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Room Temperature Deposition of Silicon Nitride Films for Passivation of Organic Electroluminescence Device Using a Sputtering-Type Electron Cyclotron Resonance Plasma

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Dense silicon nitride (SiN) films were deposited at room temperature by a sputtering technique using an electron cyclotron resonance (ECR) plasma. Film properties were studied using ellipsometry, chemical etching, Fourier transform infrared spectroscopy, and thermal desorption spectroscopy. A SiN film deposited under the optimum condition of nitrogen gas flow rate had a refractive index of 2.03 and showed a large Si–N bond number. The SiN film had a high barrier against moisture penetration relative to SiN films prepared by chemical vapor deposition at 900°C. This indicates that the film deposited using a sputtering-type ECR plasma has the potential to be utilized as a passivation layer of devices such as organic electroluminescence, which require low temperature processing.

KEYWORDS: silicon nitride, sputter, electron cyclotron resonance, moisture penetration, thermal desorption.

1. Introduction

Organic electroluminescence (EL) devices have received much interest in the last two decades as a new kind of luminescent device. However, longevity is one of difficult problems facing EL devices. Moisture penetration is known to be the main factor which influences the lifetime of EL devices. Hence, it is necessary to protect the organic EL cells from moisture by using a passivation layer. In organic EL device fabrications, particularly high requirements are placed on final passivation layers, because organic EL cells are easily degraded if they are directly exposed to temperatures higher than 100°C. Therefore, the passivation layers have to be formed at a very low temperature, around room temperature. Also, the passivation layers must have high electrical resistance.

Silicon nitride (SiN) films are now widely used as passivation films to protect semiconductor devices from moisture and alkaline metals because of their characteristics of high density and high electrical resistance.¹⁾ From the view point of physical and chemical structure, high quality SiN films have been usually fabricated using thermal chemical vapor deposition (CVD) at high temperature ranging 700–1000°C.²⁾ As stated above, such a high deposition temperature is obviously undesirable for organic EL device fabrications. By contrast, plasma-enhanced (PE) CVD, using silane (SiH₄) and ammonia (NH₃),^{3,4)} has the advantage that the substrate can be held at a relatively low temperature of around 20–400°C. However, the PECVD process using SiH₄ generally suffer from the problem of hydrogen incorporation into deposited films,^{5,6)} which causes quality degradation and large residual stress.⁷⁾ In particular, it has been recognized that SiN:H films are not applicable for final device passivation when processing temperatures are less than 150°C because the film porosity becomes excessively large.⁸⁾ In order to satisfy the strict requirements of passivation layers for organic EL devices, an alternative deposition is strongly desired, by which a film having high barrier against moisture penetration can be deposited at around room temperature.

A novel sputtering technique using an electron cyclotron

resonance (ECR) plasma has been developed recently.^{9–11)} We have reported that Si oxide and oxynitride films having good electrical properties can be deposited by this ECR sputtering technique at low temperature.^{12–14)}

In this study, we report the deposition of high density SiN films at room temperature using the sputtering-type ECR plasma. The quality of the deposited films was studied as a function of the gas flow rate of nitrogen. It is shown that the SiN films deposited at the optimum gas flow rate have a high barrier against moisture penetration and are superior in this characteristic to thermal CVD SiN films deposited at 900°C.

2. Experiment

All depositions were performed in a sputtering-type ECR plasma system. A detailed description of this system is given elsewhere.^{9–14)} Microwave power (P_{μ}) of 500 W at an frequency of 2.45 GHz was introduced into the plasma chamber for generating the Ar and N₂ plasmas. A cylindrical single-crystal Si target was placed just outside the ECR plasma and surrounded the plasma stream. A radio frequency power (P_{RF}) of 500 W was applied to the sputter target. The process gas used was a mixture of Ar and N₂. The depositions were carried out at room temperature. The gas flow rate of Ar was kept at 16 sccm for all depositions while the gas flow rate of N₂ (F_{N_2}) was changed from 1 to 7 sccm. The chamber pressures during the deposition were in the range of $1.23\text{--}1.46 \times 10^{-3}$ Torr. Since we just focused our attention on the investigation of the barrier strength against moisture penetration for the deposited films, silicon wafers instead of EL devices were used as substrates in this study.

The thicknesses and the refractive indices of the deposited films were measured using standard ellipsometry. Chemical etch rates of the films were measured using 0.5% HF solution. Fourier transform infrared (FTIR) transmission measurements were performed in the range of 400–4000 cm⁻¹.

The barrier strength against moisture penetration was evaluated by a thermal desorption spectroscopy (TDS) apparatus equipped with a quadrupole mass spectrometer. The chamber was evacuated using a 261 l/s turbomolecular pump and the ultimate base pressure of this system was 3×10^{-8} Torr.

All deposited samples, having almost the same thickness of 5000 Å and area of 3.75 cm², were first treated for 240 h exposed to atmosphere at a constant temperature of 80°C and humidity of 80%. The samples were then placed in the chamber, evacuated and externally heated with an infrared radiation lamp, which was controlled at a linear heating rate of 0.55°C/s and were heated from room temperature to 900°C without significant increase in the temperature of the chamber wall. The detected mass number was 18, corresponding to that of H₂O. Final water desorbing fluxes were evaluated by subtracting the background from the measured water desorbing flux.

3. Results and Discussion

The refractive indices and the chemical etch rates for the deposited films are shown in Fig. 1 as a function of F_{N_2} . For comparison, the chemical etch rate of a SiN film deposited by thermal CVD at 900°C (hereafter referred as thermal CVD SiN) is also shown, by a broken line, in Fig. 1. When F_{N_2} were 1 and 2 sccm, the refractive indexes were 3.2 and 2.3, respectively, suggesting that the films were silicon rich. The refractive index showed a value of 2.03 at F_{N_2} of 3 sccm, which equals that of stoichiometric Si₃N₄. The chemical etch rates decreased with increasing F_{N_2} up to 3 sccm and reached a minimum value of 4.45 nm/min at F_{N_2} of 3 sccm, implying an increase in the density of the film. The etch rate of the film deposited at 3 sccm was very close to that of thermal CVD SiN films, suggesting that the density is also close to that of thermal CVD SiN films. This result demonstrates that dense SiN films can be deposited at room temperature by using this ECR sputtering technique. On the other hand, the chemical etch rates increased rapidly with increasing F_{N_2} from 3.5 to 7 sccm. The fact suggests that N ≡ N triple bonds were formed and trapped inside the films.¹⁵⁾ These N₂ molecules form many voids and defects and create disorder in the network, which seem to cause the lower density and higher chemical etch rates. In the range above 3.5 sccm, the refractive indices decreased slowly to 1.98, which some-

what deviates from the refractive index (2.03) of stoichiometric Si₃N₄. This fact is probably due to the incorporation of gaseous N₂ in the films.

The deposition rates are shown in Fig. 2 as a function of F_{N_2} . The maximum deposition rate of 7.8 nm/min was obtained at F_{N_2} of 2 sccm and decreased gradually in the range above 2 sccm. The decrease in deposition rates is understood by considering the thin SiN film which is formed on the Si target surface because of the large number of nitrogen ions hitting the surface. In general, the sputtering yield for SiN is known to be much lower than that for Si. Thus, the number of Si atoms and SiN molecules being sputtered from the target become small and consequently the deposition rates decrease.

In order to understand the structural properties of these deposited SiN films, IR absorption measurements were carried out as a function of F_{N_2} . The IR absorption coefficient per unit (absorption coefficient/thickness) for the films deposited at F_{N_2} of 1, 3, 5, 7 sccm are shown in Fig. 3, where the peaked signals are attributed to the main Si–N stretching vibration mode. According to the Lambert-Beer rule,¹⁶⁾ the IR integrated intensity is proportional to number of Si–N bonds in the film. Thus, it is a useful method to evaluate the densities of the films by comparing the number of Si–N bonds in the films.⁵⁾ We calculated the integrated intensities per unit (=integrated intensity/thickness) of the respective signals. The results are shown in Fig. 4. For comparison, the integrated intensity per unit for the thermal CVD SiN film is also shown, by a broken line, in Fig. 4. The increase in the integrated intensities with increasing F_{N_2} up to 3 sccm is caused by the increase of the number of Si–N oscillators. The film deposited at F_{N_2} of 3 sccm showed a maximum value which is the same as that of the thermal CVD SiN film, implying that the film has the largest number of Si–N bonds among the ECR deposited films. By contrast, the intensities decreased with the increase of F_{N_2} above 3 sccm. These results are well understood by the fact that voids and defects increased and consequently the number of Si–N oscillators decreased because of the formation of gaseous N₂ molecules in the deposited SiN film, as discussed above. These results

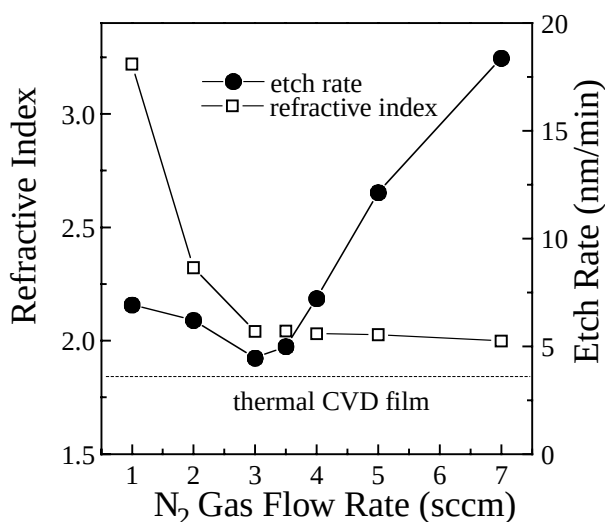


Fig. 1. Refractive index and etch rate as a function of N_2 gas flow rate at a constant Ar gas flow rate of 16 sccm. P_μ : 500 W; P_{RF} : 500 W; gas pressure: $1.23\text{--}1.46 \times 10^{-3}$ Torr; deposition temperature: room temperature; etching solution: HF : H₂O = 1 : 7. The broken line shows the etch rate for the SiN film deposited by thermal CVD at 900°C.

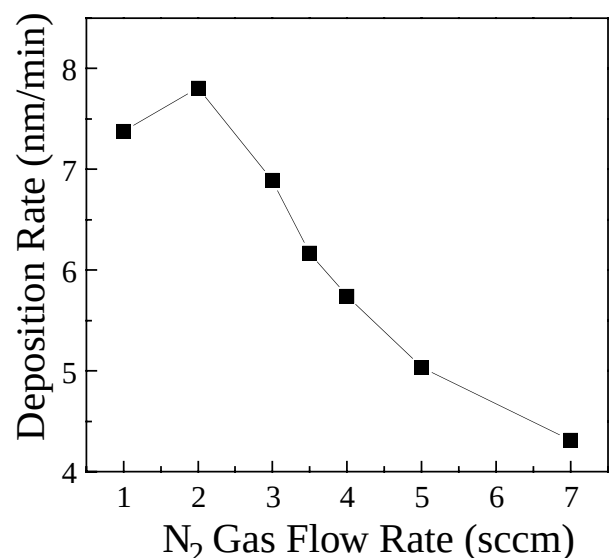


Fig. 2. Deposition rate as a function of N_2 gas flow rate at a constant Ar flow rate of 16 sccm. Plasma conditions: see Fig. 1.

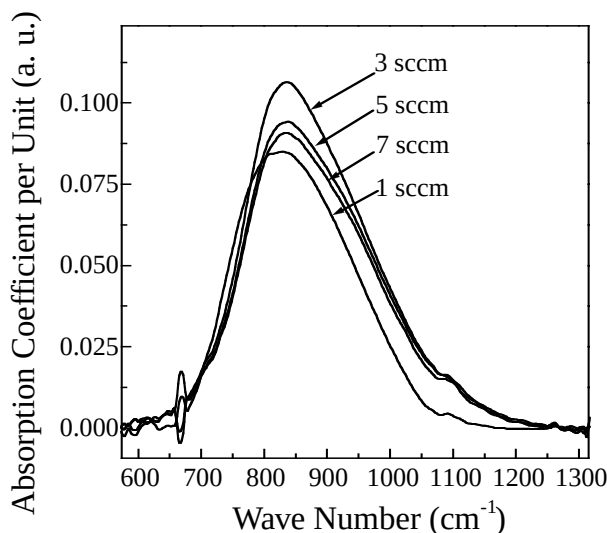


Fig. 3. IR absorption spectra for the SiN films deposited at N_2 gas flow rate of 1, 3, 5, 7 sccm and a constant Ar gas flow rate of 16 sccm. The spectra have been corrected for the film thicknesses.

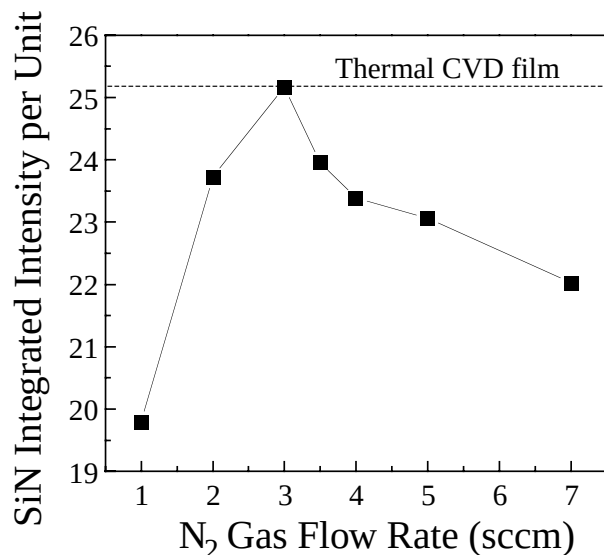


Fig. 4. Integrated intensity per unit as a function of N_2 flow rate at a constant Ar flow rate of 16 sccm. Plasma conditions: see Fig. 1. The broken line shows that for the integrated intensity per unit for the SiN film deposited by thermal CVD at 900°C.

are in good agreement with those of refractive index and etch rate measurements.

In order to investigate the water absorption characteristics in the films, the SiN films deposited at F_{N_2} of 1, 3, 5, 7 sccm were measured using the TDS system. The water desorption spectra are shown in Fig. 5. All the samples exhibited a water desorption peak at around 430°C. The films deposited at higher F_{N_2} , such as 5 and 7 sccm, showed large water desorbing intensities because of their porous structure. On the other hand, the film deposited at 3 sccm exhibited the lowest water desorbing intensity. The film deposited at 1 sccm showed a water desorbing intensity as low as that of the film of 3 sccm. However, this is not useful as a final passivation layer for organic EL devices because the film is Si rich which leads to poor electrical resistance. This was clarified by measuring the resistivities for respective films. The electrical resistiv-

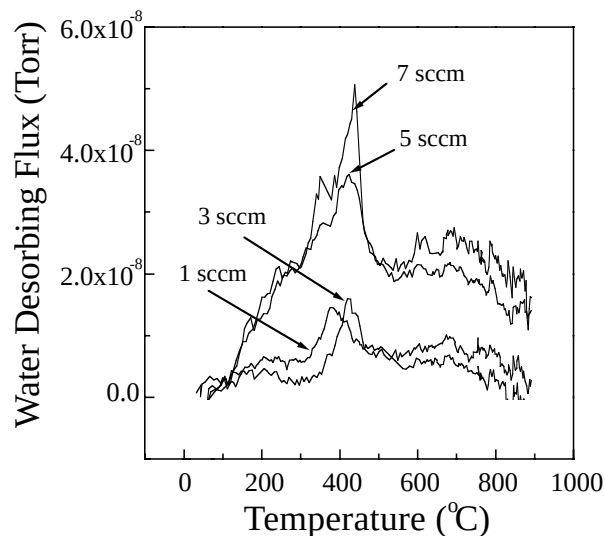


Fig. 5. Water desorbing flux for the SiN films deposited at $N_2 = 1, 3, 5, 7$ sccm and a constant Ar gas flow rate of 16 sccm.

ities were obtained by current-voltage characteristics in the range of less than 3 V using MIS structure. The resistivities were 7×10^8 , 3×10^{13} , 1×10^{12} and $6 \times 10^{11} \Omega\text{cm}$ for the films deposited at F_{N_2} of 1, 3, 5, 7 sccm, respectively. Thus, it was concluded that the N_2 gas F_{N_2} of 3 sccm is the optimum deposition condition.

SiN films prepared by thermal CVD at a high temperature are known to have compact structure in comparison with that of SiO_2 film. Thus, the comparison of the water absorption among the ECR SiN film, the CVD SiN film and the ECR SiO_2 film¹²⁾ gives us useful information. Therefore, the desorption characteristics for the ECR SiN film deposited under the optimum condition of 3 sccm, the thermal CVD SiN film and the ECR SiO_2 film deposited at 130°C, were also measured by the TDS system. The results are shown in Fig. 6. The ECR SiN film showed the lowest water desorbing intensity, while the ECR SiO_2 film showed the largest intensity. The fact that the ECR SiN film has characteristics superior to those of thermal CVD SiN films demonstrates its suitability as a passivation layer of organic EL devices.

The integrated intensity of the water desorbing signal corresponds to the water quantity contained in the film. We calculated the signal integrated intensities for the respective films from Fig. 6. The results are shown in Fig. 7. It can be seen that the thermal CVD SiN film and the ECR deposited SiO_2 film contained about 2 and 5 times more water relative to that of ECR deposited SiN film, respectively. Thus it is concluded that the SiN film deposited by ECR sputtering at room temperature has a very compact structure with a high barrier against moisture penetration.

4. Conclusion

This work demonstrated that it is possible to deposit SiN films suitable for passivation of organic EL devices by using a room temperature sputtering technique using an ECR plasma. The results of ellipsometry, chemical etching, FTIR, and TDS measurements showed that the density of the SiN films deposited at high F_{N_2} is low, which caused high moisture penetration. The formation of gaseous N_2 molecules in the deposited films is considered to be the main problem which

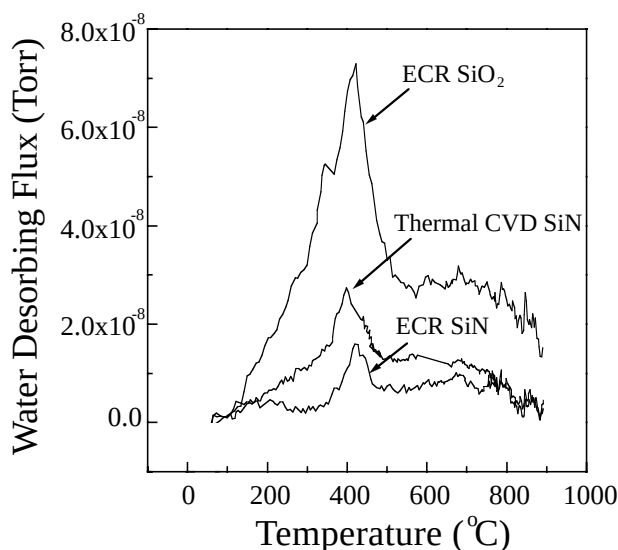


Fig. 6. Water desorbing flux for the ECR SiO₂ film, the thermal CVD SiN film and the ECR SiN film deposited at N₂ = 3 sccm.

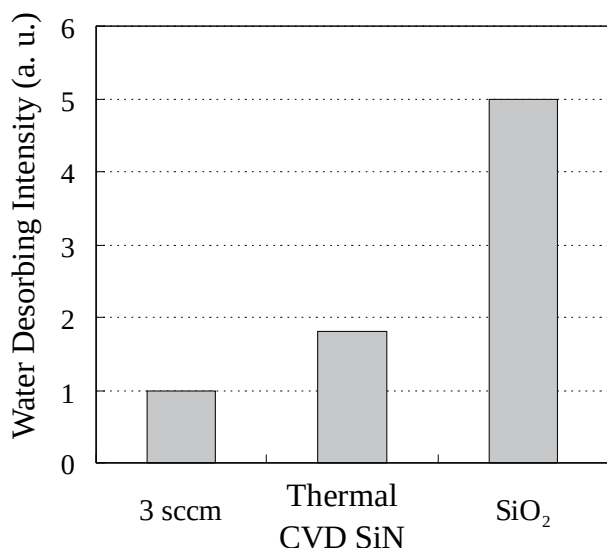


Fig. 7. Water desorbing intensities for a ECR SiO₂ film, the thermal CVD SiN film, and the ECR SiN film deposited at N₂ = 3 sccm.

increased the moisture penetration because of their porous structure. By contrast, the film deposited at the optimum condition of F_{N_2} had a refractive index of 2.03, which equals that of stoichiometric Si₃N₄. From the result of chemical etching and FTIR measurements, the film showed a lower etching rate and the largest Si–N bond number, indicating that the film has a dense structure. The results of TDS also showed a high barrier against moisture penetration. This deposition technique is believed to be applicable to EL device fabrications.

Acknowledgements

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