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Properties of Si_xN_y thin film deposited by plasma enhanced chemical vapor deposition at low temperature using $SiH_4/NH_3/Ar$ as diffusion barrier film

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ABSTRACT

Si_xN_y thin films were deposited by PECVD using $SiH_4/NH_3/Ar$ gases and by biasing the substrate at −50 V as a function of the ratio of R ($R = NH_3/(NH_3 + SiH_4)$) at a low temperature (<80 °C), and their properties as the thin film diffusion barrier were investigated. When R was lower than 0.4, the deposited Si_xN_y film showed low optical transmittance and high surface roughness due to the Si–H bonding in the deposited film. When R is higher than 0.6, the deposited Si_xN_y film was transparent, however, possibly due to the N–H bonding in the film, the film became porous and surface roughness was again increased. When $R = 0.4$, an optically transparent and smooth film could be obtained. When the WVTR was measured with a multilayer film composed of Si_xN_y ($R = 0.4$) and parylene on PES substrate, PES (200 μm)/parylene (1.2 μm)/Si_xN_y SixNy (120 nm)/parylene (1.2 μm) showed the WVTR lower than the detection limit of 0.01 g/(m^2 day).

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1. Introduction

Both H_2O and O_2 in the atmosphere can degrade the device performance of next generation organic devices such as organic light emitting diodes (OLEDs), organic thin film transistors (OTFTs), etc. [1,2]. In the case of OLEDs, H_2O and O_2 can oxidize metallic electrodes and reduce the electron injection in the OLED structure, thereby, drastically decrease their performance. For OTFTs, H_2O attacks to the boundaries and captures charges generated in the channel leading to the decrease of on-current and field effect mobility [3–5]. Therefore, to increase the lifetime of those organic devices, a protection of the devices from the permeation of oxidizing species such as H_2O and O_2 is required and one of the methods is the multilayer thin film diffusion barrier deposited on the devices.

Among the various thin film materials, $Si_xN_ySi_xN_y$ films are known to be suitable as the thin film diffusion barrier because of their good physical and chemical properties. To form $Si_xN_ySi_xN_y$ films on the organic devices without damaging the devices, the deposition of the films should be carried out at a low temperature and one of the techniques that can deposit at a low temperature is PECVD. In addition, to use various polymer materials such as polyethyleneterephthalate (PET), polyethersulfone (PES), etc. as the flexible substrates for the fabrication of next generation organic devices, $Si_xN_ySi_xN_y$ films need to be deposited at the temperature lower than 80 °C.

In this paper, a PECVD system and the substrate biasing of − 50 V were used to deposit $Si_xN_ySi_xN_y$ films at the temperature lower than 80 °C and the effect of the ratio of $R = NH_3/(NH_3 + SiH_4)$ on the properties of thin film as the thin film diffusion barrier material such as deposition rate, optical properties, relative composition, and surface morphology was investigated. Finally, for an optimized $Si_xN_ySi_xN_y$ film, water vapor transmittance rate (WVTR) was measured.

2. Experimental

The plasma source was an inductively coupled plasma-PECVD (ICP-PECVD)-type source composed of a 3.5-turn copper coil located above a dielectric plate, which forms top plate of the vacuum chamber. The gas mixture of $SiH_4/NH_3/Ar$ was fed from the side of the chamber where SiH_4 and NH_3 gases were used as the reaction gases and Ar gas as the ignition gas. Total flow rate of ($SiH_4 + NH_3$) was maintained at 10 sccm and Ar flow rate was kept at 25 sccm. Dry pump was used to evacuate the chamber and the working pressure was maintained at 80 mTorr. 100 W of 13.5 MHz rf power was fed to the coil antenna through a matching network and the substrate was biased at − 50 V using a separate 13.56 MHz rf power. The substrate temperature was maintained at the temperature lower than 80 °C using a chiller. As the substrates, various materials such as p-type Si <110> wafer, glass and PES were used.

The film thickness was measured using an α-step profilometer (Tencor Inc., Alpha-step 500). The optical properties were measured by an ultraviolet-visible near infrared (UV/Vis/NIR) spectrometer (Varian, Cary5000). The compositions and binding states of Si_xN_ySixNy films were measured using X-ray photoelectron spectroscopy (XPS, VG Microtech Inc., ESCA2000). The binding states were also measured by a Fourier transform infrared spectrometer (FTIR; Bruker, IFS-66/S). The surface morphology of thin films was measured by a

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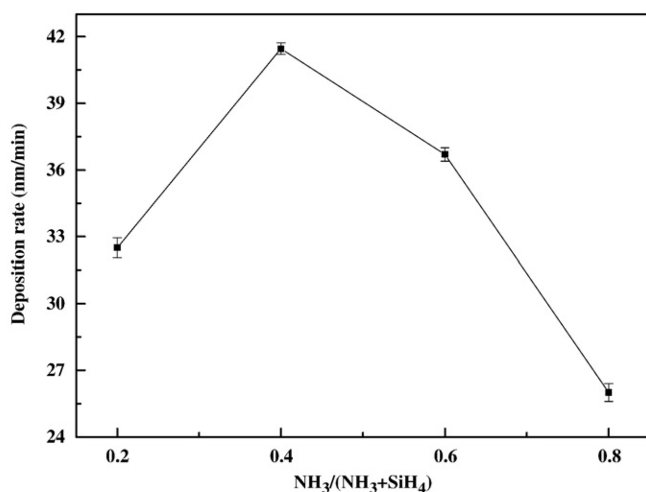

Fig. 1. Deposition rate of $Si_xN_ySi_xN_y$ films as a function of R (R=NH_3/(NH_3+SiH_4)). Deposition conditions: NH_3+SiH_4=10 sccm, Ar=25 sccm, source power 100 W, dc bias voltage −50 V, substrate temperature under 80 °C.

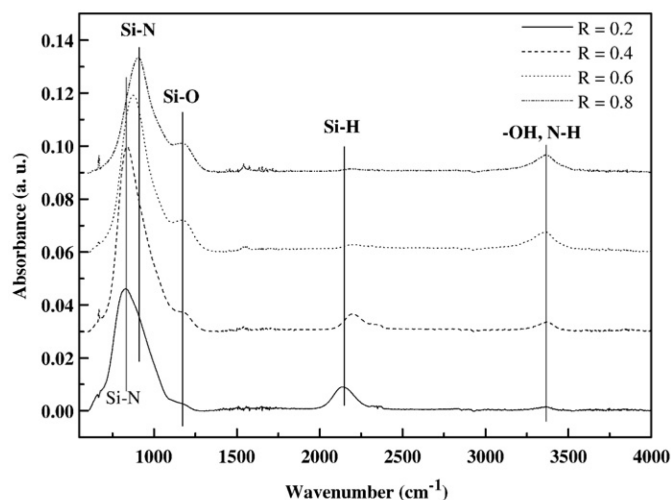

Fig. 2. FTIR absorption bands for various ratios of NH_3/(NH_3+SiH_4). All the films have the same 150 nm thickness. The deposition conditions are the same to Fig. 1.

field emission scanning electron microscope (FE-SEM; Hitachi S-4700). Using the multilayer thin films deposited on the PES, the WVTR was measured using a WVTR measurement system (MOCON Inc., PERMATRAN-W Model3/33).

3. Results and discussion

Fig. 1 shows the deposition rate of Si_xN_y films measured as a function of R=NH_3/(NH_3+SiH_4) at 100 W of rf power and − 50 V of dc bias voltage and 80 mTorr of operating pressure. Total flow rate of (SiH_4+NH_3) was maintained at 10 sccm and Ar flow rate was kept at 25 sccm. The substrate was maintained at the temperature lower than 80 °C using a chiller. The increase of the R from 0.2 to 0.4 increased the deposition rate from 32.5 to 41.5 nm/min, however, the further increase of the ratio to 0.8 decreased the deposition rate to 26 nm/min. The initial increase of deposition rate with increasing the ratio R appears to be related to the increased reaction of Si from SiH_4 and N from NH_3 for the formation of $Si_xN_ySi_xN_y$ in the film. However, due to the decrease of silicon source in the gas mixture with increasing the ratio R, the deposition rate was decreased with increase of R from 0.4 to 0.8. Therefore, at R=0.4, the maximized reaction between SiH_4 and NH_3 could be obtained.

Fig. 2 shows FTIR spectra measured to estimate the chemical bonding states for the 150 nm thick of $Si_xN_ySi_xN_y$ thin films deposited as a function of the ratio R shown in Fig. 1. All the spectra showed strong absorbance bands at around 840, 1170, 2150, and 3350 cm^{-1} originated from Si–N bonding [6], Si–O bonding [7], Si–H bonding, and the bonding from –OH and N–H [8], respectively. The Si–N absorbance peak at the wave number around 840 cm^{-1} was shifted to the high wave number (to 904 cm^{-1}) with increasing the ratio R. It is reported that Si–N band is shifted depending on the relative concentration of Si–H (2100 – 2200 cm^{-1}) and N–H (around 3350 cm^{-1}) in the deposited films [9]. In fact, with increasing the ratio R, the bonding peak related to Si–H was decreased with increasing the ratio R and the peak related to N–H was increased with increasing the ratio. Therefore, the shift of Si–N stretching to higher wave number observed in the experiment is believed to be related to the change of concentration of Si–H and N–H in the film. In addition, the peak intensity of Si–N bonding was the highest for R=0.4 indicating the optimum $Si_xN_ySi_xN_y$ compound formation at this condition in addition to the highest deposition rate observed in Fig. 1. The bonding peak observed at around 3350 cm^{-1} can be originated not only from N–H bonding but also from –OH bonding. With increasing the ratio R, due to the increase of NH_3 flow rate, the amount of N–H bonding should be increased as investigated by Lin et al. [10]. Therefore, the increase of the bonding peak at around 3350 cm^{-1} with increasing the ratio R appears to be mostly related to the increase of N–H bonding in the film. It is known that the $Si_xN_ySi_xN_y$ deposited with a higher NH_3 shows a porous structure and is easily oxidized [3]. Therefore, Si–O bonding observed at 1170 cm^{-1} appears to be related not only to oxygen impurity in the vacuum system but also to the oxidation during the air exposure before the measurement. The bonding peak related to Si–O appeared to be increased with the increase of the ratio R. Because the $Si_xN_ySi_xN_y$ film deposited at the higher ratio of R has more porous structure, the increase of Si–O bond peak intensity observed with the increase of the ratio R appears to be related to the enhanced oxidation of $Si_xN_ySi_xN_y$ during the air exposure.

In addition to FTIR, the atomic concentration of the deposited $Si_xN_ySi_xN_y$ thin films was measured by XPS as a function of the ratio R and the results are shown in Fig. 3. As the components in the film, Si, N, C, and O were found. Even though the bonding related to hydrogen was found by FTIR, due to the detection limit of XPS, the atomic percentage of hydrogen in the deposited film could not be estimated. The ratio of Si/N was decreased with the increase of the ratio R similar to the result obtained by other researchers [11]. However, compared to the stoichiometric composition of Si_3N_4 having the ratio of Si/N=0.75,

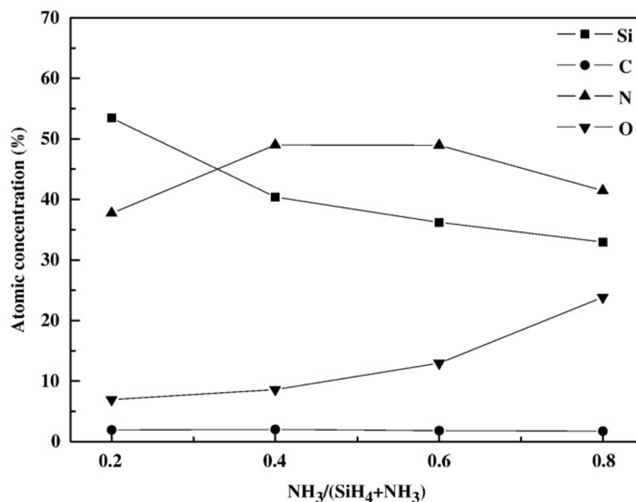

Fig. 3. Atomic concentrations of silicon (Si), nitrogen (N), oxygen (O) and carbon (C) as a function of NH_3/(NH_3+SiH_4). All the films have the same 150 nm thickness. The deposition conditions are the same to Fig. 1.

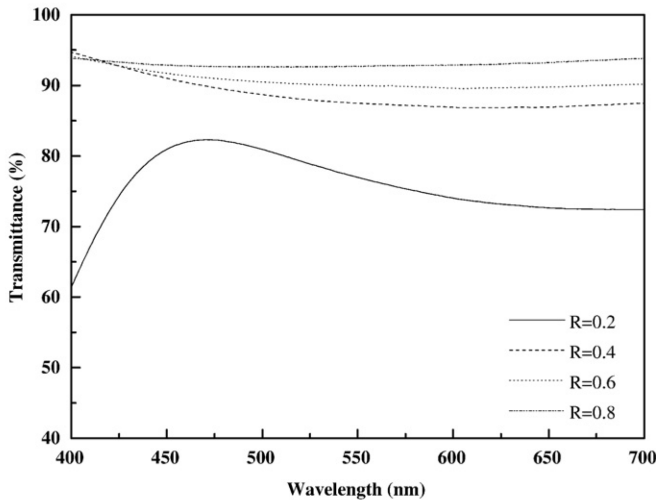

Fig. 4 Optical transmittance of $Si_xN_ySi_xN_y$ thin films deposited at various ratios of NH_3/(NH_3+SiH_4) on glass substrates. All the films have the same 150 nm thickness. The deposition conditions are the same to Fig. 1.

the ratio of Si/N at R=0.2 was about 1.41 showing highly silicon-rich $Si_xN_ySi_xN_y$ and, with increasing R, the ratio was decreased close to the stoichiometric composition of Si_3N_4 (at R=0.4: Si/N=0.82, at R=0.6: Si/N=0.74, at R=0.8: Si/N=0.79). Especially, at R=0.4, the Si/N close to the stoichiometric composition of Si_3N_4 could be obtained which appears to indicate the optimum deposition condition of Si_xN_y. With increasing the ratio R, oxygen percentage in the film increased from 6.93 to 23.84% as observed also by FTIR possibly due to more porous film structure observed with the higher ratio of R which resulted in the enhanced oxidation of the film during the air exposure. Carbon percentage in the film was in the range from 1.72 to 2% and was not dependent on the deposition condition.

Optical transmittance of the $Si_xN_ySi_xN_y$ films deposited as a function of the ratio R was measured and the results are shown in Fig. 4. The films were deposited on the glass substrates with the same thickness of 150 nm and deposition conditions in Fig. 1. The color of the deposited films was light brown and the deposited films were hard enough not to be scratched by a tweezers. When the ratio R is 0.2, the optical transmittance was lower than 75% at 550 nm but, with the increase of the ratio R, the optical transmittance was increased and the optical transmittance higher than 85% could be obtained for the ratio of R higher than 0.4. The increase of optical transmittance with the increase of the ratio R appears to be related to the removal of Si–H bonding in the film which absorbs visible wavelength range. In addition, the more incorporation of oxygen in the $Si_xN_ySi_xN_y$ film with increasing the ratio R has lead towards lower refractive index [12].

The morphology of the $Si_xN_ySi_xN_y$ film surfaces was observed by FE-SEM and the results are shown in Fig. 5 for the 150 nm-thick $Si_xN_ySi_xN_y$ thin films deposited on p-type <100> silicon wafers. (a), (b) and (c) are for the ratio R=0.2, 0.4, and 0.8, respectively. When R=0.2 or 0.8, the surface was rough and, in the case of the film deposited at R=0.8, the surface appeared to contain bubble-like structure while the $Si_xN_ySi_xN_y$ deposited at R=0.4 showed the smooth surface. The surface roughness obtained at R=0.2 appears to be related to the formation of Si-based particle having Si–H bond by the excessive SiH_4 in the gas mixture. The bubble-like structure shown for the thin film deposited at R=0.8 is believed to be from the redundant NH_3 in the gas mixture which is more than enough for the deposition of $Si_xN_ySi_xN_y$ thin film as investigated by other researcher [13]. However, as shown for R=0.4, when the ratio R is adequate in the deposition of stoichiometric Si_3N_4, Si from the SiH_4 gas reacted completely with N from NH_3 gas, therefore, a smooth surface could be obtained.

Multilayer thin films composed of Si_xN_y film (deposited at R=0.4) and parylene were deposited on PES (200 μm) substrates and the effect of the Si_xN_y films on the WVTR was investigated. For the multilayer thin film structure, parylene (an organic layer) and Si_xN_y film (inorganic layer) were alternatively deposited to increase the flexibility of the deposited film, to decrease WVTR for possible pin hole formation on the inorganic layer, to decrease stress induced defect formation of the Si_xN_y film, etc. The environment for the WVTR test was 100% RH, 37.8 °C, and 11.5 sccm of N_2 flow rate. The multilayer thin film structures investigated were 1-cycle structure consisted of PES/parylene (1.2 μm)/Si_xN_y Si_xN_y(120 nm)/parylene (1.2 μm) and 2-cycle structure consisted of PES/parylene (1.2 μm)/Si_xN_y Si_xN_y (120 nm)/parylene (120 nm)/Si_xN_y Si_xN_y(120 nm)/parylene (1.2 μm). The results are shown in Fig. 6. In the case of PES itself and PES /

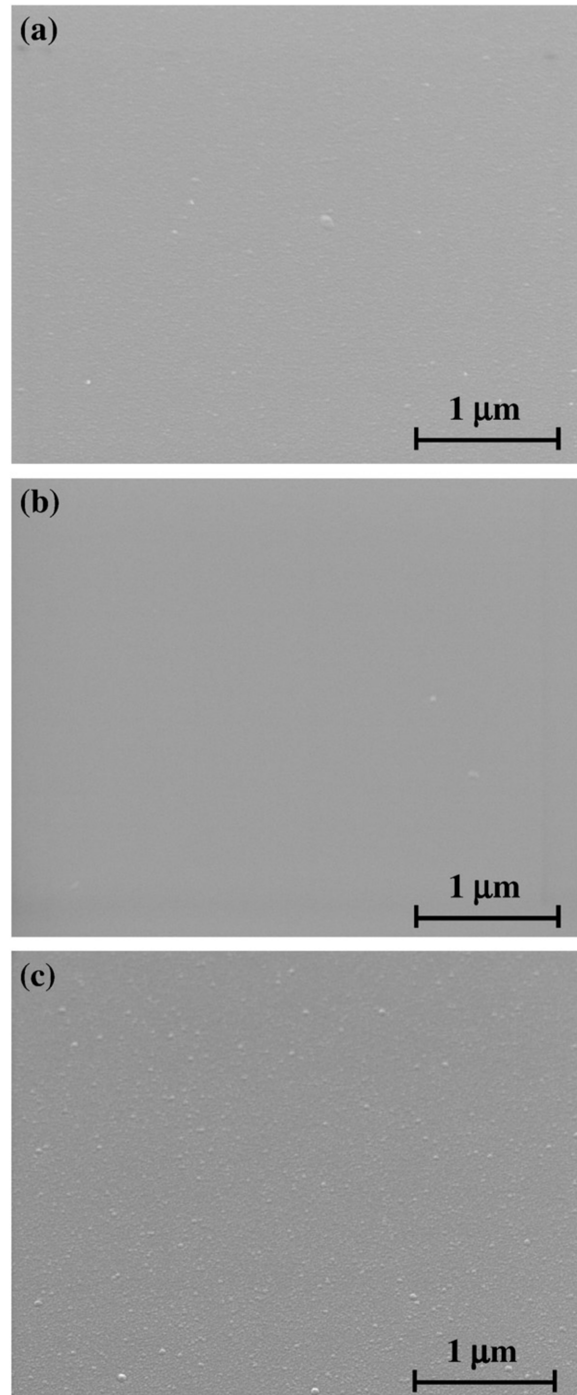

Fig. 5. SEM surface morphologies of (a) R=0.2, (b) R=0.4, (c) R=0.8. The deposition conditions are the same to Fig. 1.

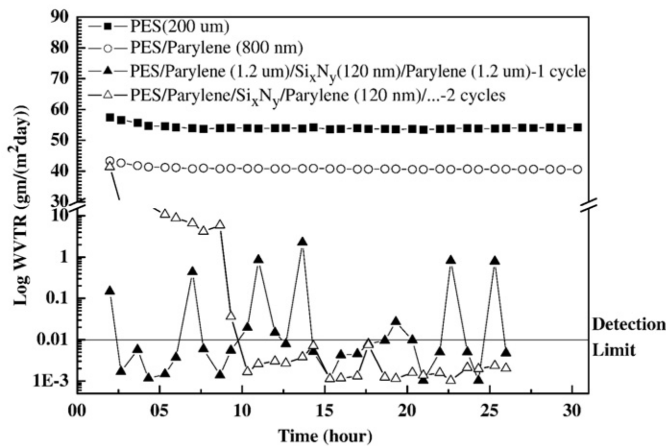

Fig. 6. WVTR results of multiple layer thin films composed of Si_xN_y (120 nm at R=0.4) and parylene (1.2 μm) on PES (200 μm). 1-cycle structure consisted of PES/parylene/$Si_xN_ySi_xN_y$/parylene and 2-cycle structure consisted of PES/parylene/$Si_xN_ySi_xN_y$/parylene (120 nm)/$Si_xN_ySi_xN_y$/parylene are measured. WVTRs of PES (200 μm) and PES (200 μm)/parylene (800 nm) were compared.

parylene (800 nm), the measured WVTRs were 54.1 and 40.4 g/(m^2day), respectively. Even though the deposition of parylene on PES decreased the WVTR slightly, both PES and parylene layer (800 nm) on PES were not enough as the diffusion barrier for preventing water permeation. However, as shown in the figure, all of the multilayer thin film structures having one layer (1-cycle structure) and two layers (2-cycle structure) of 120 nm-thick $Si_xN_ySi_xN_y$ showed the WVTR lower than 0.01 g/(m^2 day) which is the detection limit of the WVTR measurement machine.

4. Conclusions

Si_xN_ySixNy thin films were deposited at the low temperature lower than 80 °C as a function of the ratio of $NH_3/(NH_3+SiH_4)$ in NH_3/SiH_4/Ar gas mixtures using a PECVD by biasing the substrate at −50 V and the characteristics of the deposited thin films as the thin film diffusion barrier material were investigated.

The $Si_xN_ySi_xN_y$ thin film deposited at R=0.2 showed low optical transmittance and high surface roughness possibly due to the Si-rich particles formed in the film by the excessive SiH_4 in the gas mixture required for the formation of $Si_xN_ySi_xN_y$. The $Si_xN_ySi_xN_y$ thin film deposited at the ratio R higher than 0.6 also showed high surface roughness even though the optical transmittance is higher than 90% possibly due to N–H bonds in the material by the excessive NH_3 in the gas mixture. When the R=0.4, the ratio of Si/N was similar to the stoichiometric Si_3N_4 and the surface roughness was the lowest due to the optimum gas mixture in the formation of $Si_xN_ySi_xN_y$. The optical transmittance was about 85%. When WVTR was measured with multilayer thin films composed of Si_xN_y (120 nm at R=0.4) and parylene (800 nm) deposited on PES (200 μm), both PES/parylene/$Si_xN_ySi_xN_y$/parylene and PES/parylene/$Si_xN_ySi_xN_y$/parylene (120 nm)/$Si_xN_ySi_xN_y$/parylene showed the WVTR lower than the detection limit of 0.01 g/(m^2 day). Therefore, it is believed that the Si_xN_yixNy thin film deposited in this study could be applied as the thin film diffusion barrier material for next generation devices such as organic devices, devices deposited on the plastic substrate, etc. by using a multilayer structure containing at least one layer of the Si_xN_yixNy thin film.

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