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Formation of Large-Area Gas Barrier Films by Cat-CVD Method Using Organic Silicon Compounds

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1. Introduction

In recent years, sealing techniques using thin films for organic light-emitting diodes (OLEDs) and food wrappings have been required. Silicon nitride (SiN_x) films prepared by catalytic chemical vapor deposition (Cat-CVD) method at 80 °C or less have high gas barrier ability as well as high transparency and low stress, [1)] and thus can be utilized as gas barrier films on polymeric materials. Recently, it has also been clarified that Silicon oxynitride (SiO_xN_y) films can be formed by Cat-CVD method and stacking structures consisting of SiN_x and SiO_xN_y films indicate low water vapor transmission rates (WVTRs). However, these films are formed using SiH_4 which has a risk of explosion and demands extra safety equipment with high costs. Since such high-cost and dangerous processes are not suitable for production line of OLEDs and food wrappings, formation of barrier films using hexamethyldisilazane (HMDS), which is safe and inexpensive, is expected, and there have been reports about SiC_xN_y films. [2)] However, formation of SiO_xN_y films using HMDS has not been studied so far. We have also reported formation of SiN_x films using HMDS and suppression of carbonization by controlling NH_3 flow rates and gas pressure. Moreover, since deposition of SiN_x films using HMDS has been established only in a small chamber with effective deposition area of 5 cm × 5 cm, large-area deposition should be attempted for mass-production. In this study, I prepared SiO_xN_y films with high gas barrier ability by small Cat-CVD apparatus. AND I also prepared SiN_x, and SiO_xN_y films using large Cat-CVD with depositon area of 20 cm × 20 cm apparatus based on the experimental obtained in case of small Cat-CVD apparatus.

2. Experimental Details

A schematic diagram of the small Cat-CVD apparatus for deposition of SiN_x and SiO_xN_y films is shown in Fig. 1. The SiN_x films deposition condition is summarized in Table.1.

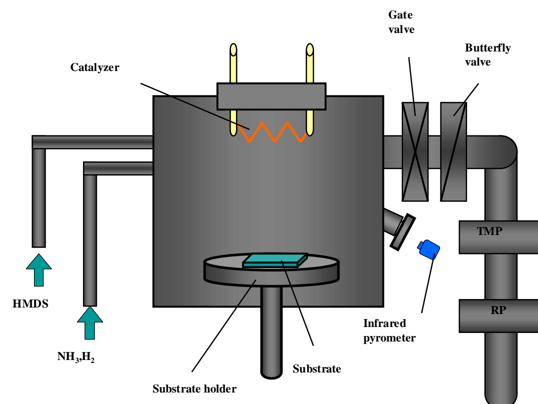

Fig. 1: Schematic diagram of small Cat-CVD apparatus

W wires with 0.4 mm in diameter and 350 mm in length were used as the catalyzer. For deposition of SiO_xN_y, O_2 gas at a flow rate of 0-8 sccm was added to the condition of SiN_x films deposition. Si and polycarbonate ethylene terephthalate (PET) substrates were heated at 80-120 °C during deposition.

A schematic diagram of the large Cat-CVD apparatus is shown in Fig. 2. W wires with 0.5 mm in diameter and 2800 mm in length were used as the catalyzer. The material gases for deposition are same as the case of small apparatus. The gases flow rate, catalyzer temperature, holder temperature, total gas pressure were adjusted under varying conditions. The WVTRs were measured by an equal-pressure method under 40 °C and 90%RH.

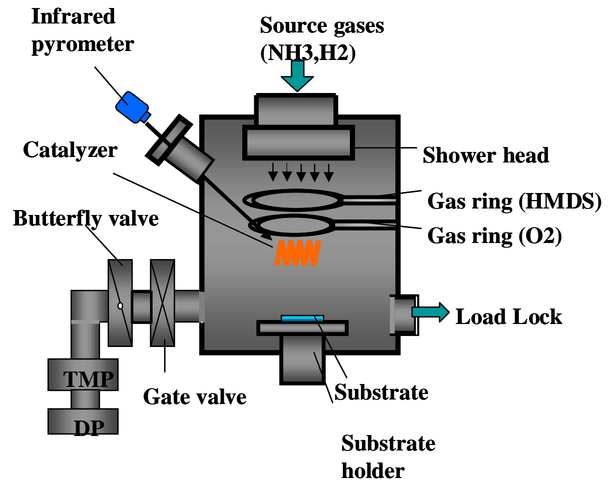

Fig. 2: Schematic diagram of large Cat-CVD apparatus

HMDS	: 0.5	sccm	NH_3	: 100	sccm
H_2	: 100	sccm	Gas pressure	: 2.3	torr
Holder temp	: 100	℃	Catalyzer (W) temp	: 1800	℃
Distance cat-sub	: 80	mm	O_2	: 0-6	sccm

Table 1: Deposition conditions for SiN_x films

3. Results and Discussions

Figure 3 shows XRD patterns of W catalyzers. Blue line is example of carbonization of W catalyzer. The reason why W catalyzer was carbonized, HMDS contain carbon and the atom of carbon reacted W. However, compared Black line, which is XRD patterns of pure W, with red line, which is XRD pattern of W after deposition, W catalyzer was not carbonized. The reason why it says [3] that carbonization was prevented adjustment of NH_3 flow rate and gas pressure. We confirmed that W catalyzer was prevented. And it considered quite well for W catalyzer that was apprehended whether W to be oxidized.

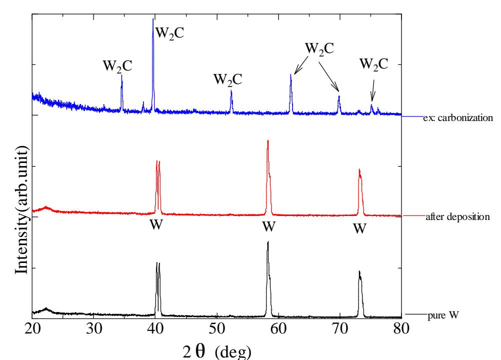

Fig.3: XRD patterns of W catalyzers

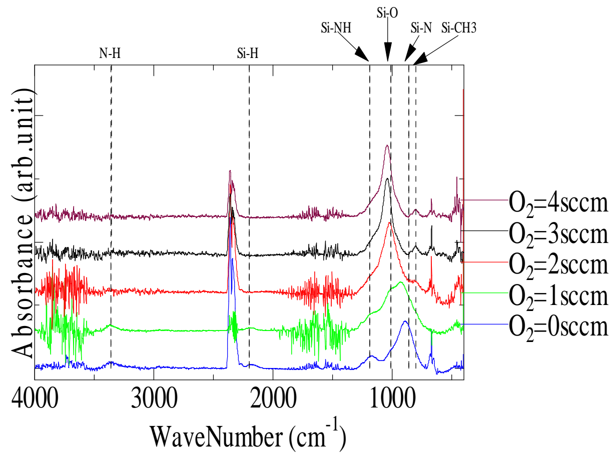

Fig.4: FT-IR spectra of the films as a function of O_2 flow rate

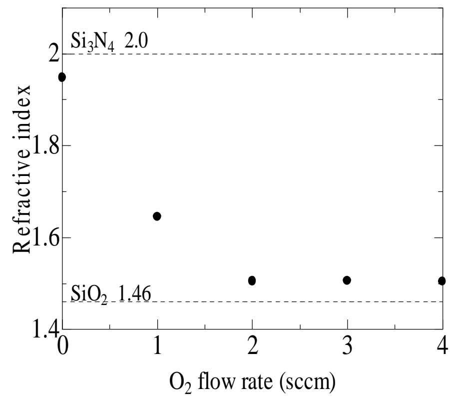

Fig.5: Refractive index of the films as a function of O_2 flow rate

Fourier transform infrared (FTIR) spectra of SiO_xN_y films prepared by small Cat-CVD apparatus as a function of O_2 flow rate are shown in Fig 4. As the O_2 flow rate increases, Si-N and $Si\text{-}CH_3$ bonds decrease, while Si-O bond increase. When O_2 flow rate is over 3 sccm, Si-N bond becomes unobservable and the spectra get close to that of SiO_2. Same tendency can be confirmed in O_2 flow rate dependence of refractive index as shown in Fig.5.

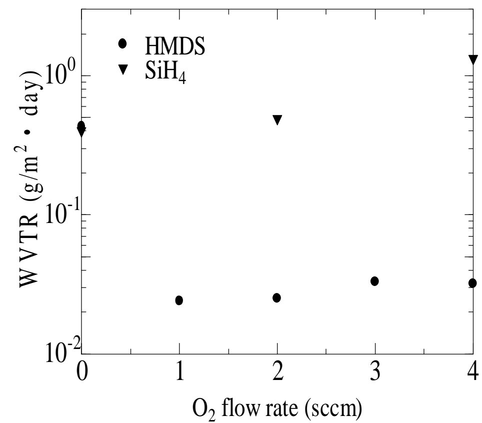

Fig.6: WVTRs of the SiO_xN_y films on PET substrates

Figure 6 shows WVTRs of SiO_xN_y films deposited on PET substrates with WVTR of 5.72 $g/m^2 \cdot day$. The WVTR for the SiN_x films on PET substrates is 0.42 $g/m^2 \cdot day$, which is equivalent to that, prepared using SiH_4 gas. Surprisingly, WVTRs of SiO_xN_y films can be decrease to 0.03 $g/m^2 \cdot day$, which is one order of magnitude lower than that of SiN_x films. This tendency is opposite to the case of SiO_xN_y films using SiH_4 showing higher WVTRs than SiN_x. Therefore, deposition of SiO_xN_y films using HMDS can be utilized as an effective sealing technique.

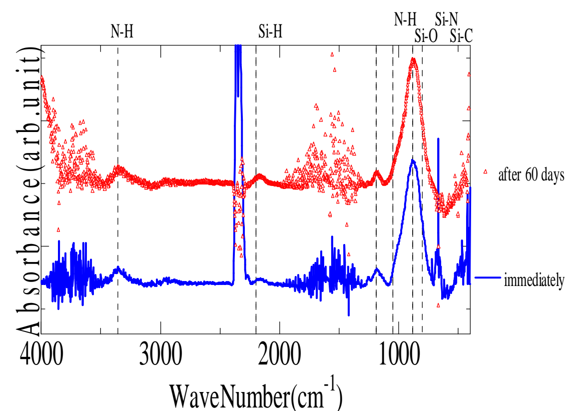

Fig.7: FT-IR spectra of the films

Next, I show the experimental result by large Cat-CVD apparatus. FTIR spectra of the film prepared by large Cat-CVD apparatus are shown in Fig 7. Blue line was measured immediately after deposition, and red dot was measured after 60 days. Compared the blue line in Fig 4 with that in Fig.7, two FTIR spectra are almost the same. However, these WVTRs were different as show in Fig.8. The possibilities of the ties reason are as follows,

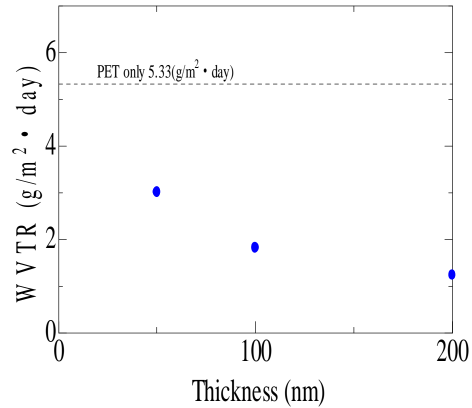

Fig.8: Relation of each films thickness to WVTRs

①the films contain large amount of nitrogen, the nitrogen-rich SiN_x films are prepared,

②the films contain large amount of hydrogen, resulting in low film density,

③the films contain large amount of carbon since the composition of prepared SiN_x films is close to SiC_xN_y films containing large number of Si-C bond .

4. Conclusion

We have successfully fabricated SiN_x and SiO_xN_y films by Cat-CVD method using HMDS by small Cat-CVD apparatus. By changing O_2 flow rate, composition of the SiO_xN_y films can be controlled. SiO_xN_y monolayer films prepared using HMDS have high gas barrier ability than that formed using SiH_4 and can be utilized for actual gas barrier films.

On the contrary, the case of large Cat-CVD apparatus, SiN_x films with stoichiometrical refractive index of 2.0 and high gas barrier ability, were not prepared. Because, the size of chamber is different, the deposition mechanism is probably changed.

Further investigation of deposition conditions for SiN_x films stoichiometrical with refractive index close to and 2.0 high gas barrier ability should be performed.

References

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3) k. Tsurumaki et al: Ext. Abstr. (53th Spring Meet. 2006), Jpn. Soc. Appl Phys. 23a-N-3.