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Deposition of SiC_xN_y Thin Film as a Membrane Application

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Abstract : SiC_xN_y film is deposited by electron cyclotron resonance plasma chemical vapor deposition system using SiH_4 (5% in Ar), CH_4 and N_2. Ternary phase SiC_xN_y thin film deposited at the microwave power of 600 W and substrate temperature of 700 contains considerable amount of strong C-N bonds. Change in CH_4 flow rate can effectively control the residual film stress, and typical surface roughness of 34.6 (rms) was obtained. Extremely high hardness (3952 Hv) and optical transmittance (95% at 633 nm) was achieved, which is suitable for a LIGA mask membrane application.

1. Introduction

Membrane has several applications in sensors, actuators and microelectronic fabrication processes. Pressure sensor and micropump are examples of their applications. LIGA (Lithographie Galvanoformung and Abformung) process, which can provide extremely high aspect ratio patterns, also requires membrane structure to obtain the contrast under synchrotron radiation. The membrane should meet some critical requirements such as high strength, moderate tensile stress, high optical/ x-ray transmittance and good surface smoothness. Recently, SiN_x has been widely used as a membrane material due to high optical transmittance, easy fabrication process and good chemical stability[1]. However, this material has some drawbacks such as poor mechanical strength for handling and considerable radiation-induced damage. In the meanwhile, there have been quite a few efforts to synthesize the -C_3N_4 compound, which is expected to have extreme hardness character (higher than that of diamond) due to strong covalent C-N bonds[2,3]. In most of the cases, however, very low deposition rate and nitrogen-deficient composition were obtained.

In this paper, SiC_xN_y was synthesized and evaluated for membrane application, because SiC_xN_y has potential advantages in microelectronics and sensor technologies due to its excellent mechanical and electrical properties[4].

2. Experiment

In this experiment, SiC film was deposited by electron cyclotron resonance (ECR) plasma chemical vapor deposition (CVD). The substrate was a 4-inch, (100), p-type Si wafer and predeposition cleaning with aceton and methanhol was executed. Deposition of SiC_xN_y was performed with various gas flow ratios ($SiH_4/CH_4/N_2$) at deposition temperature of 400-700 and microwave power of 300-600 W. Film stress was calculated from the change of the substrate curvature measured by laser reflection before and after the deposition.

Chemical composition and surface roughness of de-posited thin film were analyzed with energy-dispersive X-ray (EDX) instrument installed in the scanning electron microscope (SEM), secondary ion mass spectroscope (SIMS), Fourier transform infrared spectroscope (FTIR) and atomic force microscope (AFM). To evaluate the mechanical behavior of the SiC_xN_y film, micro hardness test was carried out. After the backside window was opened, the wafer was immersed in KOH solution (23 wt%, 85) to etch off silicon from the backside and to form the free standing membrane. And then the optical transmittance of this SiC_xN_y membrane was measured by spectrophotometry.

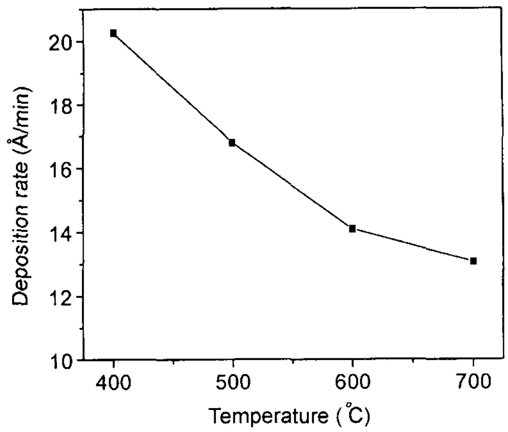


Fig. 1. Deposition rate as a function of (a) substrate temperature at microwave power of 600 W, (b) microwave power at deposition temperature of 700.

3. Results and Discussion

Deposition of SiC_xN_y as a membrane is aimed to synthesize optimum ternary phase SiC_xN_y thin film. Figure 1(a) and (b) show the deposition rate as a function of deposition temperature (at a microwave power of 600 W) and microwave power (at deposition temperature of 700), respectively. The deposition rate decreases with substrate temperature, but no significant change in film composition is observed. This is considered to be due to the reduction in the adsorption of film-forming precursors on the growing surface and/or thermal desorption of absorbed radicals from the surface[5]. The higher microwave power results in an increased deposition rate due to enhanced dissociation of source gases[6]. This en-hanced dissociation effect is more significant for CH_4 and N_2 gases with higher bonding energies compared to SiH_4, which is readily dissociated by thermal energy. This results in a slight increase in N/Si and C/Si ratios with microwave power (not shown). Figure 2 compares SIMS depth profiles of SiC_xN_y films, and hydrogen content is reduced by an order of magnitude by increasing deposition temperature from 400 to 700. Slightly increase of Si-C and Si-N bonds with temperature can be observed in FTIR spectra of Figure 3. Also, decrease in CN (2200-2500 cm^{-1}) triple bonds and increase in strong C-N bonds are observed at higher temperature of 700[7-9]. From these results, it can be con-

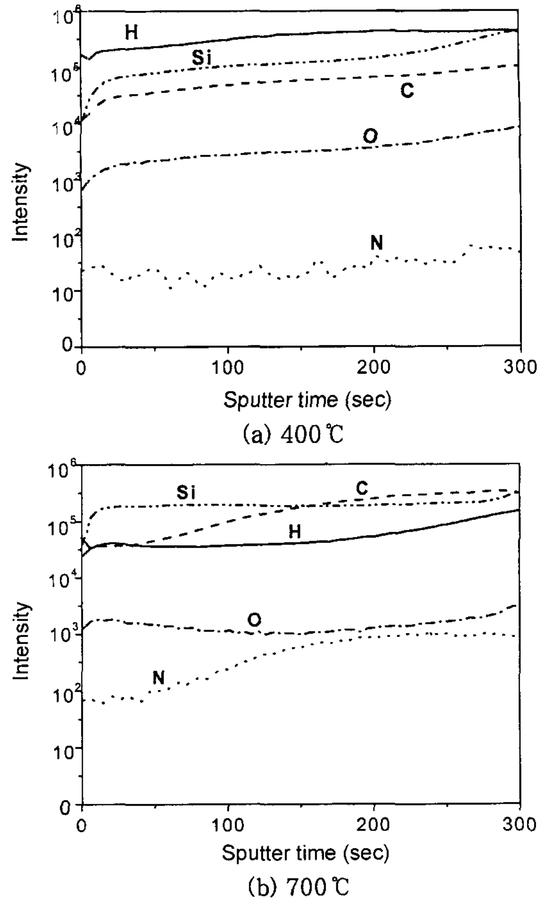


Fig. 2. SIMS depth profile of SiC_xN_y films deposited at different temperatures.

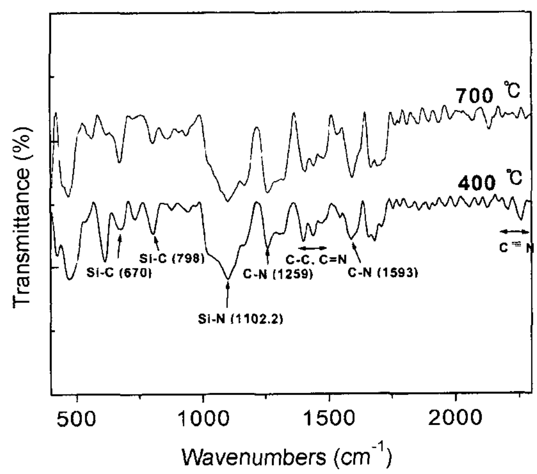
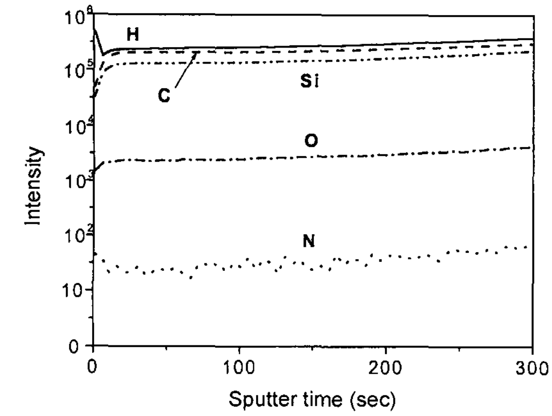
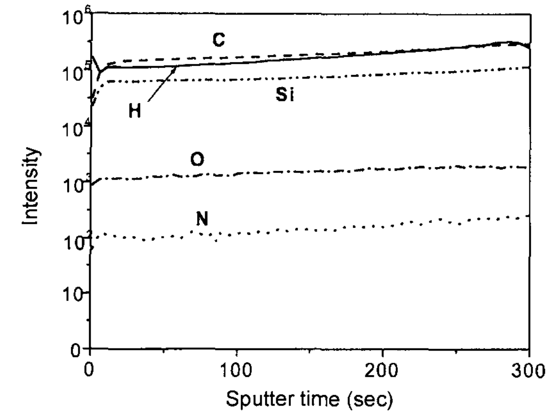


Fig. 3. FTIR transmittance spectra of SiC_xN_y films deposited at different substrate temperatures.

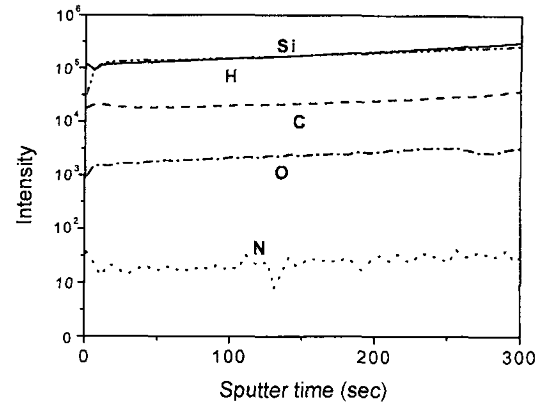


(a) N_2 flow rate: 10sccm

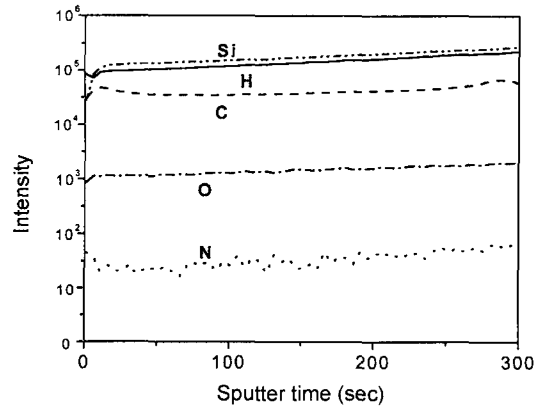


(b) N_2 flow rate: 20sccm

Fig. 4. SIMS depth profile of the film deposited with different N_2 flow rate at 700, 600 W.



(a) CH_4 flow rate: 4sccm



(b) CH_4 flow rate: 8sccm

Fig. 5. SIMS depth profile of the film deposited with different CH_4 flow rate at 700, 600 W.

cluded that weak Si-H and CN bonds are dissociated at high temperature 700, and partly replaced by stronger Si-C, Si-N, or C-N bonds. A deposition temperature of 700 and a microwave power of 600 W were selected in the following experiments.

Figure 4 and 5 show the SIMS depth profiles of the films deposited with different N_2 and CH_4 flow rates, respectively, at a fixed SiH_4 flow rate of 50sccm. Slight increase in N and C contents is observed at higher flow rate of N_2 and CH_4 flow rates, respectively. Slight decrease in H content is observed only with higher N_2 flow rate. Again, this can be explained by replacement of H in relatively weak Si-H or C-H bonds with C and N[10]. This can be confirmed by FTIR spectrum, which shows increased Si-N (1092 cm^{-1}) bonds at higher N_2 flow rate (Figure 6 (a)) and increased Si-C (672 cm^{-1}) and C-N (1560 cm^{-1}) bonds at higher CH_4 gas flow rate (Figure 6 (b))[6-9].

The residual stress of film is an important parameter to realize the self-supporting membrane structure.

Figure 7 shows the residual stress of SiC_xN_y film as a function of CH_4 flow rate. The residual stress can be controlled by the change of CH_4 flow rate (6 sccm) to the appropriate tensile value for membrane application. The shift of residual stress to compressive side with the increase of CH_4 flow rate is believed to result from the replacement of H by larger C.

The surface roughness of SiC_xN_y film was measured to be 34.6 (rms), which is slightly higher than that of SiN_x film (11) but lower than that of SiC (37), both deposited at the same reactor. Micro hardness of SiC_xN_y, SiN_x and SiC films was measured to be 3952

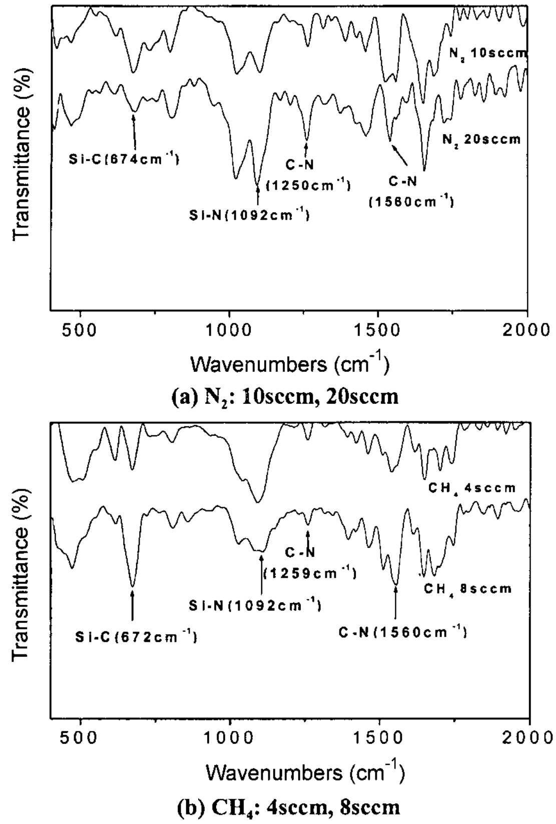


Fig. 6. FTIR transmittance spectra of SiC_xN_y films deposited at CH_4 flow rate of (a) 4 sccm and (b) 8 sccm.

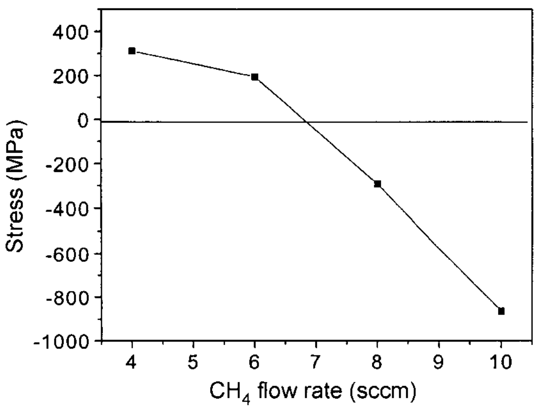


Fig. 7. Residual film stress as a function of CH_4 flow rate at 700, 600 W.

Hv, 3017 Hv and 2092 Hv (Vickers hardness), respectively. The highest value in SiC_xN_y is believed to be due to the strong C-N bonding states. The optical transmittance of 1.3-thick free-standing membrane measured by

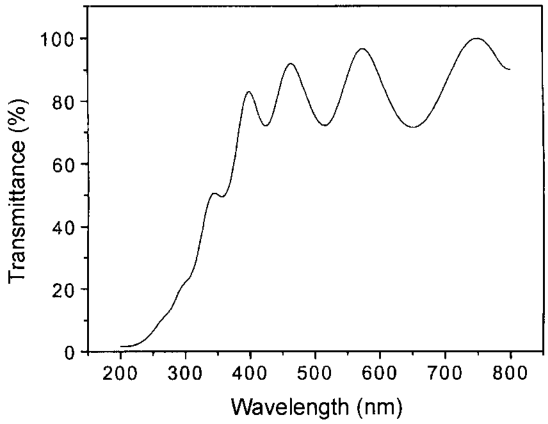


Fig. 8. Optical transmittance of SiC_xN_y.

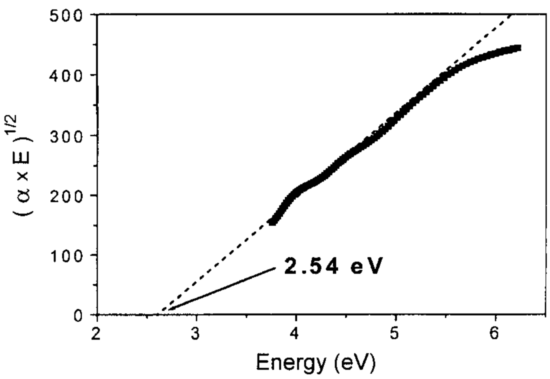


Fig. 9. Taucs plot to determined the optical bandgap.

spectrophotometry in the 200-900 nm wavelength range is shown in Figure 8. The peak transmittance of 95% is obtained at 633nm, and the optical bandgap ($E_{g,opt}$) deduced from the transmittance data by Taucs equation[11] is 2.54 eV.

4. Conclusions

SiC_xN_y thin film was deposited by ECR plasma CVD using SiH_4, CH_4 and N_2. The film deposited at a deposition temperature of 700 and microwave power of 600 W contains considerable amount of strong C-N bonds. Low residual tensile stress and fair surface roughness can be obtained. The micro hardness value is 3902 Hv, which is much higher than that of SiN_x and SiC. The optical transmittance at 633 nm is 95% and the optical bandgap is measured to be 2.54 eV. In conclusion, SiC_xN_y film is suitable for LIGA mask membrane application.

Acknowledgement

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