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The optical properties of silicon-rich silicon nitride prepared by plasma-enhanced chemical vapor deposition

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A B S T R A C T

This research investigated the optical properties of silicon-rich silicon nitride (Si-rich SiN) and conventional silicon nitride (SiNx) layers, which are commonly used in anti-reflective coating (ARC) to improve the light absorption in solar cells. We found that the change in the refractive index of Si-rich SiN was due to the annealing temperature that was considerably higher than that of conventional SiNx. In addition to the mass density variation in the SiNx layer that generally governed the change of refractive index in previous studies, this study found another important factor influencing the change of the refractive index. The Si–N bond, which was the main component in SiNx controlled the refractive index, while the amount of Si-Si bond in Si-rich SiN after annealing governed the change of the refractive index. The structural analysis presented for the Si-rich SiN and the SiNx explained the effect of the annealing process on tuning the refractive index of the Si-rich SiN.

1. Introduction

Silicon nitride (SiNx) is widely used in various electronic devices and silicon solar cells because SiNx effectively passivates the material's surface and suppresses surface recombination [1–8]. Hydrogen atoms, which are included in the SiNx layer, terminates the Si dangling bonds. The positive fixed charges in the layer bend the Si energy band to evacuate the carriers from the surface, leading to a lower surface recombination rate. Consequently, SiNx yields a high carrier lifetime of the Si substrate, which is strongly required to achieve high-efficiency crystalline Si solar cells [3]. SiNx (refractive index (n) ~ 2) is also well known for anti-reflective coating (ARC), which improves the amount of absorbed light in the bulk of solar cells. SiNx deposited on a random pyramid texture at the surface of crystalline Si, which is usually fabricated by isotropic etching with an alkaline solution, reduces a surface reflectance of the Si surface to suppress the surface reflection effectively. Besides solar cells, SiNx is also utilized in several electronic devices, such as high dielectric constant material in memory devices and distributed Bragg reflectors (DBR) used for a laser [4–7].

SiNx has been prepared using several deposition methods. Thermal chemical vapor deposition (thermal CVD), plasma-enhanced CVD (PECVD), and catalytic CVD (Cat-CVD), as have been reported in recent years [8,9]. It is possible to change the refractive index of SiNx by varying the composition ratio of Si and N. In the PECVD method, SiNx's refractive index can be changed by controlling the flow rate of source gases, namely SiH_4 and NH_3 [10]. By using this technique, multi-layers of SiO_2/Si-rich SiN were formed [11,12]. In another method, it is also possible to change the refractive index of SiNx by varying the deposition temperature [13–15].

By better understanding the reasons behind the refractive index change in SiNx after annealing or by varying the deposition temperature one can better control the refractive index. Chen et al. suggested that the change in the refractive index of conventional SiNx, by varying the deposition temperature, also resulted in the mass density change [13]. Hence, that report also expected an increase in mass density after a variation of the deposition and annealing temperatures in Si-rich SiN (n ~ 3) during our effort in increasing the refractive index. However, we found that the increase of mass density could not thoroughly explain the increasing trend of the refractive index of Si-rich SiN after the thermal annealing. In this study, we investigated the annealing effect on the optical properties of Si-rich SiN and suggested a structural diagram for Si-rich SiN to explain the changes in the refractive index after thermal annealing.

2. Experimental procedure

The SiNx (n ~ 2 at 605 nm wavelength) and Si-rich SiN were prepared on a cleaned floating-zone (Fz) p-type Si (resistivity ~ 10 Ωcm) and on a quartz substrate by PECVD (PD-2000, Samco Inc.) with 13.56 MHz plasma excitation frequency. Table 1 shows the details of the deposition condition for each material. The timed increases of the substrate temperature and the deposition time were kept at 30 min and 3 min, respectively. The deposited layer's thickness was kept at approximately 40 nm. The utilized source gases were a mixture of SiH_4 and NH_3 for Si-rich SiN and a mixture of SiH_4, NH_3, and N_2 for SiNx. We used Ar-diluted SiH_4 (20.11%) for the Si source gas. The deposited

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Table 1
Deposition conditions and materials for Si-rich SiN and SiNx in PECVD.

	SiH_4 [sccm]	NH_3 [sccm]	N_2 [sccm]	Pressure [Pa]	Rower [W]	Temp. [°C]
Si-rich SiN (200 °C)	100	15	–	60	50	200
Si-rich SiN (350 °C)	100	15	–			350
SiNx	75	60	100			

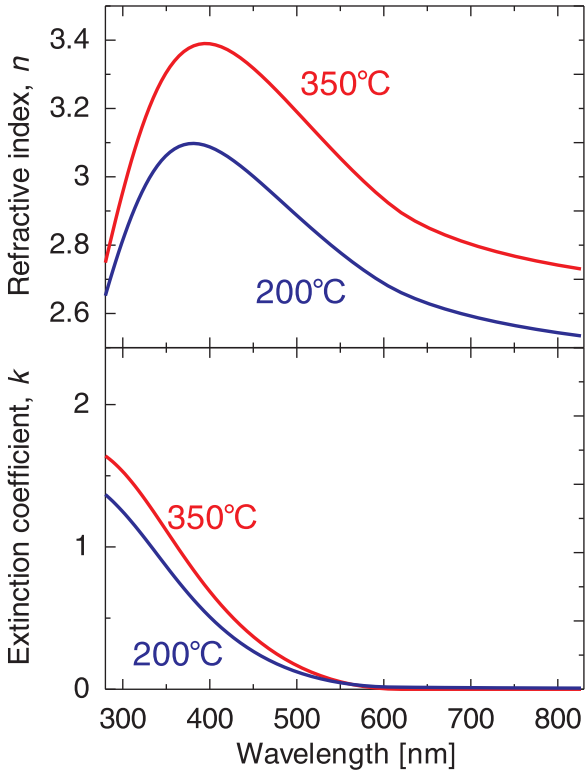

Fig. 1. Optical properties of Si-rich SiN deposited at 200 °C and 350 °C.

materials were annealed at 250 °C, 400 °C, and 650 °C for 1 h in ambient N_2 in a tubular furnace. We utilized spectral ellipsometry (UVISEL, Horiba, Ltd.) to investigate the optical properties thereof. Hereafter, the refractive index used in this paper is the value at 605 nm of the light wavelength. The mass density was evaluated by X-ray reflectivity method (XRR, RINT-TTRIII/NM, Rigaku Co.). The incident angle of X-ray was varied from 0.5° to 5°. The semiquantitative atom ratio and bonding state were evaluated by X-ray photoelectron spectroscopy (XPS, PHI5000 VersaProbe II, ULVAC-PHI, Inc.) with an Al Kα monochromatic X-ray source at 1486.6 eV under 10^{-4} Pa or less. The infrared absorption property was measured by the transmission mode of Fourier-transform infrared spectroscopy (FT-IR, FT/IR-6100, JASCO Co.) to estimate the hydrogen (H) concentration in the layers. The crystallization of Si was confirmed by Raman spectroscopy (NRS-4100, JASCO Co.) using 532 nm laser excitation.

3. Results and discussion

Fig. 1 shows the optical properties of Si-rich SiN deposited at 200 °C and 350 °C. The refractive index of the Si-rich SiN deposited at 200 °C was lower than that deposited at 350 °C. The refractive index of Si-rich SiN was 2.68 for the deposition at 200 °C and 2.92 at 350 °C. As reported previously, a lower deposition temperature for Si-rich SiN yielded a lower refractive index [10]. A slightly higher extinction coefficient was also confirmed for Si-rich SiN owing to the increase of Si/N ratio.

Fig. 2 shows the optical properties of Si-rich SiN and SiNx annealed at various temperatures from between 250 °C and 650 °C. The annealing temperature of 250 °C had no effect on the change of optical property for all the examined samples, while the annealing processes at 400 °C and 650 °C remarkably changed the refractive indices and the extinction coefficients of Si-rich SiN. The refractive indices of the Si-rich SiN deposited at 200 °C and 350 °C, which were then annealed at 650 °C both increased remarkably from 2.68 to 3.44. This is interesting behavior because the refractive index showed the same value after the annealing at 650 °C despite the different deposition temperatures. In addition, the extinction coefficient also displayed similar behavior as it was increased by a higher annealing temperature. Contrarily, for conventional SiNx, such high annealing temperature only yielded a slight increase in the refractive index from 1.92 to 1.98, as shown in Fig. 2(c),

As reported, one of the reasons for the increased refractive index was the change in mass density [13]. To validate that, we examined the mass density by XRR measurement. Fig. 3 shows the mass densities of Si-rich SiN and SiNx after annealing at various temperatures. Initially, the mass density was 1.76 and 1.86 for the Si-rich SiN deposited at 200 °C and 350 °C, respectively. A similar result previously reported that a lower deposition temperature for Si-rich SiN resulted in a lower mass density and, thus, a lower refractive index [13]. Concurrently, the mass density of SiNx was 2.42, which was also similar to the previous report, despite being much higher than that of Si-rich SiN [16,17]. The mass density of Si-rich SiN was also increased significantly by annealing at 650 °C, but there were no remarkable differences noted until 400 °C.

It should be noted that the refractive index of Si-rich SiN was also changed over 400 °C after annealing, as shown in Fig. 2. The significant increase of the refractive index and mass density for Si-rich SiN after annealing at 650 °C was observed, suggesting that one of the reasons in the increasing refractive index might be the change of mass density. This was supported by a study that reported the drastic mass density increase after high-temperature annealing in Si-rich SiN by the formation of the quantum dot of Si [18–20]. However, this mechanism could not explain the increase of refractive index after the annealing at 400 °C. At the same time, the mass density of SiNx after annealing was only increased at 250 °C but decreased at 400 °C or 600 °C, although the refractive index kept increasing. This result suggests that we would require another mechanism to explain the change in refractive index of Si-rich SiN and SiNx after the post-deposited annealing.

Besides mass density, another possible factor for the increase in the refractive index could be the composition ratio. We evaluated the semiquantitative atomic ratios of Si-rich SiN and SiNx by XPS. Table 2 shows the estimated atomic ratios using Si 2*p* and N 1*s*. The estimated atomic ratios of Si-rich SiN and SiNx did not change despite the variation in annealing and deposition temperatures. The ratio of N increased slightly because the annealing was done under N_2 atmosphere. Therefore, we presumed that the composition ratio did not result in the increase of refractive index in Si-rich SiN.

We then checked the bonding states of the prepared films by XPS in order to further examine the rationale behind the refractive index increase due to the annealing process in Si-rich SiN. Si 2*p* spectra were deconvoluted to Si–Si (99.3 eV), Si–N (100.5 eV for Si-rich SiN and 101.5 eV for SiNx), and Si–O from the native oxide layer (103 eV). The Si 2*p* spectra were calibrated to the carbon peak at 285 eV. Fig. 4(a) shows the Si–Si peak counts from the Si 2*p* spectra of the Si-rich SiN deposited at 200 °C and 350 °C and of the SiNx deposited at 350 °C annealed at different annealing temperatures. The Si–Si peak count of

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