

N₂ Plasma Treatment Effects of Silicon Nitride Insulator Layer for Thin Film Transistor Applications

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Abstract

We investigated to decrease the leakage current of SiN_x film by employing N₂ plasma treatment. The insulator layers were prepared by two step process; the N₂ plasma treatment and then PECVD SiN_x deposition with SiH₄, N₂ gases. To prove the influence of the N₂ plasma treatment, the Si substrate was exposed to the plasma, which was generated in N₂ gas ambient. Without plasma treatment SiN_x film grow at the rate of 7.03 nm/min, has a refractive index $n = 1.77$ and hydrogen content of $2.16 \times 10^{22} \text{ cm}^{-3}$ for N₂/SiH₄ gas flow ratio of 20. The obtained films were analyzed in terms of deposition rates, refractive index, hydrogen concentration, and electrical properties. By employing N₂ plasma treatment, interface traps such as mobile charges and injected charges were removed, hysteresis of capacitance-voltage (C-V) disappeared. We observed plasma treated sample were decreased the leakage current density reduces by 2 orders with respect to the sample having no plasma treatment.

1. Introduction

Silicon nitride (SiN_x) thin film have been used extensively in the semiconductor industry for over two decades, an application of particular recent importance being as the insulator in hydrogen amorphous silicon (a-Si:H) thin film transistor [1]. To further improve device performance, device stability, as well as long-term reliability, gate dielectric material becomes one of the most critical issues. Also, plasma treatment has been adopted as surface treatment, etch and deposition processes in many industrial applications [2]. Plasma treatment has proven to be very efficient for the enhancement of adhesion, and advances in this area have recently been reviewed [3]. The principal reason for this is that the

plasma-surface interactions controlled by the energetic ions, photons and free radicals present in the plasma, act in synergy [4]. Such interactions lead to (1) surface cleaning (removal of both contaminants and weak boundary layers), (2) the grafting of chemical groups (functionalization) capable of reacting to form strong bonds to subsequently deposited layers, (3) surface ablation (microetching), leading to an increase in surface microroughness that serves to enlarge the surface contact area, and (4) an increase in mechanical stability of the near-surface region through cross-linking [5].

In case of N₂ plasma treatment, SiN_x film improved to electrical properties after plasma treatment. Further, it presents the advantage of being one of the precursor gases in the deposition of SiN_x film [6]. The present work, we have investigated the properties of SiN_x film for various gas flow ratio of N₂/SiH₄ and resulting from N₂ plasma treatment.

2. Experimental

Before being introduced in the reactor, the used silicon substrate (4", (100), p-type, 25.5-42.5Ω cm). A silicon substrate was cleaned by RCA method to remove substrate contamination [7]. Just before being transferred to the vacuum deposition chamber, substrate were etched in HF:H₂O (1:10) for 10 second. The SiN_x film was deposited in planar coil plasma enhanced chemical vapor deposited (PECVD) reactor. To study the influence of the N₂ plasma treatment, the Si substrate was exposed to the plasma, which was generated in N₂ gas ambient. Substrate temperature during the N₂ plasma treatment was kept at 300 °C and the applied rf power of 400 W. Treatment time was 3 minute at the fixed pressure of 49mTorr. N₂ gas flow was 30sccm. After the N₂ plasma treatment, the insulator deposition was carried

out. At the condition using pure nitrogen and a helium dilution of silane gas. We also studied of 30mTorr working pressure, 300°C substrate temperature, 3-50 nitrogen-to-silane gas flow ratio, 200W PECVD rf power (13.56 MHz). The thickness of SiNx film was kept unchanged at 400Å. After the insulator deposition, aluminum top electrodes (about 1000Å) were deposited by thermal evaporation. The thickness and the refractive index of the films were measured by ellipsometry and chemical bonds were determined using FT-IR measurement [8]. MIS structures were characterised by high Frequency (1MHz) capacitance-voltage (C-V) characteristics study with Boonton 7200 and the current-voltage curves (I-V) with a Keithley 617, Fluke 5100B system.

3. Results and discussions

The SiNx film shows IR spectral features at frequencies characteristic of the local bonding of the Si, N, and H atoms. The nature of the chemical bonding groups was analyzed using FTIR spectroscopy. Figure 1 shows that FTIR transmission spectra from 450 to 4000 cm⁻¹ for films prepared at N₂/SiH₄ gas flow ratios of 5, 10, 20 and 50 at 300 °C. The calculations were made for the absorbance at the absorption peak position and molecular extinction coefficients 5.7×10⁻²⁰ cm² for Si-H and 4.8×10⁻²⁰ cm² for N-H [9]. Figure 1 shows that the hydrogen content of Si-H bond is decreasing as gas ratios increasing. On the contrary, hydrogen content of N-H bond is increasing. Additional re-bonding of silicon to nitrogen is expected as hydrogen is evolved from the film at these conditions. The reduction of bonded hydrogen and Si-H bond healing are responsible for the improved electrical and passivation properties of SiNx film.

Figure 2 shows the hydrogen concentration in the as-deposited films is in the form of Si-H and N-H bonds. It was observed that all of the detectable hydrogen in the SiNx film was bonded to nitrogen and detected as N-H groups for the nitrogen-to-silane gas flow ratio at the 10~50 range. It was observed that the hydrogen content is about 2.0 × 10²² cm⁻³ for SiNx film deposited at nitrogen-to-silane gas flow ratio more than 5 as shown was observed in Figure 2. The hydrogen content of about 2.14 × 10²² cm⁻³ for the gas flow ratio equal to 50. For the sample made of using gas flow ratio of 20 and at the substrate temperature of 300°C, the Si-H bonding concentration was detected as 2.47× 10²¹ cm⁻³ and that of N-H bonding

as 1.91× 10²² cm⁻³. To optimize the properties of SiNx film, the gas flow ratio of 20 was selected.

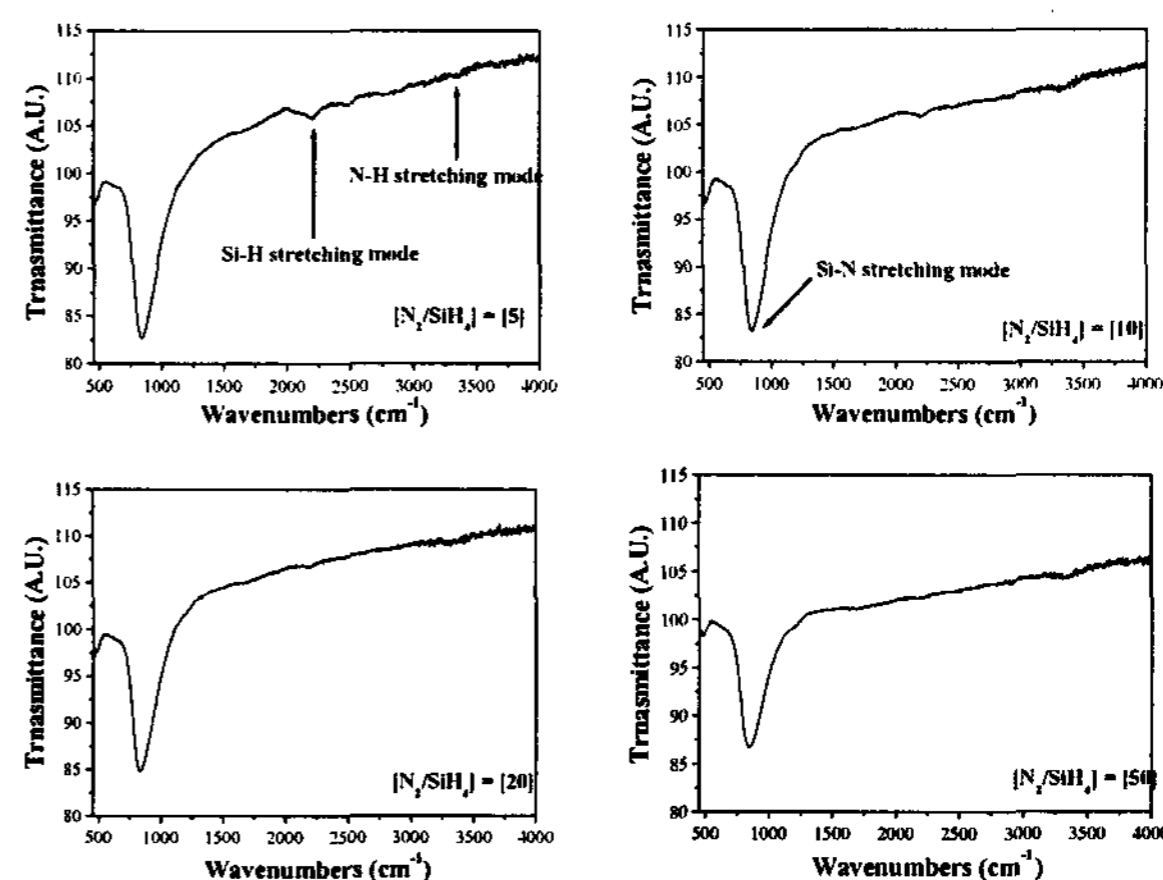


Figure 1. FT-IR transmission spectra of SiNx films that is deposited in various N₂/SiH₄ gas flow ratios, 200W source power, 30mTorr discharges at 300 °C

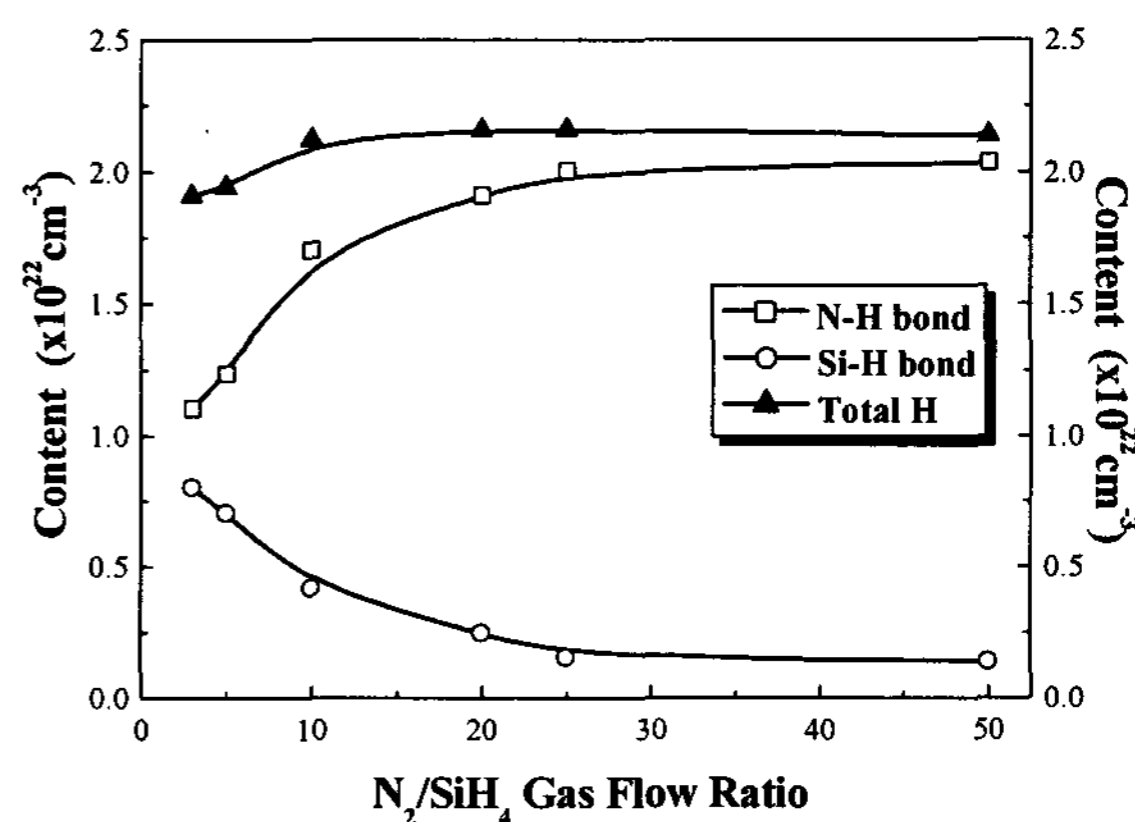


Figure 2. hydrogen concentration for the SiNx films prepared by different N₂/SiH₄ gas flow ratio

Figure 3 shows deposition rate and the refractive index of SiNx film as a function of N₂/SiH₄ gas flow ratio and existence and nonexistence of N₂ plasma treatment. The N₂ plasma treatment reduces the deposition rate and increases the refractive index from its original value of SiNx film without plasma treatment. The deposition rate is 11.1 nm/min no N₂ plasma treatment at the gas flow ratio of 5. After N₂ plasma treatment, deposition rate reduces 9.3nm/min. The refractive index increases about 0.2 magnitudes after plasma treatment than before plasma treatment.

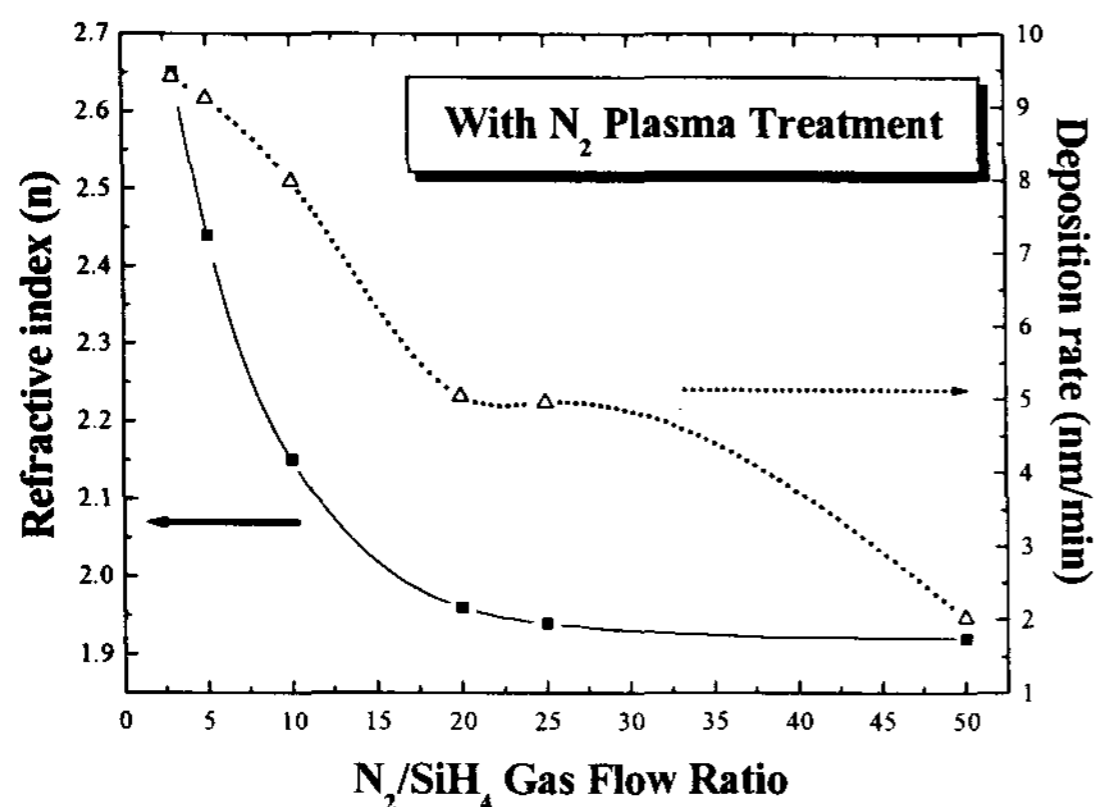
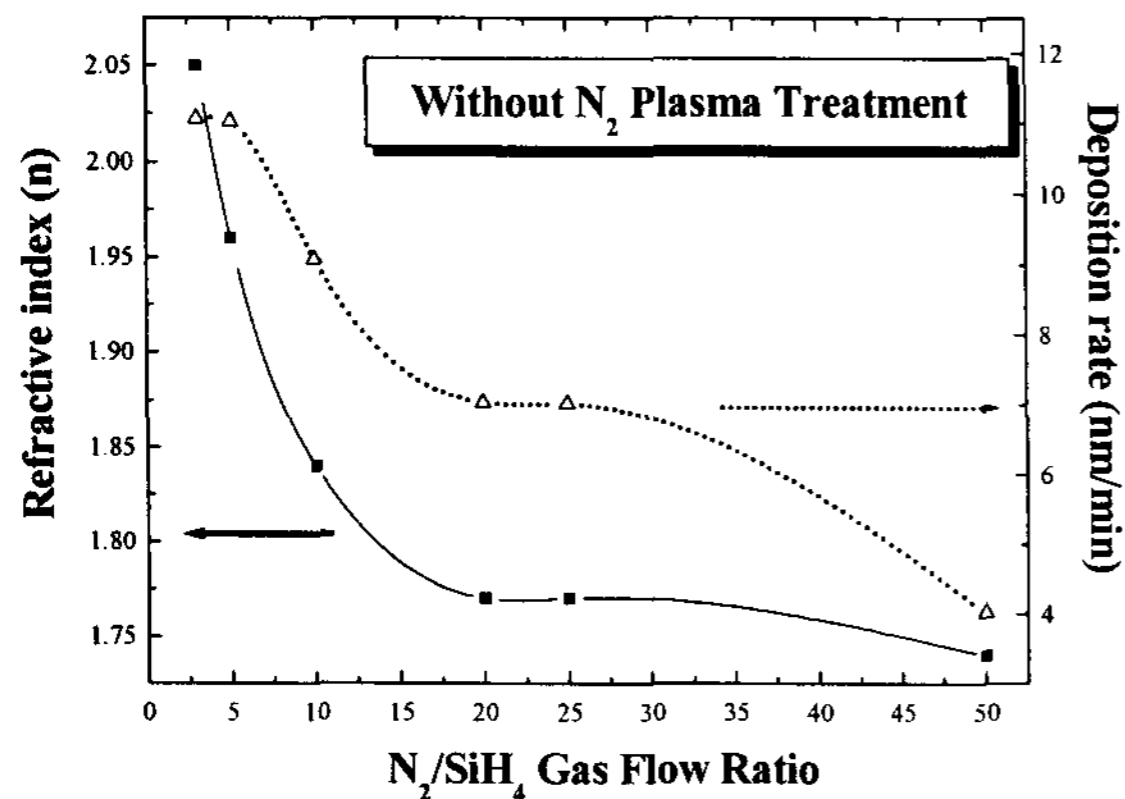


Figure 3. Refractive index and deposition rate as existence and nonexistence of N₂ plasma treatment

Figure 4 shows the capacitance-voltage (C-V) curve of Al/SiN_x/Si with and without N₂ plasma treatment. The main difference between the two curves is in the amount of hysteresis observed in their transfer characteristics. As can be seen from Figure 4, the direction of hysteresis was clockwise, which is contributed by the mobile charge. It can be attributed that by employing N₂ plasma treatment, interface traps such as mobile charges and injected charges were removed, which helps to show a very narrow hysteresis of C-V curve, and shift the flat band voltage towards negative voltage. These results indicate that N₂ plasma treatment induces a small number of slow interface states, which produce an important hysteresis phenomenon. These phenomena are probably related to the nitridation induced by this plasma treatment [6]. The reduction of mobile charge (naturally positive) improves the insulating property of SiN_x film.

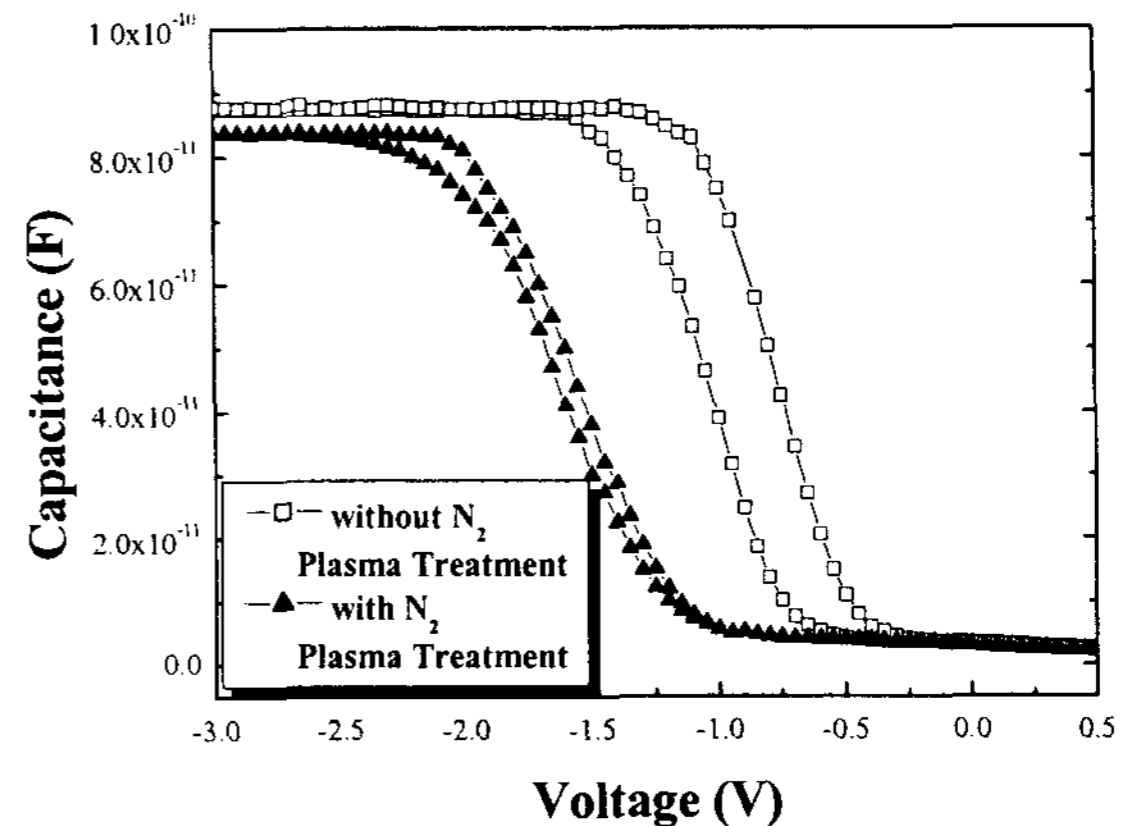


Figure 4. Comparison of the CV characteristics for SiN_x films with N₂ plasma treatment and without N₂ plasma treatment

Figure 5 corresponds to the leakage current density of the SiN_x film prepared by different N₂/SiH₄ gas flow ratio. At the electric field of -0.6 MV/cm is the leakage current density of $7.29 \times 10^{-6} \text{ A/cm}^2$ for the gas flow ratio was observed 5. An increase in the gas flow ratio from 20 to 50 causes an increase in the leakage current density from $5.45 \times 10^{-8} \text{ A/cm}^2$ to $2.34 \times 10^{-7} \text{ A/cm}^2$. Addition of N₂ reduces peak intensity of Si-H bond and increases peak intensity of N-H bond. These results were reduced leakage current density for addition of N₂. But, in case of the gas flow ratio of 50, the electrical properties of an insulator layer become poor, because of the presence of excess nitrogen in the films.

Figure 6 shows the effect of N₂ plasma treatment process on the I-V characteristics of the SiN_x film. For N₂ plasma treated samples, the leakage current density was reduced by two orders with respect to the sample having no N₂ plasma treatment. The decrease in the leakage current density has two possible causes. One is the plasma treatment plays a cleaning role on a silicon substrate. The N₂ plasma treatment can also remove impurities left on the surface after conventional wet etching. The other is related to the nitridation induced by N₂ plasma treatment. As we know from the C-V curve, reduction of interface defects like mobile and injected charges decreases the leakage current density.

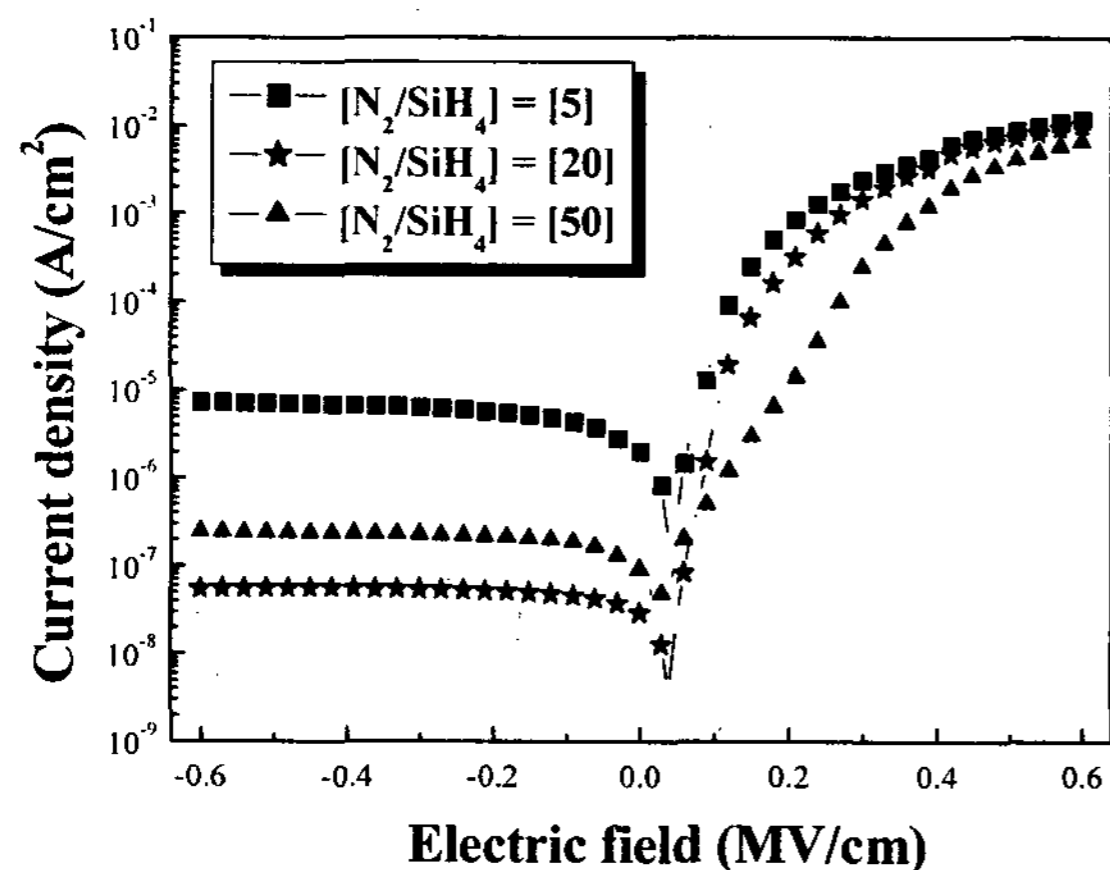


Figure 5. Fig. 5. I-V characteristics of SiNx films without N₂ plasma treatment

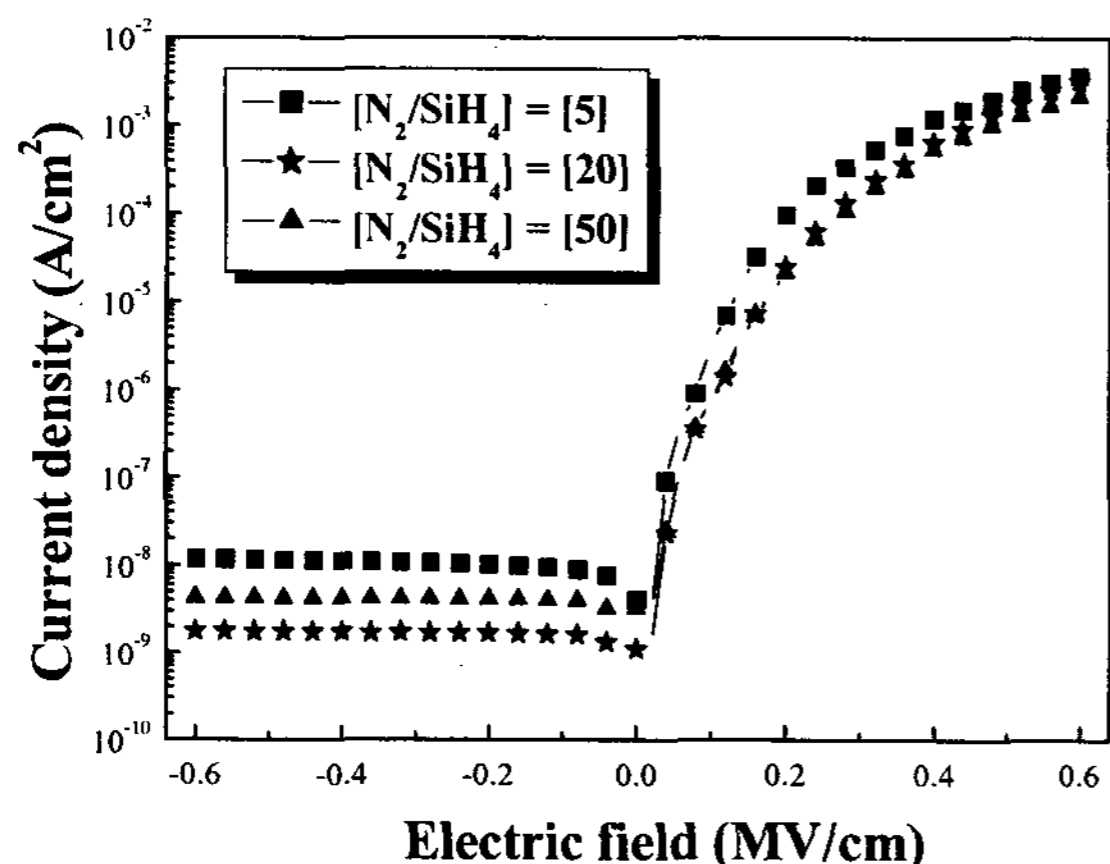


Figure 6. I-V characteristics of SiNx films with N₂ plasma treatment

4. Conclusions

From the present work it can be concluded that, it is possible to get a good quality SiNx film at low temperature by PECVD. Our research gave evidence that by proper choosing the nitrogen-to-silane gas flow ratio, H-atom release from the growing SiNx film may be obtained at as low temperature as 300 °C. It can be adapted to TFT that need a low temperature processing. Also, it is proved that N₂ plasma treatment removed a mobile and injected charges existing in SiNx layer and interface. It means that the electrical and physical properties were improved. So the hysteresis of C-V curve was reduced to a negligible value almost all and a leakage current was decreased.

Therefore, the process of N₂ plasma treatment can be used for low temperature deposition of SiNx film and to maintain to a good quality of SiNx films.

5. References

- [1] D.T. Murley, R.A.G. Gibson, B. Dunnett, A. Goodyear, I.D. French, *J. Non-Cryst. Solids*, p. 187, (1995).
- [2] Jean-Jong Kim, Hyung-Ho Park, Song-Hoon Hyun, *Thin Solid Films*, p. 377-378, (2000).
- [3] M.R. Wertheimer, L. Martinu, E.M. Liston, in: D.A. Glocker, S.I. Shah (Eds.), *Handbook of Thin Film Process Technology*, IOP Press, Bristol, Chapter E3.0, (1996).
- [4] J.E. Klemberg-sapieha, G. Czeremuszkina, in: K.L. Mittal, A. Pizzi (Eds), *Adhesion Promotion Techniques*, Marcel Dekker, New York; p. 139, (1999).
- [5] D.-Q. Yang, L. Martinu, E. Sacher, A. Sadough-Vanini, *Applied surface science* 177, pp. 85-95, (2001).
- [6] E. Redondo, M.N. Blanco, I. Martil, G. Gonzalez-Diaz, *Microelectronics Reliability* 40, p. 837-840, (2000).
- [7] W. Kern, and D.A. Puotinen, *RCA Review*, p. 187, (1970).
- [8] Luis da Silva Zambom, Ronaldo Domingues Mansano, Rogerio Furlan, *Vacuum*, volume 0, (2001).
- [9] W. A. Lanford, M. J. Rand, *J. Appl. Phys.* 49(4), p. 2473-2477, (1978).