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Optical properties, infrared spectroscopy and photoluminescence at low temperature of LPCVD silicon oxynitride thin films

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Low pressure chemical vapor deposition (LPCVD) silicon oxynitride (SiON) films of various compositions between SiO_2 and Si_3N_4 were grown by changing the relative ratio (Ro) of nitrous oxide (N_2O) to silane (SiH_4) pressures while keeping constant the ammonia (NH_4) pressure. The SiON films were deposited at 700° C on p-type silicon substrates (with a carrier concentration of 10^{15} cm^{-3}), varying Ro from 0.32 to 1.38. Some samples were subsequently annealed at 700° C for times up to 150 min, whereas other samples were annealed at 1000° C for times up to 60 min in nitrogen. In this work, we present results of the effect of Ro upon the refractive index, the infrared spectrum, and the growth rate of the LPCVD SiON layers. In particular, we show that as Ro increases, the refractive index decreases from values very close to those of SiN to values very close to those of SiO_2. In addition, the infrared spectrum shows that the peak associated to the Si-O stretching vibration mode decreases as compared to the Si-N stretching local mode when Ro increases. The annealing processes seem not to modify the films as thickness and refractive index remain constant as a function of the annealing time. In addition, we made photoluminescence spectroscopy measurements at low temperature (9-10º K) and found luminescence in the range between 1.4 eV and 2.4 eV with a peak around 2 eV. Finally, we also discuss the effect that a thermal annealing at 700º C for 90 minutes has upon the photoluminescence spectra.

1. Introduction

Silicon oxynitride (SiON) is a material of great interest for the development of integrated devices and sensors in the microelectronics and opto-electronic industries because the variation of its stoichiometry may allow a wide range of properties [1, 2]. For example, it may have a variable refractive index, of interest for integrated optics [3], and it may induce low stress on silicon substrates, what is useful for micro-mechanical devices. Also, the excellent passivating properties of silicon oxynitrides on the surface of silicon allow their use as active layers in transistors and memory devices [4].

In this work, we study the variation of the refractive index and the infrared spectrum of SiON films, obtained by low pressure chemical vapor deposition (LPCVD), as a function of the relative ratio Ro of nitrous oxide (N_2O) to silane (SiH_4) pressures while keeping constant the ammonia (NH_4) pressure. We also study the possible photoluminescence of the SiON films obtained by LPCVD.

2. Experimental

LPCVD SiON films were grown at 700° C using ammonia, silane and nitrous oxide as the reactive gases and were deposited on (100) p-type silicon substrates with a carrier concentration of 10^{15} cm^{-3}. By changing the relative ratio Ro of the nitrous oxide $(N_2O)_P$ to silane $(SiH_4)_P$ pressures while maintaining the ammonia pressure at 1.1 Torr, we deposited SiON films for Ro values of 0.32, 0.52, 0.71, 1.07, and 1.38. The total pressure changed from 1.75 Torr for Ro = 0.32 to 2.25 Torr for Ro = 1.38. To investigate the effect of thermal treatments upon the refractive index of SiON layers, three groups of samples were annealed at 700° C in a nitrogen ambient for times of 30, 90 and 150 min, respectively. Two other similar groups were annealed at 1000° C for times of 20 and 60 min, respectively. Film thickness and refractive index were measured with a Gaertner ellipsometer employing a He-Ne laser beam (wavelength of 632 nm), at an angle of 70º. Finally, the IR spectrums were determined using a Magna-IR 750 Nicolet spectrophotometer. The photoluminescence before and after the annealing at 700º C was measured at low temperature (9-10º K) using a focused 20 mW laser (λ = 4579 A) as the excitation source.

3. Results

One of our main purposes in this work was to have a variation of the refractive index of the films so that we may apply them to integrated optical devices in the near future. This variation can be observed in fig. 1 for our LPCVD films. The variation of the index of refraction is shown as a function of the annealing time at 700º C and 1000º C in Fig. 2. Notice that the refractive index of the annealed samples is almost the same as that for the non-annealed ones.

This result is important because it means that the refractive index of the SiON films obtained by LPCVD is stable and they can be processed at such high temperatures without a significant change

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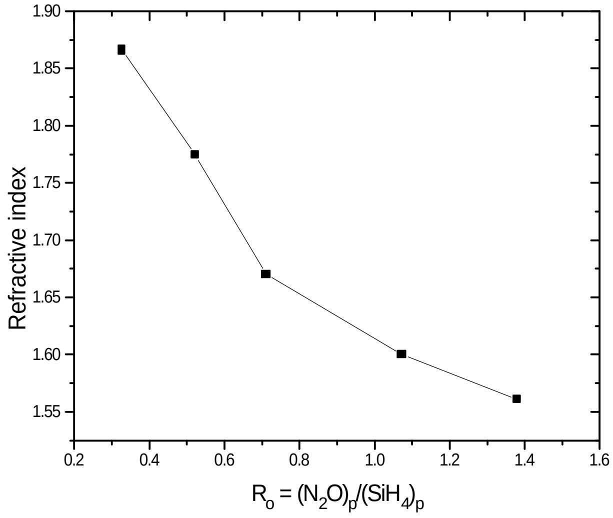


Fig. 1. Index of refraction as a function of Nitrous Oxide to Silane relative pressures.

As expected from the above result, the sample thickness (in the range from 40 to 100 nm) also remained constant when they were annealed at these high temperatures.

In order to observe, qualitatively, the variation of the chemical composition as a function of the gas mixture composition we determined the infrared absorption spectra of the SiON films on silicon wafers, after eliminating the silicon substrate effect. They can be seen in Fig. 3, for 4 non-annealed samples. There are 2 wide bands that change when Ro is varied from 0.32 to 1.07.

The highest band around 1025 cm^{-1} is associated to stretching vibrations of the Si-O bonds and the band around 850 cm^{-1} is affected by stretching vibrations associated to the Si-N bonds. As expected, as we increase the relative N_2O pressure, we have a higher amount of Si-O bonds as compared to Si-N bonds, giving rise to the variation of the refractive index observed in fig. 1. In future experiments we shall try an even wider variation of properties by changing also the ratio of the relative silane to ammonia pressures.

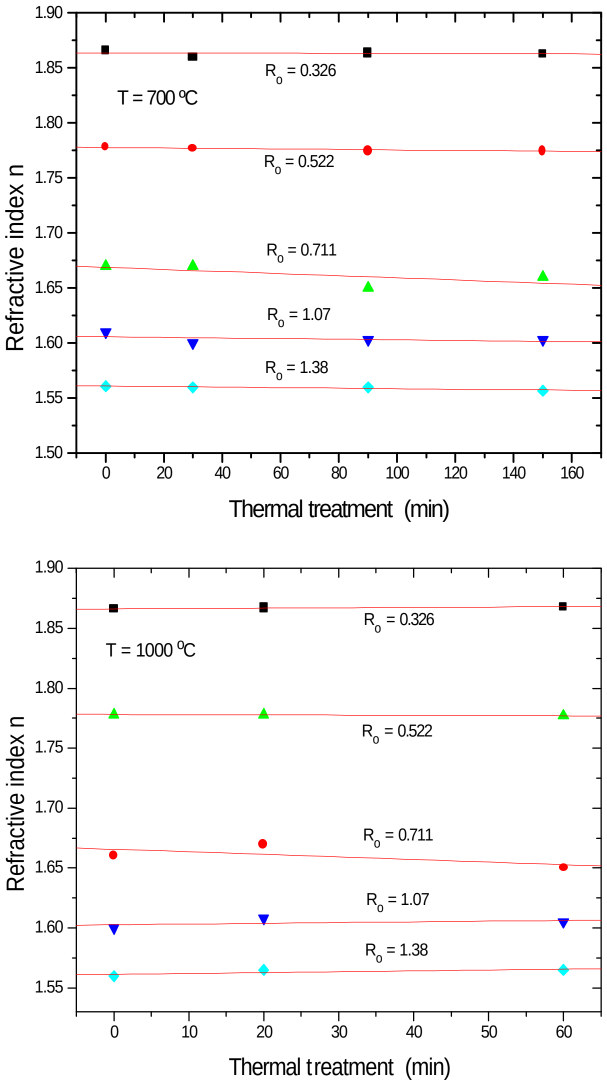
We show the results for the photoluminescence of only 2 samples with Ro = 0.71 and Ro = 1.07 labeled as samples 3 and 4, respectively. These samples had a thickness between 88 to 100 nm. In Fig. 4 we observe that for sample 3, there is an increase of the photoluminescence (PL) signal after the annealing at 700º C. The maximum occurs around 2 eV, both before and after the annealing.

On the other hand, for sample 4 we also observe the growth of the PL signal as a consequence of the annealing, but there is a shift of the peak from around 2 eV to around 2.25 eV, before and after the annealing, respectively. The luminescence observed before the annealing in other samples was similar to that shown in Fig. 3.

The origin of the photoluminescence is not known as the films are amorphous. We think of 2 possibilities:

The formation of microcrystals of silicon within the SiON film matrix as a consequence of a lack of stoichiometry during the growth, or the presence of defects that cause luminescent carrier traps. In any case, this result is important because it means that it may be possible to have electroluminescence (EL) from MIS devices with SiON thin films as the insulator, even at room temperature, if carriers are injected into the films by means of an appropriate polarization.

We shall investigate further in order to determine the cause of luminescence from the films and will try to make electroluminescent devices. If this is achieved we expect to have the basis for a truly integrated optoelectronics based on silicon technology, since waveguides from SiON and photodetectors for the wavelength range of luminescence observed here are already fabricated on silicon.



Fig, 2. Variation of the refraction index as a function of annealing time in N_2 at (A) 700º C and (B) 1000º C.

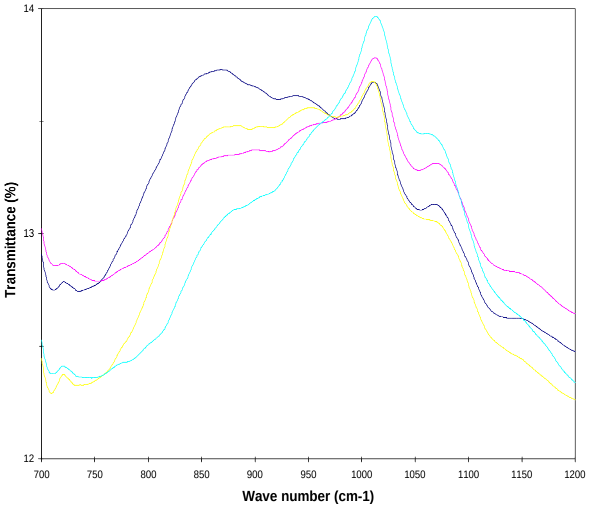


Fig. 3. Infrared Absorption spectra for (A) Ro = 0.32, (B) Ro = 0.52, (C) Ro = 0.71 and (D) Ro = 1.07.

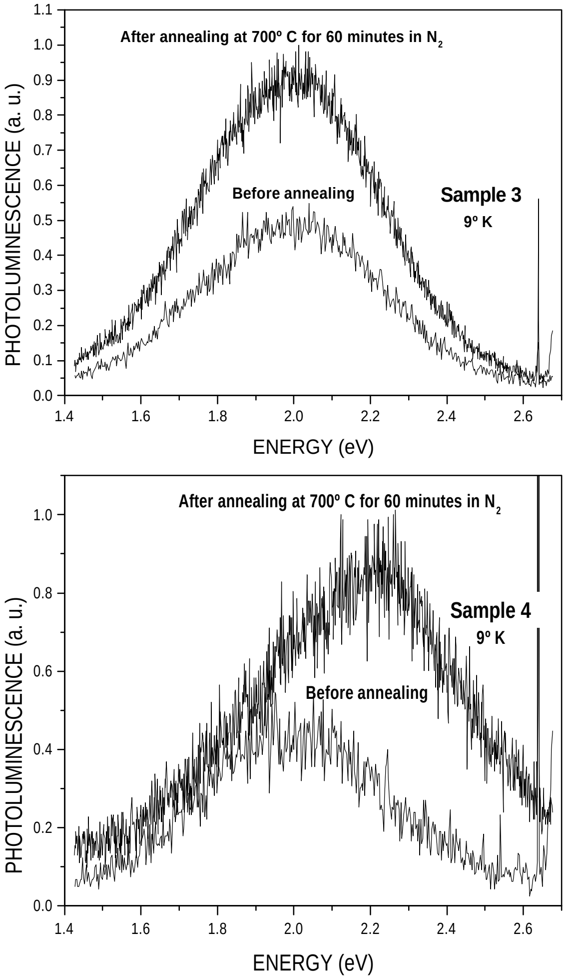


Fig. 4. Photoluminescence spectra for sample 3 and sample 4, respectively, before and after an annealing at 700º C in N_2.

4. Conclusions

In summary, we have shown that it is possible to have SiON thin films by LPCVD with variable index of refraction due to a variation of the chemical composition of the films as the gas mixture is changed during their deposition. We also have shown that, at low temperature, photoluminescence is observed for the SiON films possibly associated to the non-stoichiometry of the samples or the presence of defects that cause radiative carrier traps within the band-gap. This fact may be useful .for making optoelectronic devices compatible with modern VLSI silicon technology, making it possible the development of a real integrated optoelectronics in the near future.

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