CHAPTER 6 . CONCLUSIONS

Hydrogenated silicon nitride SiN_x:H alloy thin films have been deposited onto silicon and glass substrates by a home-built DC Plasma Glow Discharge system, with silane and ammonia gases as precursors. In this present work, the compositional, bonding and optical properties of the silicon nitride films have been studied as a function of deposition parameters, i.e. the gas flowrate ratio $R = [NH_3]/[SiH_4]$ and the deposition temperature.

IR absorption revealed the incorporation of nitrogen into the Si-matrix through the near-symmetric broad Si-N stretching mode vibration in the region 700 to 1000 cm^{-1} and centred around 860 cm^{-1}. A closer analysis on the IR spectrum yields the following bonding configuration; the Si-N bonding with two stretching absorption modes around 860 and 960 cm^{-1}; the N-H groups, characterized by stretching vibration around 3330 cm^{-1} and bending vibration at 1175 cm^{-1}; the Si-H groups, namely the stretching vibration at 2100 cm^{-1} and the wagging vibration near 630 cm^{-1}; and finally the Si-O stretching vibration detected around 1000 cm^{-1}. At deposition temperature below 150°C SiH_2 scissoring mode absorption is observed around 750 cm^{-1} which is assigned to incomplete bond-breaking at low deposition temperature.

The Si-N vibrational mode which peaks around 860 cm^{-1} is assigned to the isolated SiN_3 trigonal site while the vibrational mode which peaks around 970 cm^{-1} is assigned to the formation of the minimum stoichiometric cluster site of Si-$(NSi_2)_4$. As the NH_3 to SiH_4 flowrate ratio was increased more SiN_3 trigonal site is replaced by the formation of the stoichiometric cluster site. Higher deposition temperature promotes reaction probability and it is manifested through the increasing intensity of the 860 cm^{-1} Si-N peak absorption as the substrate temperature was increased. The growth of a more ordered Si-N network is also favoured when the deposition temperature was increased. This has been indicated with the increasing intensity of the 960 cm^{-1} Si-N absorption peak. Higher deposition temperature however also has an effect of reducing the sticking coefficient of the plasma active species and therefore the intensity of both the Si-N absorption peaks decreases when the substrate temperature was increased further.

Absorption due to Si-H and N-H stretching bonds around 2100 cm^{-1} and 3500 cm^{-1} respectively , whose concentrations are regarded as a measure of the hydrogen content of the film, increases markedly with nitrogen content. The hydrogen is mainly bonded to Si. Hydrogen incorporation into the film is comparatively low, in the magnitude of 10^{-21} to 10^{-22} cm^{-3}. Nitrogen seems has a role in retaining the hydrogen effusion from the solid phase during plasma deposition. The hydrogen content decreases almost exponentially when the substrate temperature was increased from 31°C to 300°C, which is due to the re-evaporation of weakly bonded hydrogen from the films and increasing decomposition rate of H-containing species with increasing temperature.

An appreciable oxygen incorporation into the films is detected in the form of Si-O stretching absorption around 1000 cm^{-1}. The amount is non-dependent on the gas flowrate ratio or the nitrogen content of the film. Possible source of oxygen contamination are the moisture trapped in the surfaces of the reaction chamber, and also the glow discharge sputtering of the inner wall of the reaction chamber and of the glass substrates. The concentration of the oxygen contamination however decreases prominently as the deposition temperature increases. This variation is as a result of a temperature sensitive preference of the radical adsorption, in which chemical reaction on the substrate surface favours oxygen precursors at a lower deposition temperature.

The film composition has been expressed in terms of mole fraction x=N/Si estimated through a quadratic dependence of x on optical energy gap E_g and this approximation is shown to be in a fair agreement to the x values estimated from the IR absorption intensity of the Si-N bond. The mole fraction x increased smoothly from zero towards 0.88 as the NH_3 to SiH_4 flowrate ratio R was increased from zero to 5. The N/Si ratio is found to be strongly dependent on the gas flowrate ratio R in the form $x=CR^a$, and in this work the values of C=0.6 and a=0.3 was obtained.

The variation of the Si-N bond IR absorption parallels to that the changes in the optical energy gap as the NH_3 to SiH_4 ratio was increased. E_g increases gradually and roughly linearly from for $x \leq 0.55$, and later rapid E_g widening occurs as the stoichiometry is approached. At low N contents the optical gap is mainly determined by the Si-Si bond concentration which is similar to those of a wide gap a-Si:H while at higher N contents the Si-Si bonds have been substituted by the Si-N bonds, and when the number of the Si-Si bonds becomes too small to allow the existence of a connected Si-network the optical gap widening occurs. The transition observed around N/Si=0.72 is a result of the conversion from the tetrahedral network to a Si_3N_4 network. The increase of bonded H atoms has an influence towards widening the optical gap and its role appears to be less dominant as the film becoming N-rich. The energy gap shifted gradually from 3.66 eV towards 2.71 as a the substrate temperature was increased from 31°C to 300°C. Below the deposition temperature of 150°C it seems that the hydrogen content of the films or the hydrogen loss from the layers due to the increasing growth temperature has a great influence on the optical gap. The higher rate of hydrogen loss in the temperature range of 31°C to 150°C may have contributed to the decrease in E_g within this temperature range. Beyond 150°C the film N/Si ratio content factor plays a more dominant role in determining the E_g.

The static refractive index n_0 displayed a decreasing tendency as the films becoming N-rich which is attributed to the denser Si-N amorphous network compared to the Si-Si network due to the shorter Si-N bond (1.75Å) than the Si-Si bond (3.01Å). Therefore the refractive index closely is related to the film composition x. The static refractive index however increased with increasing substrate temperature regardless of the change in the N/Si content of the film. Higher temperature stimulates the rearrangement of atoms and ions on the substrate surface hence resulting films with fewer defects and higher density. The density effect overshadows the N/Si ratio effect. The slightly lower refractive index values obtained in the present work are most probably due to the non-negligible oxygen incorporation.

The variation of the average growth rate as a function of NH_3 to SiH_4 flowrate ratio R exhibited 2 opposite trends. A decreasing film growth rate was due to the limited supply rate of silane reacting species to the substrate surface region. At higher flowrate ratio the film average deposition increased slightly as a result of an increase in the fast electron concentration with an increase in ammonia gas supply which in turn enhances the ionization efficiency. A decrease in film growth rate with substrate temperature is caused by the increase in the diffusion rate of reactive species on the substrate surface. Although the reaction probability of the reacting source gases is supposed to increase at higher temperature, however, the sticking coefficient of the active species decreases with increasing substrate temperature and therefore lead to overall decrease in the film growth rate.

As for all glow discharge SiN_x:H thin films, DC glow discharge thin films are found to have compositional, structural and optical properties very dependent on deposition conditions, and in particular the ammonia to silane flowrate ratio R and the substrate temperature.