Comparison of Hexamethyldisilazane and Hexamethyldisilazane/Nitrogen Gas Mixture Plasma Deposited *SiOx* films by Atmospheric-pressure Plasma Cyclone

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Abstract: The aim of this study is to find the correlations between the surface characteristics of atmospheric plasma cyclone deposited films and the process parameters. The influence of process parameters on the characteristics of *SiO_2/SiOx* films deposited in hexamethyldisilazane (HMDSN) and HMDSN/N_2 gas mixture plasmas at atmospheric pressure were studied. The water contact angle meter, Fourier transform infrared spectroscopy, and scanning electron microscopy were used to analyse the film surface characteristics. A possible film growth that prevails in atmospheric-pressure plasma deposition is proposed based on atmospheric-pressure plasma chemistry, nitrogen gas addition, and experimental observations.

Keywords: Hexamethyldisilazane, Atmospheric-pressure plasma, Film, Surface characteristics, Plasma Cyclone,

1. Introduction

Silicon dioxide (SiO_2) is widely used thin film material. It is the most common dielectric in semiconductor technology, serves as corrosion protection or permeation barrier in the packaging industry or is used as a scratch resistant coating on polymers [1]. For the deposition of SiO2 thin films, plasma chemical vapor deposition (PCVD) is suitable for the formation of thin films at a low temperature. However, SiO_2 films are generally deposited with low pressure/vacuum plasma discharges and has been extensively studied in the past decades. Atmospheric pressure plasma (APP) is a promising technique for deposition of thin films. This technique consists of feeding organic monomer into plasma glow discharge and chemically depositing organic/inorganic materials onto various substrate surfaces [2] The use of APPs is a promising procedure for the thin film deposition. This procedure involves feeding organic monomers into glow discharge and chemically forming organic/inorganic thin films onto various substrate surfaces. For researchers, the formation of APP-deposited films and their detailed surface analyses are particularly exciting because plasma-deposited films contain a variety of chemical species. To our knowledge, there is a lack of attempts to evaluate the gas effect of nitrogen gas addition for the organosilicon thin film deposition by atmospheric pressure plasma cyclone. The plasma cyclone deposited thin-film properties will be analytically studied using the HMDSN/N_2 plasma deposition method to clarify and provide insights on atmospheric-pressure plasma deposition processes.

2. Experimental Procedure

This plasma cyclone uses two rotating double-pipe-type plasma jets to create a discharging cyclone to enlarge the deposited sample size and the cyclonic APP treatment were like those reported in earlier studies. Argon gas at a high flow rate (10 slm) and nitrogen gas (20 sccm) were induced from the upper part of the plasma and passed through the gas section as the ionization gas. The water contact angles of the cyclonic APP-deposited organosilicon thin films were measured by taking sessile droplet resting on the film surface image with a contact angle goniometer (Sindatek Instruments). To find out the phenomena of the surface alteration of cyclonic plasma deposited organosilicon thin films, the polar and the dispersion components and the surface energies were estimated using Kaelble–Owens–Wendt method.

$$\gamma_{LV}(1+cos\theta)=2\left(\gamma_L{}^d\gamma_S{}^d\right)^{1/2}+2(\gamma_L{}^p\gamma_S{}^p)^{1/2}$$

The hydrophilic and hydrophobic properties are derived from the polar and dispersed components, respectively. An attenuated total reflection ATR-FTIR spectrometer (PerkinElmer Spectrum 100) was used to distinguish the chemical structures of APP-deposited organosilicon films. Each spectrum was obtained from an average of 256 scans in the range of 650–4000 cm^{-1} at a resolution of 4 cm.

3. Results and discussion

The water contact angles of the cyclonic APP-deposited films were measured, and the average value for both HMDSN and HMDSN/N_2 was 128.7 ± 1.2°, as shown in Fig. 1. The wettability of thin films indirectly specifies its predisposition to molecular interactions with the liquid phase and the presence of polar groups on the film surface. Similar water contact angle values for HMDSN and HMDSN/N_2 gas mixture cyclonic APP-deposited films are the related surface characteristics. It also refers the variation in film surface energy for HMDSN and HMDSN/N_2 gas mixture cyclonic APP-deposited thin films. The surface energy of the HMDSN cyclonic APP-deposited film was 16.24 mJ/m^2, and the relatively lower value obtained for the HMDSN/N_2 gas mixture cyclonic APP-deposited film was 14.47 mJ/m^2. The effect of adding nitrogen gas plasma on surface energy and contact angles of both liquids, which shows that the HMDSN and HMDSN/N_2 cyclonic APP-deposited films have similar static water contact angles and surface energies. These results show that adding nitrogen gas to the film did not affect the surface tension/surface free energy of cyclonic APP-deposited films.

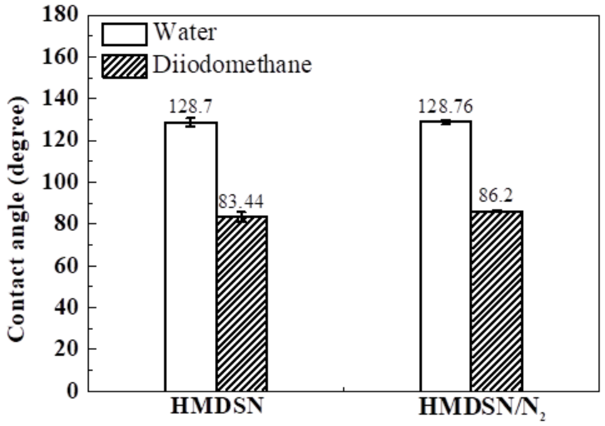

Fig. 1. Average contact angles of HMDSN and HMDSN/N_2 cyclonic plasma deposited films.

The cyclonic APP-deposited films were inspected by ATR–FTIR spectroscopy and the results are shown in Fig. 2. The FTIR spectra showed that the Si–O–Si group band peaks were located at 800, 1080, and 1170 cm^{-1}, the SiRx (X=1-3) peaks were at 796-840 cm^{-1}, the CHx peaks were at 1300-1500 cm^{-1}, and the C=O peaks were at 1720 cm^{-1}. Conversely, the ratio of the shoulder area of the Si–O stretching mode at 1170 cm^{-1} to the primary peak area at 1080 cm^{-1} was correlated with the degree of porosity of silicon dioxide films. In this context, many studies assert that the chemical composition of these thin films is permanently a mix of polydimethylsiloxane (PDMS) and a resembling silica structure. In this regard, this large band in the section from1,075 to 1,200 cm^{-1} can be attributed to the formation of silica networks (Si–O–Si) and the occurrence of Si–C bonds.

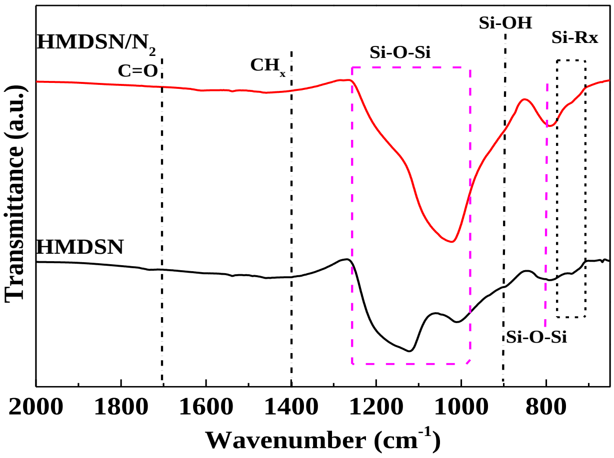

Fig. 2. ATR-FTIR spectrum of HMDSN and HMDSN/N_2 cyclonic plasma deposited films.

The evolution of the Si–Si bonds could be analyzed by Raman spectroscopy. Fig.3 depicts the features of cyclonic APP-deposited films by Raman spectra. As can be seen in Fig. 3, the Raman peaks at 520 cm^{-1} is crystalline silicon on APP HMDSN/N_2 deposited films. It is also found the amorphous feature of APP HMDSN deposited films. The influence of monomer feed in APPCVD and the film structure transition are determined from this study.

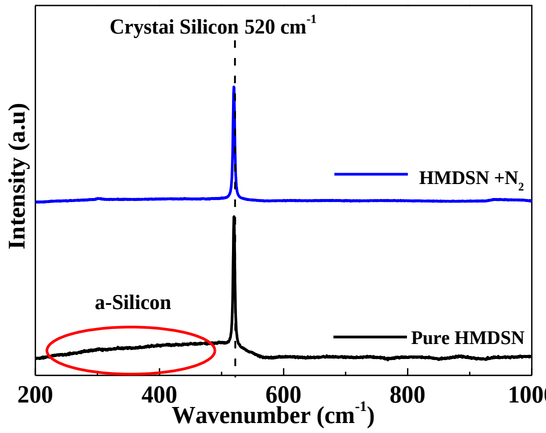

Fig. 3. Raman spectra of HMDSN and HMDSN/N_2 cyclonic plasma deposited films

4. Conclusion

The cyclonic APP-deposited films exhibit mainly low carbon content characteristics even without nitrogen; however, when nitrogen gas was added, the chemical structure of the film was altered. The surface morphology became rough, the Si-O-Si group peaked at approximately 1050 cm-1, the degree of porosity was relatively low, and the SiCHx group decreased with the addition of nitrogen gas during atmospheric-pressure plasma deposition. The addition of nitrogen gas substantially affected the structural and chemical properties of the organosilicon film. Si–O–Si bonds in HMDSN/N2 discharge resulted in a higher film deposition rate than that of the HMDSN discharge. Despite the absence of Si–O–Si bonds, HMDSN discharge could still be activated with plasma cyclone to grow the organosilicon film formation. Therefore, it can be concluded that hexamethyldisilazane (HMDSN) with nitrogen gas addition method could have led to the inorganic features of the organosilicon film.

5. References

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