti in the solution.

Key words: TiO₂, Ga-doping, spin-coating, optical properties

1. Introduction

Solar cells have been intensively investigated and they are at present widely used all over the world. However, deposits of silicon are not sufficient to supply all the demand for fabricating silicon solar cells. Since a high price of silicon material will result in a high price of silicon solar cells, further lowering in cost is required in silicon solar cell fabrication.

In general, off-grade silicon wafers which are not suitable for IC (integrated circuit) fabrication are used for solar cells. P-type silicon wafers are normally used for silicon solar cells because the lifetime of minority carriers in p-type silicon is longer than that in n-type silicon. However, it is reported that solar cells made on boron-doped Czochralski silicon substrates often exhibit poorer cell performance.[1] In recent research, silicon solar cells using n-type silicon wafers have been reconsidered.[2-4]

We have proposed to use n-type wafers as a substrate for silicon solar cells in which p-type layers are formed in the front side of the cells.[5] Thin TiO₂ films are often used as an antireflection coating (ARC) and manufacturing process of solar cells will be simplified if impurities of group-III, such as gallium, are doped in the TiO₂ films in advance, and they are diffused into silicon during annealing process.

In this study, we investigated the influence of Ga-doping on optical properties of TiO₂ films.

2. Experiments

Ga-doped TiO₂ films were prepared by spin-coating method. They were spin-coated at 400 rpm for 5 sec and 1000 rpm for 20 sec on n-type Si(100) substrates with

resistivities of 1-8 Ω cm and on quartz substrate. In the spin-coating process, two types of solutions for forming TiO₂ and Ga₂O₃ films (named "T" and "G", respectively) were mixed. The sample name T $\overline{G}$ ab means that the sample was prepared using the solution in which T and G were mixed with the ratio of $a : b$. The small letters "s" or "q" after T $\overline{G}$ ab represent the samples being deposited on silicon or on quartz substrate, respectively. Table 1 shows the sample reference. After drying at 120°C for 5 min in air, they were annealed at 850°C for an hour in Ar ambient.

The refractive index and film thickness of Ga-doped TiO₂ films were measured by ellipsometry (Mizojiri Kogaku Kogyosyo, DVA-FL). The reflectance and transmittance of the films were measured by

Table 1. Sample reference

T:G <small>T,G→Solution for forming TiO₂ and Ga₂O₃ films</small>	substrate	
	silicon	quartz
10:0	TG10s	TG10q
9:1	TG91s	TG91q
8:2	TG82s	TG82q
5:5	TG55s	TG55q
2:8	TG28s	TG28q
1:9	TG19s	TG19q
0:10	TG01s	TG01q

UV/Vis/NIR spectrophotometer (Shimadzu, UV-3100). The structural properties of the films were evaluated using X-ray diffractometry (Shimadzu XRD-6000) using Cu-K α radiation. XRD measurement was carried out with the incident angle of the X-ray fixed at 3° and the sample holder continuously rotated during measurement. The incident X-ray angle was fixed at a low angle because only the diffraction signal from the thin film, but not from the substrate, needs to be detected. This technique is known as the grazing incidence XRD method.[6]

3. Results and discussion

3.1 XRD measurements

Figure 1 shows the XRD spectra of TG10s, TG91s, TG82s, TG55s, TG28s, TG19s and TG01s. The peaks in each XRD spectrum were identified using ICDD cards. Si (311) peaks around 56° were observed in all XRD spectra. In the XRD spectra of TG10s and TG55s, a peak around 27.5° which corresponds to rutile-TiO₂ (110) can be observed.[7] Therefore, the sample annealed at 850°C contained crystalline rutile-TiO₂. In the XRD spectra of TG01s and TG19s, peaks of β -Ga₂O₃ (400) and β -Ga₂O₃ (002) were observed around 30° and 31°, respectively.[8] Rutile-TiO₂ (110) peaks around 27.5° were observed for the samples from TG10 to TG55, but Ga₂O₃ peaks around 30° and 31° were hardly observed for these samples. These results indicate that few Ga₂O₃ crystals exist in the films prepared using the solution which contains a small amount of solution for forming Ga₂O₃.

Fig. 1. XRD spectra of TG10s, TG91s, TG82s, TG55s, TG28s, TG19s and TG01s.

Fig. 2. The film thickness and the refractive index of TG10s, TG91s, TG82s, TG55s, TG10q, TG91q, TG82q and TG55q.

3.2 Film thickness and refractive index

Figure 2 shows the film thickness and the refractive index of TG10s, TG91s, TG82s, TG55s, TG10q, TG91q, TG82q and TG55q. The film thickness of TG10 was about 50nm, and that of TG55 was about 150nm. The thickness of the films prepared on either substrate increased with increasing the ratio of Ga to Ti in the solution, which may be attributed to the fact that the viscosity of the solution for forming Ga₂O₃ is higher than that of TiO₂. The refractive index of TG10 was about 2.4, and that of TG55 was about 1.5. The refractive index decreased with increasing the ratio of Ga to Ti in the solution. It is known that the refractive indices of rutile-TiO₂ and Ga₂O₃ are 2.7 and 1.4, respectively.[9] Ga-doping affected the optical properties and lowered refractive indices although the amount of Ga₂O₃ crystals in the films were very small as can be seen in Fig. 1.

3.3 Reflectance and transmittance

Figure 3 shows reflectance spectra of TG10s, TG91s, TG82s and TG55s. The minimum values in the spectra of TG91 and TG82 shifted to a longer wavelength compared to TG10. The wavelength where the reflectance takes the minimum value is expressed using the following equation,

$$\lambda_{\min} = 4nd, \quad (1)$$

where n is the refractive index and d the film thickness. The calculated $\lambda_{\min}$ for TG10s, TG91s, TG82s and TG55s using the values of n and d in Fig. 2 were 493nm, 566nm, 550nm and 715nm, respectively, which showed fairly good agreement with the measured ones. The reflectance of TG91s and TG82s were smaller than that of TG10 in the wavelength range between 550 nm and 1200 nm. These results indicate that Ga-doping has little influence on reflection properties of TiO₂ films as long as doping concentration is not too high.

Fig. 3. Reflectance spectra of TG10s, TG91s, TG82s and TG55s.

Fig. 5. Absorption coefficient of TG10q, TG91q, TG82q and TG55q.

Fig. 4. The transmittance of TG10q, TG91q, TG82q and TG55q.

Figure 4 shows transmittance spectra of TG10q, TG91q, TG82q and TG55q. The transmittance of TG91, TG82 and TG55 became larger than that of TG10, although the film thickness of TG91, TG82 and TG55 were larger than that of TG10. The transmittance of TG91 and TG82 was more than 70% and that of TG55 was more than 90% in the wavelength range over 400 nm. The transmittance increased with increasing the ratio of Ga to Ti in the solution, which is considered to be due to a large bandgap of Ga_2O_3 . The large bandgap of Ga_2O_3 leads to a high transmittance in the wavelength over 400 nm and a shift of the absorption edge to a shorter wavelength.

Fig. 6. Optical absorption spectra of TG10q, TG91q, TG82q and TG55q, plotted as $(\alpha h\nu)^{1/2} = f(h\nu)$.

3.4 Absorption coefficient and bandgap

Figure 5 shows absorption coefficients of TG10q, TG91q, TG82q and TG55q calculated using the measured reflectance and transmittance of each sample. When the incident light is completely absorbed and a multiple reflection in the film can be neglected, the absorption coefficient can be calculated using the following equation, [10]

$$\alpha d = \ln \frac{1}{T_{obs}} + \ln(1 - R_{obs}) + \ln \left(1 - R'_{obs} + \frac{1}{2} R_{sobs} \right), \quad (2)$$

where α is the absorption coefficient, d is the thickness

of the film; T_{obs} , R_{obs} and R'_{obs} are the transmittance, the surface reflectance and the rear reflectance of the sample, respectively; and R_{sobs} is the reflectance of a quartz substrate. As shown in Fig. 5, in the UV wavelength region, absorption coefficients became smaller with increasing the ratio of Ga to Ti in the solution, which may be attributed to the fact that gallium oxide existed in the film even if the amount of Ga₂O₃ crystals were very small and that therefore the ratio of TiO₂ in the film decreased.

The optical bandgap of the films is determined by the following relation,[11]

$$(\alpha h\nu)^\gamma = A(h\nu - E_g) \quad (3)$$

where $h\nu$ is the photon energy, E_g is the optical bandgap and A is a constant which has no dependency on photon energy and γ has four numeric values (2 for allowed direct, 1/2 for allowed indirect, 1/3 for forbidden direct and 2/3 for forbidden indirect optical transitions). Figure 6 shows the $(\alpha h\nu)^{1/2}$ versus photon energy plot for the sample TG10q, TG91q, TG82q and TG55q. The indirect E_g values for TG10q, TG91q, TG82q and TG55q are estimated as 3.29eV, 3.35eV, 3.31eV and 3.36eV, respectively. It is known that the bandgaps of Ga₂O₃ and rutile-TiO₂ are ~5eV and 3eV, respectively.[12,13] In our experiments, the E_g values for all non-doped and Ga-doped TiO₂ films were almost constant at 3.3eV and showed little dependency on doping concentration. At present, it is not clear why Ga-doping had little influence on optical bandgap of TiO₂ films although it had great influence on transmittance of the films.

4. Summary

Ga-doped TiO₂ films were prepared by spin-coating method and optical properties of non-doped and Ga-doped TiO₂ films were investigated. In the films prepared using low concentration of Ga to Ti in the solution, few Ga₂O₃ crystals exist in the TiO₂ films. The thickness of Ga-doped TiO₂ films increased and the refractive index of the films decreased with increasing the ratio of Ga to Ti in the solution. In the reflectance measurements, there was little dependency of doping concentration as long as the concentration was not too high. The transmittance increased with increasing the ratio of Ga to Ti in the solution. The bandgap of the non-doped and Ga-doped TiO₂ films were obtained using absorption coefficients calculated with reflectance and transmittance spectra. The bandgap of the films was almost constant regardless of the ratio of Ga to Ti in the solution.

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