CHARACTERIZATION OF POROUS SILICON NITRIDE FORMED BY PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION

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The Si nitride films are widely used for the passivation of devices and for the core layer of the optical waveguides [1]. A Si nitride film deposited by plasma-enhanced chemical vapor deposition (PECVD) is generally stable. However, we found that at certain deposition condition, an unstable porous Si nitride film is deposited. And the refractive index and the thickness is gradually changed with time at even room temperature.

The Si nitride film was deposited by using the parallel plate type plasma CVD apparatus using SiH_4 and NH_3 mixture gas. The refractive index and thickness of the film were measured by spectroscopic ellipsometry (WVASE32, J. A. Woollam Co., Inc.). The annealing of the film was carried out by using the hot plate in the clean room air at humidity of 35~40 %.

It was found that the refractive index of the film deposited at low plasma power is decreased with time even at room temperature within a few days. However, we used the raised temperature to save the experiment time. The change in the refractive index is larger for the lower plasma power, which suggests that the unstable porous Si nitride film is formed. Examples of the changes of the refractive index and thickness are shown in Fig. 1.

The growth temperature dependence of the refractive-index change is shown in Fig. 2. The peak of the refractive-index change is observed at a growth temperature of 200°C. At low growth temperature (23°C) and low power, the as grown film includes relatively large amount of oxygen because the SiH_4 reacts with the residual H_2O or O_2 in vacuum chamber and the nitridation with NH_x radicals is not enhanced due to the small plasma power. Then the additional oxidation reaction by the annealing is not large. On the other hand at the high growth temperature (300°C), the dense film is generated and then the property change by annealing is small. As a result, in the medium growth temperature, the film becomes most unstable. In Fig. 1, the thickness increases at the beginning and then decreases gradually. This reason is considered as follows. Both of the thickness expansion due to the inclusion of oxidation precursors (O_2 or H_2O) and the densification due to the annealing simultaneously take place, which makes the peak in Fig.1. Figure 3 shows the FT-IR spectra of the as deposited and annealed film (growth temperature=23˚C, RF Power=100 W). By the annealing, the Si-N and N-H absorption peaks decrease, instead the Si-O absorption peak is increased.

The Si nitride film contains a lot of hydrogen atoms (usually more than 20%). By annealing, hydrogen bonds may be dissociated and the oxygen atoms are incorporated into the film, which may lead to the reduction of the refractive index as shown in Fig. 1.

As a result of the above mechanism, the film color is drastically changed by the annealing as shown in Fig. 4. Even at room temperature the film color is changed with time. Therefore, it can be used as the low-cost rough timer. The local change of the film property by electron [2] or laser beam can be applied to the electronic and optical devices such as optical waveguides without using the etching process.

References

[1] T. Nagata *et al.*, Jpn. J. Appl. Phys. **34** (1995)1282.
[2] M. Hirose, *et al.*, J. Photopolym. Sci. Technol. **17**(1994) 599.

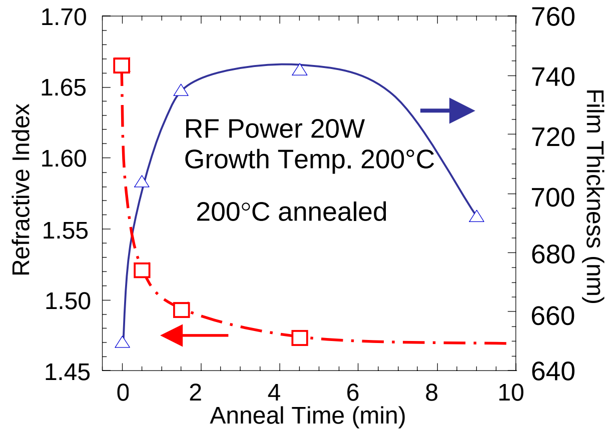

Fig. 1. Refractive index and film thickness versus anneal time for the sample grown at 200°C.

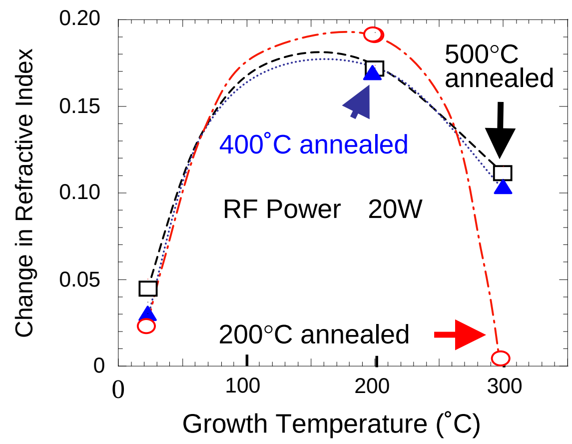

Fig. 2. Growth temperature dependence of the refractive-index change.

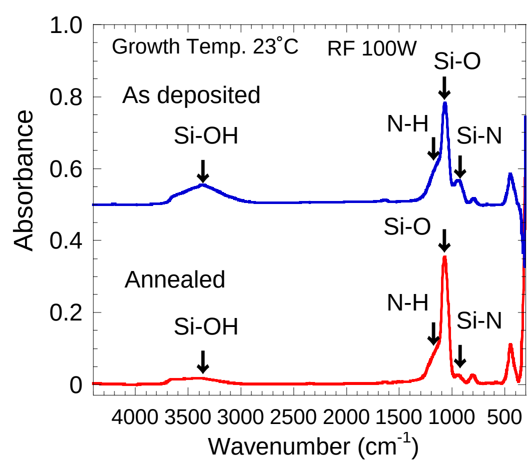

Fig. 3. FT-IR spectra of the as deposited and annealed (400°C, 30min) films.

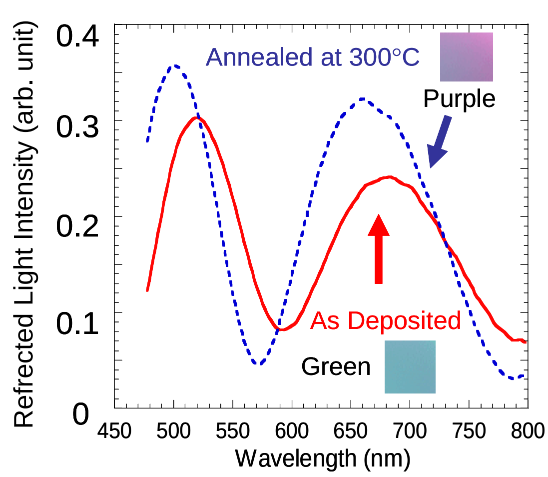

Fig. 4. Interference color change by the annealing. Growth temperature=300˚C, initial thickness=610 nm, anneal temp=300˚C, and anneal time=90 min.