Photoluminescence from C⁺-implanted SiNₓOᵧ films grown on crystalline silicon

L. S. Liao,a) Z. H. Xiong, X. Zhou, X. B. Liu,b) and X. Y. Hou

Surface Physics Laboratory and T. D. Lee Physics Laboratory, Fudan University, Shanghai 200433, People’s Republic of China

(Received 3 March 1997; accepted for publication 25 July 1997)

Carbon ions at an energy of 35 keV with a dose of 5×10¹⁶ cm⁻² were implanted into SiNₓOᵧ films grown on crystalline silicon by plasma enhanced chemical vapor deposition. Intense photoluminescence (PL) peaked at about 550 nm is observed in the implanted films under an excitation of 441.6 nm laser line. The PL intensity varies with annealing temperature, and reaches a maximum at the annealing temperature of 600 °C. The luminescence may originate from the complex of Si, N, O, and C in the films. © 1997 American Institute of Physics.

In the studies of Si⁺-based light-emitting materials, the luminescence properties of SiO₂ films attract much attention. SiO₂ films as passivation layers or dielectric layers are widely used in Si integrated circuits. If this kind of film possesses good luminescence properties, Si-based optoelectronic integration could be realized easier than other materials due to its complete compatibility with the current Si planar technique. There are several methods to prepare luminescent SiO₂ films, such as radio frequency magnetic sputtering, plasma enhanced chemical vapor deposition (PECVD), ion implantation, etc. The luminescence behaviors of Ge⁺ or Si⁺-implanted thermal SiO₂ films were reported. Shimizu-Iwayama et al. implanted Si⁺ ions into SiO₂ films with high dose and MeV energy, and observed the photoluminescence (PL) bands at the energies of ~2.0 and ~1.7 eV. Mutti et al. studied the Si⁺-implanted SiO₂ films and observed a blue-light emission. We investigated the photoluminescence in the blue, green, and red bands as well as the electroluminescence from Si⁺-implanted SiO₂ films.

Besides SiO₂ films, SiNₓOᵧ films are also used in Si integrated circuits as a promising alternative passivation layer or gate insulator due to their high radiation hardness, low defect density, and low impurity diffusion. It is thus natural to consider whether SiNₓOᵧ could also be a luminescent material. In this letter, we report our observations on the PL from C⁺-implanted SiNₓOᵧ films.

Boron doped p-type silicon (100) single crystal wafer with the resistivity of 5–8.5 Ω cm was used as the substrate. A layer of ~120 nm SiNₓOᵧ film with the refractive index n≈1.7 was grown on the substrate surface by PECVD method. C⁺ ions were then implanted into the SiNₓOᵧ film at an energy of 35 keV with a dose of 5×10¹⁶ cm⁻². The average projection range is about 60 nm. The C⁺-implanted samples were thermally annealed in a N₂ ambient at 200, 400, 600, 800, and 1000 °C for 30 min, respectively, or at 1100 °C for 2 min. The 441.6 nm line of an He–Cd laser with the light power of 75 mW and the light spot diameter of 1 mm on the sample surface was used as the excitation source for PL measurements at room temperature. The wavelength scale of the instrument was calibrated before the measurements. A PHI-550 Auger electron spectrometer (AES) was used for atomic content profile measurements and a Bruker ER-200D electron spin resonance (ESR) spectrometer, with a detector sensitivity of ~10¹² spin, was used for ESR measurements.

Shown in Fig. 1 are the PL spectra of the samples. Under our experimental conditions, the SiNₓOᵧ film without ion implantation does not exhibit any PL [curve (a)]. After C⁺-implantation, the sample shows PL properties [curve (b)], and the luminescence could be seen by the naked eye under daylight conditions. After annealing in N₂ ambient at 600 °C for 30 min, the PL from the implanted sample increases enormously, and the sample exhibits intense green–yellow light with the peak wavelength at about 550 nm. The peak intensity of the annealed sample is at least ten times...

FIG. 1. Photoluminescence spectra of (a) nonimplanted SiNₓOᵧ film, (b) C⁺-implanted SiNₓOᵧ film, (c) C⁺-implanted SiNₓOᵧ film annealed in N₂ ambient at 600 °C for 30 min, and (d) Si⁺-implanted SiO₂ film annealed in N₂ ambient at 1100 °C for 100 min.
higher than that of the as-implanted sample. As a comparison, Fig. 1 also shows the PL spectrum of the Si\(^{+}\)-implanted SiO\(_2\) film (implanted at an energy of 120 keV with a dose of \(5 \times 10^{16} \text{ cm}^{-2}\)) after annealing in N\(_2\) ambient at 1100 °C for 100 min. (The Si\(^{+}\)-implanted SiO\(_2\) film does not show red emission after annealing at 600 °C, but shows the most intense red emission after annealing at 1100 °C, so we choose the sample annealed at 1100 °C for comparison.)

Figure 2 shows the PL spectra of the samples annealed at 600 °C for 30 min and etched in a buffered HF solution for different times. Curve (a) is the PL spectrum of the sample before dipping in the buffered HF solution (sample 1); curves (b) and (c) are that of the samples dipped in the HF solution for 10 s (sample 2) and 150 s (sample 3), respectively. The thicknesses of SiN\(_x\)O\(_y\), measured by an ellipsometric method, are about 120, 100, and 50 nm, corresponding to curves (a), (b), and (c), respectively. Comparing curve (b) with curve (a), we may notice that the PL intensity is enhanced after removing the upper part of the SiN\(_x\)O\(_y\) film. It means that the surface layer of the SiN\(_x\)O\(_y\) film is a nonluminescence area. Comparing curve (b) with curve (c), we may also notice that the bottom part of the SiN\(_x\)O\(_y\) film near the Si interface is a nonluminescence area also. So the luminescence originates from the middle part of the SiN\(_x\)O\(_y\) film.

In order to analyze the composition of the SiN\(_x\)O\(_y\) film, AES measurements of samples 1, 2, and 3 (denoted as above) were performed and the approximate atomic concentration profiles are shown in Fig. 3. According to Fig. 3(a) of sample 1, we may roughly divide the profiles into three zones, the surface zone (with oxygen content >40%), the middle zone, and the bottom zone (with silicon content >50%). Figure 3(b) is the composition profile of sample 2, where only the contents of Si, N, O, and C in the middle and the bottom zones are shown because its surface zone has been etched away during the HF-dipping. Figure 3(c) is the composition profile of sample 3 which only shows the atomic contents in the bottom zone. The luminescence area is just the middle zone of the SiN\(_x\)O\(_y\) film, which consists approximately of Si (≈20%), N (30%), O (<40%), and C (>5%). Therefore, we believe that the complex of Si, N, O, and C is responsible to the light emission.

Shown in Fig. 4 is the annealing temperature dependencies of PL peak intensity [curve (a)] and of ESR signal [curve (b)] of the samples. Curve (a) possesses a maximum
at about 600 °C. The PL peak intensity increases as the annealing temperature increases from room temperature to 600 °C, and then it decreases as the annealing temperature increases further. In contrast to curve (a), the ESR signal decreases monotonically with the increment of the annealing temperature. The as-implanted sample shows intense ESR signal with a spin density of about 3.7 × 10^{14} cm^{-2}. After annealing at 200 and 400 °C, the spin density decreases to 1.9 × 10^{14} and 2.6 × 10^{13} cm^{-2}, respectively. When the annealing temperature is higher than 600 °C, no ESR signal could be detected (<10^{12} spins in the samples). Moreover, the nonimplanted SiNₓOᵧ films do not show any ESR signal either. It illustrates that there are some paramagnetic defects in the films after C⁺-implantation, and the defects could be removed by thermal annealing.

The implantation of carbon into SiNₓOᵧ film seems to create both the radiative recombination centers and the non-radiative recombination centers in the film. The two kinds of centers will affect the PL intensity of the C⁺-implanted films oppositely. The increment of the PL intensity by raising the annealing temperature from room temperature to 600 °C may be caused either by the increment of the number of the radiative recombination centers or by the decrement of the number of the nonradiative recombination centers. The decrement of ESR signal intensity in this temperature range implies that the later factor is dominated. When the annealing temperature is higher than 600 °C, the thickness of the surface zone of SiNₓOᵧ film increases due to the oxygen diffusion from the surface into the middle zone according to our AES profile measurement (it will be discussed elsewhere). As a result, the thickness of the middle zone decreases and the PL intensity decreases as well. If we optimize the sample growth conditions and control the obvious diffusion of surface oxygen, the PL intensity will hopefully not decrease even annealed at higher temperatures. Further investigation of the materials is in progress.

In summary, C⁺-implanted SiNₓOᵧ films grown on crystalline silicon are able to exhibit intense PL peaked at about 550 nm and the PL intensity could reach its maximum after thermal annealing at about 600 °C for 30 min. The luminescence may originate from the complex of Si, N, O, and C in the films. The preparation of C⁺-implanted SiNₓOᵧ film is fully compatible with the current Si planar technique. Therefore, SiNₓOᵧ film is possible to become a kind of cheap and practical Si-based light-emitting material.

The authors gratefully thank Professor X. Wang for his guidance, Z. Lin for his help in ion implantation, and Professor D. Huang for his help in PL measurements. This work is supported by China Postdoctoral Science Foundation and by Chiatai Foundation of T. D. Lee Physics Laboratory of Fudan University.