SILICON NITRIDE DEPOSITED BY INDUCTIVELY COUPLED PLASMA USING DICHLOROSILANE AND AMMONIA

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Abstract

Silicon nitride films were deposited at low temperature (350 °C and pressure of 60 mtorr, on silicon substrate, using an Inductively Coupled Plasma Chemical Vapor Deposition system (ICP-CVD). Different ammonia to dichlorosilane flow ratios (1.4 to 9.5) and RF powers (25 and 50W) were adopted for comparison. Deposition rates of the order of 2.6 to 12.3 nm/minute and refractive indexes ranging from 1.710 to 1.818 were determined by ellipsometry. FTIR spectra revealed the presence of SiN breathing and stretching mode, Si-NH-Si bending mode, NH stretching mode. The dielectric constant (4.5 - 5.8), dielectric breakdown electric field 4.3 MV/cm and conductivity 3.10^{-12} (\Omega \cdot cm)^{-1} were determined by capacitance-voltage (C-V) and current-voltage (I-V) measurements. The films present low compressive total stress but with increase of the concentration of the nitrogen in the film the total stress tend to tensile.

1. Introduction

Silicon nitride films have found several applications in the microelectronic industry. These films have a great potential as electrical insulators [1], gate dielectric in thin film transistors (TFTs) [2,3], inter metal dielectric, passivation layer for ions and water diffusion [4,5], mask at local oxidation and selective doping, mask for silicon KOH etching and present other applications in optical devices [6,7].

The film characteristics depend on several different deposition process parameters, such as the gas composition and pressure, the substrate temperature, the energy of the impinging ions etc.

The main hydrogen source in the deposited silicon nitride films, when is used silane and ammonia gases, is the ammonia. But when fluorides gases are used, SiH_{2}F_{2} [8], NF_{3} [9] and SiF_{4} [10], quantity of [Si-H] dangerous bonds decrease and Si-F bonds are formed in its place. This substitution occur because the Si-F bonds are more stable than Si-H bonds. Maybe, we can await the formation of Si-Cl bonds if we use dichlorosilane gas (SiH_{2}Cl_{2}) instead of SiH_{2}F_{2}.

In this work, we investigated the deposition of silicon nitride thin films deposited from dichlorosilane and ammonia. We study the influence of the deposition parameters considering four different dichlorosilane/ammonia mixtures ratios using a proposed high-density plasma based ICP-CVD system. This system was obtained by placing a coil at the inlet side of an LPCVD tube and applying 13.56 MHz power to it.

2. Experimental

The silicon nitride films were deposited by an LPCVD reactor (Thermco, Mini-brute 80) that was adapted to work as an ICP-CVD system [11] using: ammonia/dichlorosilane ratio of 1.4, 4.3, 7.2 and 9.5, temperature of 350 °C, working pressure of 60 mtorr, RF frequency of 13.56 MHz, process time of 8 to 20 minutes and RF power of 25 and 50W. For comparison, we deposited stoichiometric LPCVD silicon nitride at temperature of 720 °C, pressure of 500 mtorr and ammonia/dichlorosilane ratio of 16. Before the deposition the substrates (3” silicon wafers, <100>, p-type, 1-10 \Omega \cdot cm) were cleaned in an HF solution (4%). The thickness of the films and the refractive index were measured by ellipsometry (\lambda = 632.8 nm). The Si/N ratio was analyzed by RBS (Rutherford Backscattering Spectrometry). Chemical bonds were determined by FTIR (Fourier Transformed Infrared). The total stress of the silicon nitride films was obtained by using a stressmeter.

Metal/nitride/silicon capacitors were formed by thermal evaporation of 300 nm thick aluminum film. The capacitors were patterned with a mask composed of 700 \mu m pads. On the wafer backside was evaporated a 300 nm thick Al film.

C-V measurements at 1 MHz were made to determine the dielectric constant. I-V measurements were performed to determine the dielectric breakdown electric field and conductivity.
3. Results and Discussion

3.1 – Deposition rate and refractive index

The films were deposited with thicknesses between 70 nm and 110 nm. Figure 1 shows the deposition rate versus NH$_3$/SiH$_2$Cl$_2$.

![Deposition rate versus NH$_3$/SiH$_2$Cl$_2$ ratio for RF powers of 25 and 50W.](image)

The deposition rate increased with RF power and decreased with the dichlorosilane dilution. Deposition rates presented the following ranges: 2.6 nm/min. to 10.4 nm/min. for 25W and 3.4 nm/min. to 12.3 nm/min. for 50W.

The refractive index behavior as a function of the flow ratios are presented in Figures 2.

![Refractive Index versus NH$_3$/SiH$_2$Cl$_2$ ratio for RF powers of 25 and 50W.](image)

The refractive index of our stoichiometric silicon nitride was 1.99. However, the ICP silicon nitride films show lower refractive index (1.71 to 1.82 for 25W and 1.67 to 1.77 for 50W), decreasing with the increase of nitrogen concentration for 25W indicating that the films become nitrogen rich. This behavior is similar that observed by silicon nitride films deposited from silane and ammonia in LPCVD and plasma deposition and is associated with the lower adsorption of the N-N bonds, compared to that of the Si-Si bond [12]. However, for 50W, the refractive index increase with the increase the nitrogen concentration from NH$_3$/SiH$_2$Cl$_2$ ratio of 4.3. This is an unusual result of refractive index and can indicate the influence of the molecule dissociation energy.

3.2 - Film composition

FTIR spectra revealed the following absorption bands: SiN breathing mode at (480 - 500 cm$^{-1}$) and stretching mode at (835 - 845 cm$^{-1}$), Si-NH-Si bending mode at (1102 - 1128 cm$^{-1}$), NH stretching mode at (3317 - 3327 cm$^{-1}$). Figure 3 shows the FTIR spectra obtained for 25 W.

![FTIR spectra of silicon nitride films deposited from NH$_3$/SiH$_2$Cl$_2$ ratio of 1.4, 4.3, 7.2 and 9.5.](image)

The spectra in figure 3 show that the increase of the gas ratio increases the concentration of NH bonds and decrease the SiH concentration bonds. On the other hand, in figure 3b, the spectra show that the increase of the gas ratio does not affect significantly the concentration of NH bonds, indicating that 25 W is a low RF power to dissociate the N$_2$ molecule. The increase in the RF power increases the N$_2$ molecule dissociation, as the refractive index shows.

3.3 – Electrical characteristics

Typical C-V characteristics were obtained of the capacitors, figure 4, where the maximum capacitance was measured under accumulation conditions at 1 MHz.

The dielectric constant was calculated and for LPCVD silicon nitride ranged between 6.0 - 7.0. For the ICP silicon nitride films we obtained the dielectric constant ranging from 4.5 to 5.8. But we do not found any relation with the NH$_3$/SiH$_2$Cl$_2$ ratio.
Figure 4 – C-V Characteristic of the capacitors for NH$_3$/SiH$_2$Cl$_2$ ratio of 7.2.

Figure 5 and 6 present the relation between dielectric breakdown electric field and conductivity versus NH$_3$/SiH$_2$Cl$_2$ ratio, respectively, for 25 and 50 W.

We can observe that the electric field increase with the NH$_3$/SiH$_2$Cl$_2$ ratio, but for 25 W and NH$_3$/SiH$_2$Cl$_2$ ratio of 4.3 the value became constant. Anyhow, the maximum value obtained for 50 W is 4.0, what is a low value for dielectric breakdown electric field for silicon nitride films. The stoichiometric silicon nitride film we obtained values ranging between 8 - 10.

For conductivity, the RF applied power of 50 W showed the worst value. This result was unexpected because in this RF power we obtained the better values for electric field. However, for RF applied power of 25 W where we have the best values of conductivity, the better value (3.10$^{-12}$ $\Omega \cdot$cm$^{-1}$) is very high when compared with the stoichiometric silicon nitride film (10$^{14}$ - 10$^{15}$ $\Omega \cdot$cm$^{-1}$).

In both cases, the results show that the ICP silicon nitride films probably have more species that are contributing for film conduction. These species can be dangling bonds, bonds between N, H, Cl, Si and metallic contamination (from reactor).

### 3.4 - Total stress

The stress was calculated following the total stress equation [13].

Figure 7 shows the total stress for different NH$_3$/SiH$_2$Cl$_2$ ratio. We obtained low total stress values (-0.67 GPa to +0.21 GPa).

The observed behavior can be explained by the increase of the nitrogen concentration in the film [14], which
affects the internal structure, and consequently the intrinsic stress. For high nitrogen concentration, gas ratios higher than 7.2, the maximum stress is not reached, what can be associated with low defects generation in the film. However, for 50W and gas ratio of 7.2, the total stress increase to tensile stress and cracks can occur.

4. Conclusion

Silicon nitride films were deposited in an ICP-CVD system, using different mixtures of dichlorosilane and ammonia for RF applied powers of 25 and 50W.

The obtained deposition rates range from 2.6 nm/min. to 10.4 nm/min. for 25W and 3.4 nm/min. to 12.3 nm/min. for 50W. The refractive index range from 1.71 to 1.82 for 25W and 1.67 to 1.77 for 50W, decreasing with the increase of the concentrations of ammonia.

The FTIR revealed Si-N breathing mode at (480 - 500 cm⁻¹) and stretching mode at (835 - 845 cm⁻¹), Si-NH-Si bending mode at (1102 - 1128 cm⁻¹), NH stretching mode at (3317 - 3327 cm⁻¹).

The total stress values ranged from compressive to tensile, -0.67 GPa to +0.21 GPa. The increase of the total stress is associated with the increase of the nitrogen concentration in the film.

5. Acknowledgment

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6. References


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