CHARACTERIZATION OF a-SiNx THIN FILM DEPOSITED BY INDUCTIVELY COUPLED PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

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ABSTRACT

Silicon nitride thin films are deposited at low temperature using the inductively coupled plasma enhanced chemical vapor deposition.(ICP-CVD) N_2 and SiH_4 gases are used as reactant gases for deposition of silicon nitride thin films with low hydrogen content. Composition, refractive index, and hydrogen content of the films were examined with variation of N_2 flow rate, RF power and substrate temperature. As N_2 flow rate and RF power increase and substrate temperature is lowered, N/Si ratio is reduced producing higher refractive index of the film. Hydrogen content of the films is calculated by FTIR spectroscopy and is much less than those of the films deposited by conventional PECVD using SiH_4/N_2 gases since N_2 gas is used instead of NH_3 gas. Total hydrogen content is constant regardless of RF Power and N_2 flow rate. However, the hydrogen content decreases with increasing substrate temperature due to the release of hydrogen at high temperature.

Introduction

Plasma enhanced chemical vapor deposited (PECVD) amorphous silicon nitride (a-SiNx) films are extensively used in the microelectronic industry for a wide variety of applications as a passivation of integrated circuits, an oxidation mask, a dopant diffusion barrier, the gate dielectric for thin film transistors, an encapsulant for Ⅲ-Ⅴ semiconductors, and a charge storage layer in MNOS nonvolatile memories. A number of investigations of the deposition and characterizations of PECVD a-SiNx films have been reported. Usually, they used the SiH_4/NH_3 gases as reactant gases since it was more controllable.[1,2,3,4] Also, $SiCl_4$ was preferred to SiH_4 as a silicon source since it is easier and safe to use. However, this process was avoided in microelectronic applications due to the contamination of the films by Cl.

The incorporated hydrogen content in a-SiNx film is important since it has a great effect on the properties of the films.[3,4,5] Generally, hydrogen in a-SiNx film is undesirable for microelectronic applications. First, it reduces the insulating behavior of gate insulator because of formation of defects due to the presence of the hydrogen. Second, when the a-SiNx film is used as a passivation layer of MOSFET(metal-oxide-silicon field effect transistor) devices, it can cause a parameter shift due to the out-diffusion of the weakly bonded hydrogen. Also, hydrogen evolution at high temperature induces the large stress and imperfections within the films. Thus, it have been carried out investigations to reduce the hydrogen content in the PECVD a-SiNx films.[6,7,8]

In this work, a-SiNx films were deposited using inductively coupled plasma enhanced chemical vapor deposition(ICP-CVD) with SiH_4/N_2 gases as the reactant gases. The variation in the characteristics of the films including hydrogen content was investigated depending on the deposition parameters. Then, the results are compared with the others of the a-SiNx films deposited using conventional PECVD and SiH_4/NH_3 gases as the reactant gases.

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Experiment

Fig. 1. is a schematic diagram of a ICP-CVD used in this study. A RF coil is wound on an Al_2O_3 tube plasma chamber. A 13.56MHz, 1.2kW RF power is supplied to coil. The silicon nitride films on (100) p-type Si substrate were deposited using SiH_4/N_2, and Ar as diluent gases. N_2, Ar gases were premixed in a gas mixing box, and the gas mixtures were passed through the plasma chamber. The plasma gas dissociates the SiH_4 gas ejected from the gas ring. The substrate is rotated at 5rpm for uniform deposition. Deposition characterictics have been observed for three process variables. The substrate temperature, RF power, SiH_4/N_2 gas flow rate ratio were systematically changed while the rest were held constant. The deposition condition is listed in Table 1.

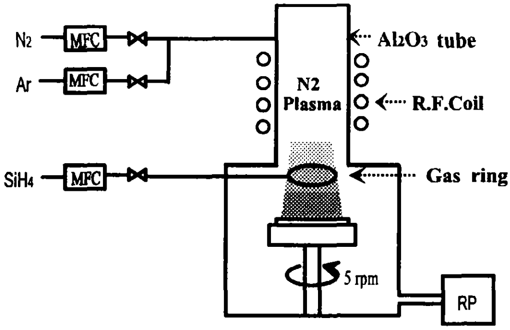

Fig. 1. Schematic view of ICP-CVD system.

Table. 1. Deposition conditions and variables of SiNx.

Deposition Variables	Power (W)	N_2(sccm)	SiH_4 (sccm)	Ar (sccm)	Temperature (℃)	Pressure (mtorr)
N_2 flow rate	200	10, 20, 30, 40	1	150	300	160
RF Power	200, 300, 400, 500, 600	10	1	150	300	140
Temperature	200	10	1	150	25, 100, 200, 300	140

Results

Compositional analysis.

The compositional analyses of SiN_x films were performed by AES. We measured the peak-to-peak height of Si_{LMM} and N_{LMM} in the spectrum and checked the height ratio of N/Si as a relative composition ratio of nitrogen and silicon. The relative N/Si ratio with various deposition conditions is shown in Figs. 2, 3. As a matter of course, the N/Si ratio increases as N_2 flow rate increases. Also, the N/Si ratio decreases with increasing substrate temperature and decreasing RF power. Generally, the generation rate of radicals is larger than that of ions since the dissociation energy of gas molecule is lower than ionization energy. Also, neutral radicals have longer lifetime than ions because positive ions meet electrons easily near the surface and chamber wall. Therefore, the concentration of radicals is much higher than that of ion and major deposition agent is neutral radical. With a very crude approximation, the molecular dissociation probability is proportional to $\exp(-\Delta E / kT_e)$, where ΔE is a dissociation energy and T_e is an electron temperature.[9]

If T_e is raised, the concentration of the reactant gas having larger ΔE is changed more widely. It results in changing of stoichiometry of the film. In N_2/SiH_4 system, the dissociation energy of N_2 gas is 9.9 eV, and SiH_4 is 3.1 eV. Therfore, as RF power increases, electron temperature increases and N/Si ratio increases. Thus, the effect of RF power is similiar to that of N_2 flow rate.

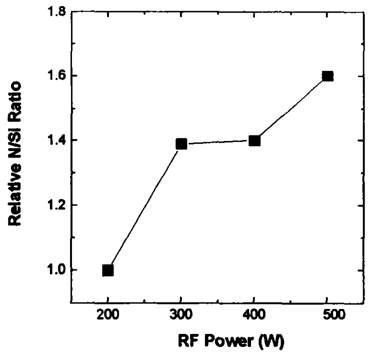

Fig.2. Relative N/Si ratio with variation of RF power.

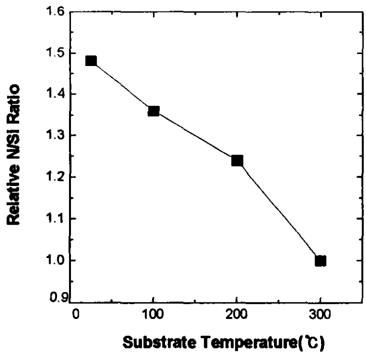

Fig.3. Relative N/Si ratio with variation of substrate substate.

<u>Refractive index and deposition rate.</u>

The refractive indices and deposition rate of the SiNx films as a function of deposition parameters are shown in Figs. 4, 5, 6.

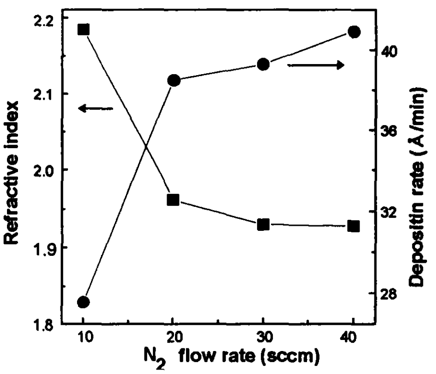

Fig.4. Refractive index and deposition rate with variation of N_2 flow rate. (SiH_4:1sccm)

Fig. 4. shows the refractive index and deposition rate with a variation of N_2 flow rate. (Squares and circles represent the refractive index and deposition rate, respectively.) Deposition rate increases with increasing N_2 flow rate since more activated N_2 gas is generated. Refractive index decreases from 2.18 to 1.93 at 200W with increasing N_2 flow rate. According to AES data, as the N_2 flow rate increases, N/Si ratio increases. Normally, the lower N/Si value will give the higher refractive index due to more absorptive Si-Si bonds in the film.

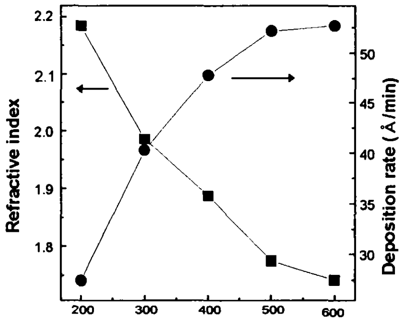

Fig.5. Refractive index and deposition rate with variation of RF power.

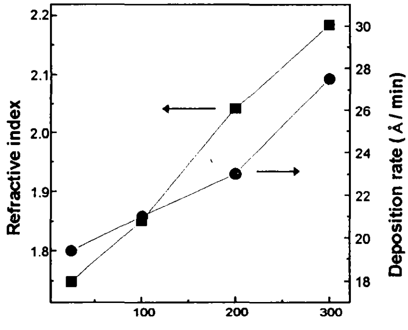

Fig.6. Refractive index and deposition rate with variation of substrate temperture.

Also, as RF power increases from 200W to 600W, more N_2 gas is dissociated (Fig.5.). Thus, the deposition rate increases and refractive index decreases extensively from 2.18 to 1.74. In particular, the decrease of refractive index of the film due to the increase of power is larger than that of N_2 flow rate, since only N_2 gas is passed through plasma chamber and dissipated directly by the RF power, while the SiH_4 gas is dissipated indirectly. Thus RF power is more controllable parameter of reaction stoichiometry than gas flow rate, which is characteristic of ICP-CVD.

Fig. 6. shows the effect of the substrate temperature on the refractive index and deposition rate. As the substrate temperature increases, the surface atom gains more energy to diffuse to a stable site. Therefore, the film density increases with substrate temperature. The increase of refractive index with substrate temperature agrees with the density trends. Also, this observation is consistent in the AES analysis which shows a decreased N/Si value with temperature.

The hydrogen content

The hydrogen content and the hydrogen bonding configuration (Si-H, N-H) depend on the deposition conditions, and have a great influence on film properties. It has been known that the hydrogen content in a-SiNx films deposited by PECVD is mainly determined by substrate temperature, and the hydrogen configuration depends on the gas flow ratio and RF power at a given substrate temperature.[10,11]

Fourier Transform IR (FTIR) spectroscopy was used for hydrogen analysis of the films deposited on the silicon substrate.[9,10,11] The main absorption peak due to the Si-N stretching bond appears at 890cm^{-1}, and the absorption peaks due to the Si-H stretching bond and the N-H stretching bond appears at 2180cm^{-1} and 3340cm^{-1}, respectively. The hydrogen content is analyzed quantitatively by using the Beer-Lambert's law, as shown below

$$A = \log(T_0/T) \quad (1)$$

$$C = \frac{k}{t}\int \frac{A(w)}{w} dw \quad (2)$$

where A is the absorbance, t is a film thickness and k is an absorption cross section which is a proportionality constant representing the vibrational strength. The absorption cross section k of hydrogen is 7.4 × 10^{-18} cm^2 for N-H and 5.3 × 10^{-18} cm^2 for Si-H which was obtained in the Lanford and Rand's result.[10] The hydrogen content with variation of deposition parameters are shown in Figs. 7, 8, 9.

Fig. 7. shows the hydrogen content with varying N_2 flow rate. The total hydrogen content is almost constant about 3 × 10^{21} atoms/cm^3. The Si-H bonding decreases and N-H increases with increase of N_2 flow rate.

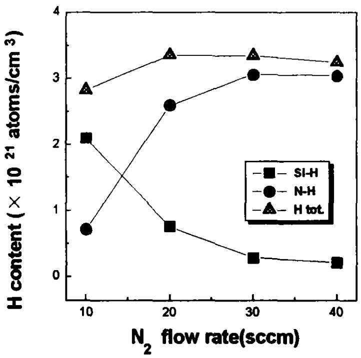

Fig. 7. Hydrogen content with variation of N_2 flow rate.

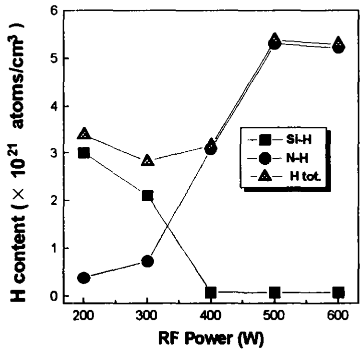

Fig. 8. Hydrogen content with variation of RF power.

Fig. 8. presents the hydrogen content with variation of RF power. The effect of RF power is similiar to that of the N_2 flow rate. N-H bonding increases and Si-H bonding is decreased but total hydrogen content is almost constant with increasing RF power. Since only N_2 gas is dissociated directly by RF power and dissociated H atoms from SiH_4 gas are more favorable to the nitrogen dangling bond than silicon dangling bond, more N-H configurations are created with increasing RF power. At high RF power, no more Si-H configuration is detected with FTIR spectroscopy, but the N-H configuration increases due to the increase of N content in the film enhances total hydrogen content.

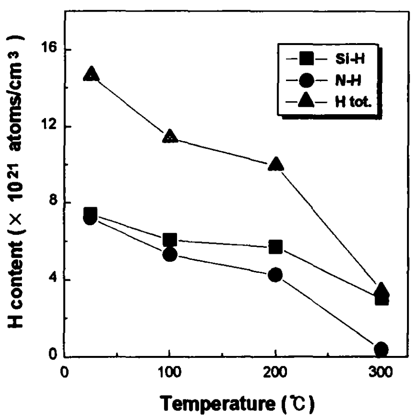

Fig. 9. Hydrogen content with variation of substrate temperature.

Fig. 9. shows the hydrogen content of the films deposited at various substrate temperatures. As the substrate temperature is increased, both hydrogen configurations as well as total hydrogen content decreases. At high temperature, the hydrogen atom obtains more energy required to release from the surface than at low temperature. Thus, Si-H configuration is lowered at high temperature although Si content increases with increasing substrate temperature. Therefore, the total hydrogen content depends only on substrate temperature. However, Si-H bonding is not decreased below 6×10^{21} atoms/cm^3 even at high temperature which means Si-H bonding is not readily dissociated.

Total hydrogen content is about (3-5.5) × 10^{21} atoms/cm^3 regardless of N_2 flow rate and R.F. power when deposited at 300 ℃. This value is lower than those which were reported in previous studies using SiH_4/NH_3 gases in conventional PECVD.[7,9,10,12] For example, total hydrogen content of a-SiNx films which were deposited at 330 ℃ by conventional PECVD using SiH_4/NH_3 gases is around (1.6-2) × 10^{22} atoms/cm^3. Thus, the hydrogen content of the a-SiNx films can be greatly reduced by deposition using SiH_4/N_2 gases, which can be dissociated in ICP-CVD.

Conclusion.

a-SiNx thin films were deposited by ICP-CVD using SiH_4/N_2 gases at the reactant gases. Compositional N/Si ratio changes extensively depending on RF power, N_2 flow rate and substrate temperature. Usually, refractive index of the films is reduced with increasing N/Si ratio obtained by increasing RF power and N_2 flow rate, and decreasing substrate temperature. Especially, the refractive index can be controlled extensively in the range of 1.7-2.2 by variation of RF power since the reaction chemistry is controlled by RF power in ICP-CVD.

The hydrogen content calculated by FTIR spectroscopy is much less than values obtained in other a-SiNx thin films deposited by conventional PECVD using SiH_4/NH_3 gases. This might be due to use of N_2 gas which can be dissociated by ICP instead of NH_3 gas.

Reference

1. M. Maeda, H. Nakamura, J. Appl. Phys. **58**, 484 (1985).
2. R. Chow, W.A. Ranford, K. Wang, R. S. Rosler, J. Appl. Phys. **53**, 5630 (1982).
3. T. P. Smirnova, V. I. Belyi and L. V. Chramova, Thin Solid Films **74**, 287 (1980).
4. R. E. Rocheleau and Z. Zhang, Thin Solid Films **220**, 73 (1992).
5. M. Gupta, V. K. Rathi, R. Thangaraji and O. P. Agihotri, Thin Solid films **204**, 77 (1991).
6. J. S. Yoon, C. V. Deshpandey and R. F. Bunshah, Thin Solid Films **220**, 80 (1992).
7. H. Kyuragi and T.Urisu, J. Electrochem. Soc. **138**, 3412 (1991).
8. H. H. Willard, L. L. Merritt. Jr., J. A. Dean, F. A. Settle. Jr., Instrumental Methods of Analysis, 7th ed. (Wadsworth, California, 1988), p.287.
9. H. Dun, P. Pan, F. R. White and R. W. Douse, J. Electrochem. Soc. : Solid-state Science and Technology **128**, 1555 (1981).
10. W. A. Lanford and M. J. Land, J. Appl. Phys. **49**, 2473 (1978).
11. P. S. Peercy, H. J. Stein, B. L. Doyle and S. T. Picraux, J. Electron. Mater. **8**, 11 (1979).
12. X. Zhang, G. Shi, A. Yang and D. Shao, Thin Solid Films **215**, 134 (1992).