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PROPERTIES OF SILICON NITRIDE FILMS PREPARED BY PLASMA-ENHANCED CHEMICAL VAPOUR DEPOSITION OF NH_3—SiH_4—Ar, NH_3—SiH_4—He and NH_3—SiH_4—N_2 MIXTURES[1]

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This paper reports on the properties of PE CVD silicon nitride obtained from a gas mixture of NH_3—SiH_4—Ar, NH_3—SiH_4—He and NH_3—SiH_4—N_2. Ellipsometric data, IR data and BHF etch rate are presented. It is shown that the carrier gas (N_2, He, Ar) and the reactant gas SiH_4/NH_3 ratio has an influence on the properties of the films. It is found that these PE CVD nitrides are best described as $Si_xN_yH_zO_t$.

I. INTRODUCTION

Silicon nitride films prepared by plasma-enhanced chemical vapour deposition (PECVD) processing have many applications in very large scale intergrated circuit (VLSI) fabrication, such as final passivation layers, multilayer resits, interlevel dielectrics for multilevel metallization structures and diffusion or photolitographic mask coating [1]. However, the use of a plasma-deposited film in electrically active regions of integrated circuits is still very limited, due to both the difficulty in controlling and the poor understanding of the film properties and the deposition mechanism.

II. EXPERIMENTAL PROCEDURE

Silicon nitride films were deposited on bare silicon *p*-type substrates in a high frequency parallel-plate plasma reactor, where the frequency, the RF power and the substrate temperature were maintained at 13.56 MHz, 0.06 W cm^{-2}, and 310 °C, respectively. The diameter of the electrodes was 12 cm and they were 2 cm apart. The RF power was fed to the upper electrode, while the lower electrode, which held the substrates was grounded. The gas mixture of SiH_4 and NH_3 was directly introduced into the reaction chamber, and the flow rates of these gases were 3—10 sccm and 10—30 sccm, respectively. The flow rates of the carrier gases (N_2, He, Ar) were maintained at 150 sccm. Film thickness and refractive index were measured by means of a He—Ne laser ellipsometer ($\lambda = 632$ nm).

III. RESULTS AND DISCUSSION

Deposition. — Figure 1a. represents the dependence of the layer grow rates on the SiH_4/NH_3 ratio. This dependence is of a linear character. For a substrate temperature of 310 °C, on the SiH_4-to-NH_3 ratio of 0.5 the dependence of the growth rate on the total pressure of the reactor is obtained (Fig. 1b). The dependence is also of a linear character. The refractive index of the layer in the pressure interval studied does not change.

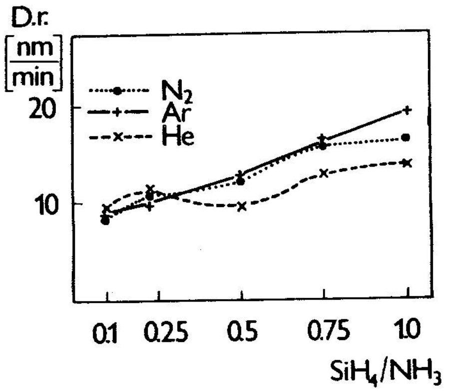

Fig. 1a. Nitride deposition rate as a funkcion of SiH_4/NH_3 flow ratio.

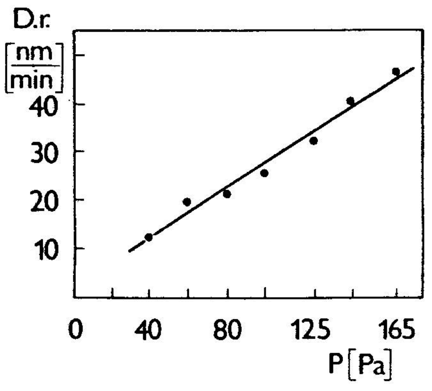

Fig. 1b. Growth of rate dependence on the pressure.

For the silicon nitride film deposition, the helium carrier gas tends to enhance the film thickness and the refractive index uniformity as compared with other carrier gases (Ar, Kr, Xe) under the same deposition conditions. This is due to a better thermal conductivity of the helium plasma and higher Penning reaction efficiencies of helium and the reactant gas in the plasma [2]. These properties suppress the runaway temperature during the deposition process and enhance the uniform distribution of the reactive species across the diameter of the plasma reactor. As a result, the deposited film thickness and the refractive index became more uniform. In Table 1. we have summarized the uniformity of the refractive index *n* and the thickness *t* of the silicon nitride films.

It is seen that both gas systems SiH_4/Ar and SiH_4/He produce acceptably uniform films, but SiH_4/He leads to somewhat more uniform films.

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Table 1

Nonuniformity of refractive index *n* and thickness *t* over a 2.5 in wafer.

	n [%]	*t* [%]
SiH_4/He	<0.4	<1
SiH_4/Ar	<0.6	<2
SiH_4/N_2	<1	<5

Etch rate. — The chemical reactivity, particularly the etch rate of silicon related nitride films, is closely relted to structure and composition [3, 5]. Figure 2. shows that the BHF etch rate is strongly dependent on the SiH_4/NH_3 ratio. Although the decrease in the etch rate is related to the increas in the silicon concentration, the hydrogen incorporation in the film as Si—H and N—H tends to have a marked influence. As the hydrogen concentration increases, the deposited films become more porous with a lower density and contain more of the weaker Si—H and N—H bonds as compared to more of the stronger Si—N in lower hydrogen concentration silicon nitride films. The weaker Si—H and N—H bonds will break more easily and facilitate the etching process.

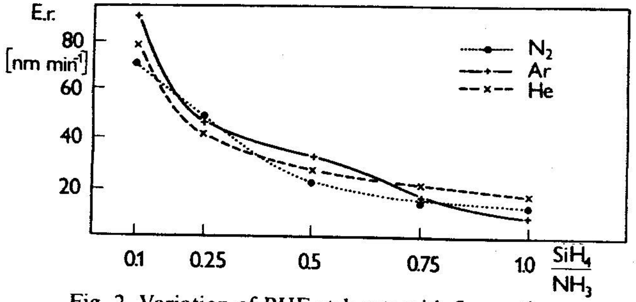

Fig. 2. Variation of BHF etch rate with flow ratio.

The decrease of the etch rate with increased silicon concentration in the films can also be explained by the use of a similar Si—Si and Si—N bonding energy difference. Since there is also a strong inversed correlation between silicon and hydrogen concentrations in the Si-rich silicon nitride film systems, the decrease in the etch rate should be attributed to the effect of both hydrogen and silicon concentrations in the films in which the effect of hydrogen is more dominat.

Refractive index. — The refractive index has been used as a quality control index for the deposition process. Experimental results have shown that the refractive index of silicon nitride films prepared by the PECVD process depends on the film composition and varies linearly with the change in the Si/N ratio of the films. The film with the stoichiometric composition of silicon nitride has a refractive index of about 1.95. The refractive index increases with increasing Si/N ratio [4].

The refractive index of the present films is plotted in Fig. 3. as a function of the gas phase composition for the films deposited at an RF power density of 0.06 W cm^{-2} and a chamber pressure of 40 Pa. The refractive index increases with increasing SiH_4/NH_3 ratio. Since we can expect that the composition of the deposited films positively depends on the gas phase composition, this variation is quite reasonable.

IR analyses. — The IR spectrum of silicon nitride films with a refractive index of 1.93 showed the presence of N—H (3353 cm^{-1}), Si—H (2171 cm^{-1}), Si—O (1107 cm^{-1}), Si—N (867 cm^{-1}), and Si—Si (610 cm^{-1}) (Fig. 4.).

Infrared spectra of silicon nitride films after annealing in the forming gas (450 °C, 120 min) showed a reduction in the intensity of Si—H and N—H bonds (Fig. 4.). These results indicate that a significant amount of hydrogen was evaporated from the film during the annealing process.

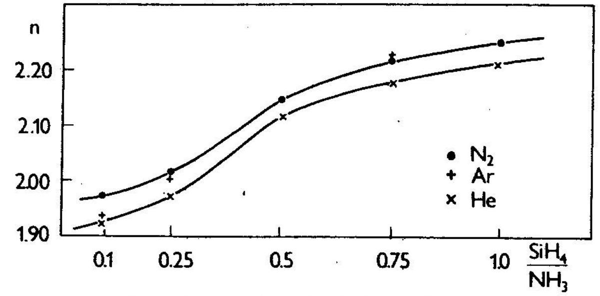

Fig. 3. Variation of refractive index with flowratio.

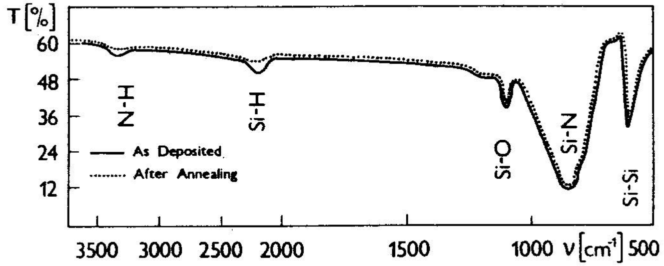

Fig. 4. IR spectra of plasma deposited silicon nitride films RI = 1.93

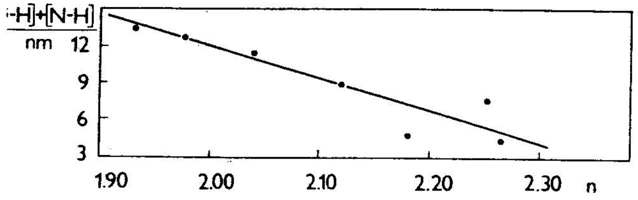

Fig. 5. Total hydrogen bond density dependence on the refractive index.

The total hydrogen bond density (absorption intensity area unit/nm film thickness) of the Si—H and N—H bonds decreased substantially with increased film refractive index. We also observed the shift of Si—H bonds to a lower absorption frequency peak as the refractive index increased, i.e. the films become more Si-rich.

The oxygen content is probably from the native oxide, and, possibly, the contamination that occurred during the deposition processing. The Si—Si bonds are probably due to both the Si substrate and the Si clusters in the film bulk [3].

IV. CONCLUSION

Good uniformity silicon nitride films with refractive indices varying between 1.93 and 2.25 were deposited on silicon substrate surfaces using the PECVD processing. Infrared analyses show that the films deposited under the described conditions contain significant amounts of hydrogen. A substantial loss of hydrogen was observed after annealing. The concentration of other elements, such as Si, N, and O, however, remains unchanged. Summarily, the results presented indicate that the properties of silicon nitride films are strongly dependent upon the reactant gas SiH_4/NH_3 ratio. Excess silicon is a primary contributor for determining film properties, but the hydrogen incorporation and the chemical bonding pattern play an important role which cannot be ignored when discussing these properties.

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СВОЙСТВА ПЛЕНОК НИТРИДА КРЕМНИЯ, ПОДГОТОВЛЕННЫХ МЕТОДОМ ПЛАЗМОХИМИЧЕСКОГО ОСАЖДЕНИЯ ИЗ СМЕСЕЙ $NH_3—SiH_4—Ar$, $NH_3—SiH_4—He$ И $NH_3—SiH_4—N_2$

В работе описаны свойства пленок нитрида кремния, полученных методом плазмохимического осаждения из газовых смесей $NH_3—SiH_4—Ar$, $NH_3—SiH_4—He$ и $NH_3—SiH_4—N_2$. Приведены эллипсометрические данные, инфракрасный спектр а скорости травления в буферном травителе. Показано, что инертный газ-носитель, (N_2, He, Ar) также как и отношение SiH_4/NH_3, влияют на свойства пленок. Из их спектра следует, что состав пленки можно записать в виде $Si_xN_yH_zO_t$.