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Transparent silicon nitride films prepared by surface wave plasma chemical vapor deposition under low temperature conditions

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ABSTRACT

Highly transparent silicon nitride films with a low absorption coefficient of only 200 cm^{-1} or lower were prepared under high NH_3/SiH_4 source gas ratio conditions at 80 °C or lower temperature using surface wave plasma chemical vapor deposition (SWP-CVD). Rutherford backscattering measurements indicated that a silicon nitride structure Si_3N_x ($x > 5$) with excess nitrogen could be prepared with the SWP-CVD method under high NH_3/SiH_4 source gas ratio conditions. X-ray photon spectroscopy (XPS) analysis provided verification that the excess nitrogen combined with the oxygen contained in the SiN_x film during low-temperature film formation and that the atomic ratio of Si and N was almost stoichiometric, i.e., Si_3N_4.

XPS study also revealed that the $Si_3N_{<4}$ structure contained suboxides, which presence may reduce the transparency of the films. In contrast, suboxides were not observed in the Si_3N_4 structure obtained under high NH_3/SiH_4 source gas ratio conditions. Fourier-transform infrared spectroscopy study confirmed that the SiN_x film becomes more stable when the SiN_x structure approaches the stoichiometric ratio. Achieving a near-transparent Si_3N_4 structure requires a sufficient amount of N atoms in the periphery of the Si atom, i.e., an adequate amount of NH_3 is necessary in the presence of the SiH_4.

1. Introduction

High-performance transparent barrier films have recently attracted much attention for flexible applications such as organic light emitting diode (OLED) displays [1]. Organic materials are susceptible to water, oxygen, and other environmental elements present in ambient conditions [2–4]. Many studies report on encapsulation methods or materials for increasing OLED display lifetimes. Transparency is particularly critical for encapsulating films that are applied to top-emitting OLED displays.

The water vapor transmission rate requirement for OLED encapsulation is less than 10^{-6} g/m^2/day [5]. Silicon nitride (SiN_x) films are the strongest candidates for a high-performance barrier film. There are many reports that discuss the transparency of SiN_x films [6–9]. These reports examine the influence of the Si/N ratio on optical characteristics, but few ones discuss the bonding states of transparent SiNx films.

For this study, we prepared SiN_x films under low temperature (less than 80 °C) conditions using a surface wave plasma chemical vapor deposition (SWP-CVD) system and elucidated the relationship between the Si/N elemental ratio and the Si – N bonding states using Rutherford backscattering spectroscopy (RBS) and X-ray photoelectron spectroscopy (XPS).

2. Experimental methods

Fig. 1 shows a schematic diagram of the SWP-CVD system [10]. This system has a plasma source with a slot antenna. Microwaves with a frequency of 2.45 GHz were introduced through the slot antenna and alumina dielectric window into the reactor. Ar, SiH_4 and NH_3 gases were fed from the upper and lower gas inlets. The distance between the dielectric window and the substrate stage was fixed at 200 mm. The films were prepared by exposing 6-inch- diameter FZ Si (100) wafers and quartz substrates to Ar, SiH_4 and NH_3 gases that were introduced from the gas inlets at flow rates of 350, 70, and 90–500 sccm, respectively. The total gas pressure was maintained at 10 Pa. The microwave power density was fixed at 1.57 W/cm^2. The deposition time was fixed at 100 s for each sample. The deposition rate was almost the same when the SiH_4 gas flow rate was constant (2.0 nm/s for the case of SiH_4 70 sccm). The substrate and the gas lines were not positively heated. The surface temperature of the substrate increased from ambient temperature and saturated at 80 °C during 100 s of deposition time.

The optical absorption coefficients of the SiN_x films were determined by transmittance and reflectance (T–R) measurement in the 300–800 nm range with a Shimadzu UV2600 spectrophotometer.

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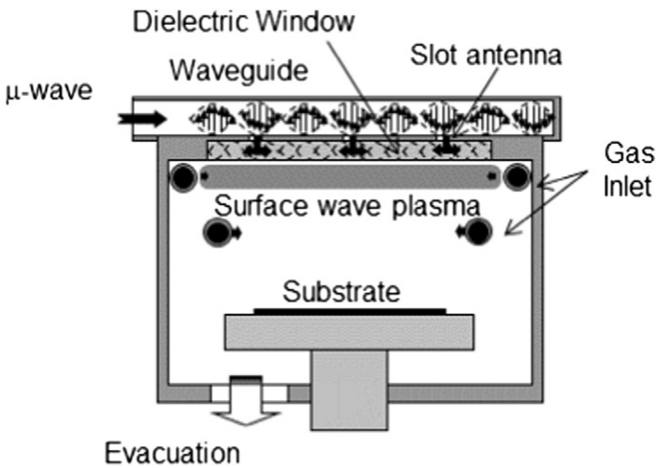

Fig. 1. Experimental apparatus of surface wave plasma chemical vapor deposition system.

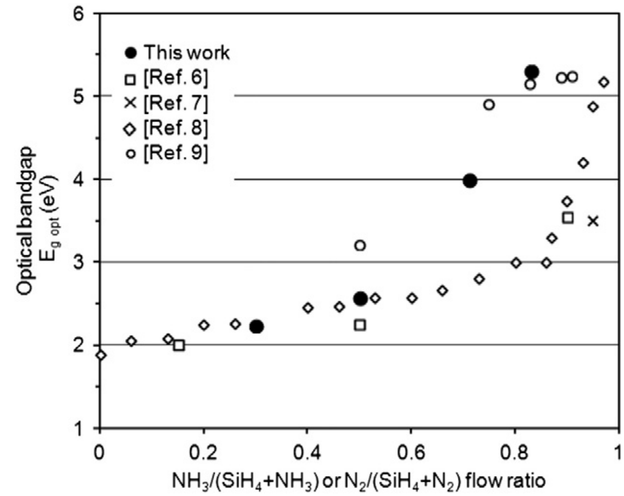

Fig. 3. Optical band gap ($E_{g\ opt}$) as a function of source gas flow ratio. The conditions for each reference are as follows: [Ref. 6] RF PE-CVD, $SiH_4 + NH_3$ at 300 °C. [Ref. 7] RF PE-CVD, $SiH_4 + N_2$ at 300 °C. [Ref. 8] RF PE-CVD, $SiH_4 + NH_3$ at 200 °C. [Ref. 9] ECR PE-CVD, $SiH_4 + N_2$ at 60 °C.

Film structures were evaluated with a Shimadzu FTIR-8400 Fourier transform infrared (FTIR) spectrometer and by XPS. XPS analysis was performed using a Shimadzu/Kratos AXIS-Nova spectrometer with a Vision 2 data system. The excitation source was a monochromated Al-Kα X-ray with 225 W-power, the size of the analysis area was 700 × 300 μm, and the emission angle of the photoelectron with respect to the sample normal was zero degrees. No ion sputtering was performed prior to the XPS analysis. For XPS data processing of Si 2p peaks, a linear background was subtracted before peak synthesis, which was performed with component peaks having a Gaussian (70%)–Lorentzian (30%) product peak shape. Without any constraints on peak position, peak height and peak width between component peaks were set during peak synthesis process. The position of the peaks was calibrated so that the highest Si 2p component appeared at 101.80 eV. The films were measured by XPS within 30 to 60 min after removal of the samples to ambient air from the vacuum tool after film formation.

The elemental ratio of the SiN_x films was also analyzed by RBS (NEC 3S-R10 and CEA RBS-400). RBS analysis can provide elemental bulk information of a film for the first several hundreds of nanometers of the surface. Measurements were performed with an incident energy of 2.275 MeV $4He^{++}$, a beam diameter of 1–2 mm, and detection angles of 160° (normal angle) and 119° (grazing angle).

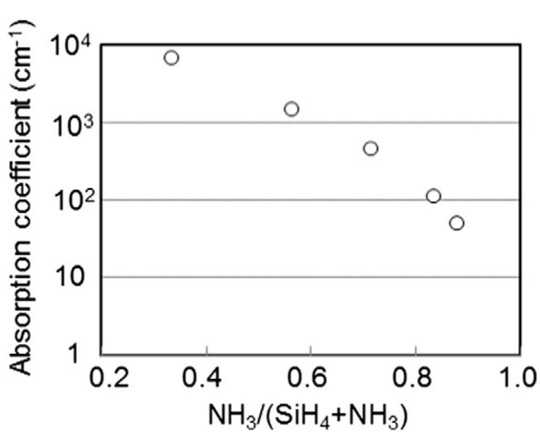

Fig. 2. Relationship between absorption coefficient of the SiN_x films and NH_3/($SiH_4 + NH_3$) source gas ratio.

3. Results and discussion

3.1. Optical properties of SiN_x films

First, the optical absorption coefficient of SiN_x films was calculated from the Beer–Lambert law for the films prepared with various SiH_4/NH_3 gas ratios. Fig. 2 shows the relationship between the absorption coefficient of the films at the wavelength of 400 nm and a supplied gas ratio of NH_3 and SiH_4. There is a noteworthy drop in the absorption coefficient down to a few hundred cm^{-1} or less at a NH_3/($SiH_4 + NH_3$) ratio of 0.7 and higher.

An optical band gap energy E_{04} was defined to be the spectra wavelength (energy) for which the absorption coefficient $\alpha = 10^4\ cm^{-1}$ in wavelength-dispersive optical absorption [11,12]. The optical band gap was plotted as a function of the NH_3/($SiH_4 + NH_3$) ratio in Fig. 3. Films with an optical absorption of lower than $10^4\ cm^{-1}$ in the measured range were not plotted. Data from previous reports [6–9] were also plotted in the figure. Refs. [6,8] used RF plasma enhanced chemical vapor deposition (PE-CVD) with SiH_4 and NH_3 as source gases. The deposition temperature was 200–300 °C. Ref. [7] used RF PE-CVD with SiH_4 and N_2. The deposition temperature was 200 °C. Ref. [9] used electron cyclotron resonance (ECR) PE-CVD with SiH_4 and N_2 and with a deposition temperature of 60 °C. Refs. [6,8] determined the optical band gap using E04 and Refs. [7,9] determined the same with Tauc's relation [13]. According to Fig. 3, the optical band gap increases with an increase in the NH_3 or N_2 ratio, indicating that adequate NH_3 or N_2 is needed for transparent SiNx films. Since the PE-CVD process is a predominantly surface reaction, the usual SiN_x film preparation involved heating at 200 °C. Since heating promotes Si – N bond formation, the SiN_x structure approaches the stoichiometric ratio, which leads to a lower absorption

Table 1
Film preparation conditions (flow rates of source gases).

Sample	SiH_4 (sccm)	NH_3 (sccm)
1	70	650
2	70	500
3	70	350
4	70	175
5	70	153
6	70	90