Properties of SiO$_x$N$_y$ Thin Films Deposited with a Single Molecular Precursor by Using RF PECVD

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We have deposited SiO$_x$N$_y$ thin films on both Si(100) and glass substrates by using a tetraethyl orthosilicate (TEOS) single precursor at nitrogen flow rates of 0 ∼ 100 sccm by using a radiofrequency Plasma Enhanced Chemical Vapor Deposition (PECVD) method. The film growth orientation and microstructural characteristics were analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Deposition at higher nitrogen flow rates results in finer clusters with smaller grain sizes. Moreover, we used UV/Vis and FT-IR spectroscopy and ellipsometry to investigate the optical properties for various nitrogen flow ratios. As-deposited SiO$_2$ films showed an amorphous structure, but samples annealed in an O$_2$ ambient at 900 °C showed increased crystallinity. Also, the leakage current densities of the SiO$_2$ and the SiO$_x$N$_y$ films annealed at 900 °C in an O$_2$ ambient were about 4.0 × 10$^{-8}$ and 1.5 × 10$^{-7}$ A/cm$^2$.

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I. INTRODUCTION

In recent years, considerable work has been done on thin silicon-oxynitride films and is increasing due to the development of the plasma enhanced chemical vapor deposition (PECVD) and the availability of metal-organic (MO) precursors [1–6]. It is well accepted that the substitution of weak Si-H or Si-OH bonds by more stable Si-N bonds at the semiconductor-insulator interface contributes to improved electrical behavior. Furthermore, the incorporation of nitrogen may reduce the interfacial strain. Consequently, knowledge of the electronic structure of the interface and the near interfacial region is a key to understanding the electrical reliability and the degradation due to high field stress. Unfortunately, the details of the role of nitrogen in the formation or removal of interface states is still not clear. Especially, silicon oxynitride has many unusual properties that make it suitable for a variety of thin film applications [7]. Recent articles have been focused on silicon oxynitride films because these materials reveal behaviors between metallic Si-N and resistive SiO$_2$ compounds.

Despite the huge amount of published scientific work on thin films of metallic oxides and nitrides over the last decades, the area of metal oxynitride has been poorly explored so far [8–12]. Based on the previous results [13], however, we realized that there were some argument of SiO$_2$N$_y$ growth behavior, such as morphology and RMS roughness properties on Si(100) and glass substrates, when using the RF PECVD method. The dependencies of some structural and optical properties on the nitrogen content were mainly examined for the purpose of obtaining the optimum effect of nitrogen addition on the film characteristics. In this work, we investigated the nitride material by using an RF plasma and focused on the general property of SiO$_2$N$_y$ coating materials.

II. EXPERIMENT

SiO$_2$N$_y$ films were deposited on Si(100) and glass substrates by using a radiofrequency PECVD reactor fabricated by using stainless-steel bodies. The PECVD apparatus was evacuated using a mechanical pump (R.P.). The general deposition conditions were a temperature of 300 °C, an RF power of 500 Watt, and a working time of 30 minutes. The Si(100) and glass substrates were pretreated with acetone, ethanol, de-ionized water, and HF solutions in an ultrasonic cleaner and sputter etched
for 15 min in Ar at 2 Pa (300 W RF power). TEOS (tetraethyl orthosilicate) was used as a single precursor without heating and without a bubbler gas. The base pressure in the deposition chamber was approximately 0.2 Pa, and depositions were carried out under the nitrogen mass flow rates and were set in order to reach N\textsubscript{2} partial fluxes of 0 ∼ 100 sccm.

After deposition, the morphology of the film was characterized with atomic force microscopy (AFM) and scanning electron microscopy (SEM) techniques to analyze their structural properties, and their optical properties were characterized with infrared spectroscopy FT-IR) and UV-Vis. spectroscopy. Furthermore, the MIS structure was used for electrical measurement. The structures were characterized by using I-V measurements at various temperatures.

III. RESULTS AND DISCUSSION

Figure 1 shows the variation of (a) the growth rate and the (b) refractive index obtained from the SiO\textsubscript{2} and SiO\textsubscript{x}N\textsubscript{y} films on Si(100) substrates at 300 °C and at 130 Pa with various nitrogen partial pressure. Figure 1(a) shows the variation of thickness with nitrogen flow rate at constant substrate temperature of 300 °C. It is clear from Figure 1(a) that with increasing nitrogen flow rate from 0 to 100 sccm, the thickness decreases from 2.4 to 1.67 nm/min. Figure 1(b) shows the variation of the refractive index obtained by ellipsometry measurement for the plasma-deposited SiO\textsubscript{2} and SiO\textsubscript{x}N\textsubscript{y} thin films as a function of nitrogen flow rate. Initially, refractive index increases slowly with the nitrogen flow rate and reaches a value of 1.8 at a nitrogen flow rate of 100 sccm. From Figure 1, we know that with increasing nitrogen content, the refractive index increases while the growth rate decreases.

Figure 2 shows the AFM images obtained from the SiO\textsubscript{2} and SiO\textsubscript{x}N\textsubscript{y} films on Si(100) substrates at 300 °C and at 130 Pa for various nitrogen partial pressure. The surfaces of SiO\textsubscript{2} and SiO\textsubscript{x}N\textsubscript{y} films grown on Si(100) substrates have RMS roughnesses of (a) 2.24 nm, (b) 1.53 nm, (c) 1.30 nm and (d) 1.19 nm with increasing nitrogen flow rate. With increasing nitrogen flow rate, we obtained smooth film, which means that of Si-O and Si-N species were formed on Si(100) substrates according to nitrogen flow rate.

Figure 3(a) and 3(c) show cross-sectional SEM images of the as-grown SiO\textsubscript{2} and SiO\textsubscript{x}N\textsubscript{y} films deposited under various conditions. Moreover, when nitrogen was implanted in the SiO\textsubscript{2} films, surfaces fo the films were smooth and did not have cracks. Figure 3(b) and 3(d) show SEM morphological images of the SiO\textsubscript{2} and the SiO\textsubscript{x}N\textsubscript{y} films that were grown on Si(100) substrates at 900 °C in an oxygen ambient. Here, the surface morphologies of the SiO\textsubscript{x}N\textsubscript{y} films after annealing were drastically changed; they had become amorphous and smooth.

Figure 4(a) shows UV/Vis. spectra for the SiO\textsubscript{2} and the SiO\textsubscript{x}N\textsubscript{y} films before and after annealing at 900 °C in an O\textsubscript{2} ambient. The measured average transmittance in the visible range of the SiO\textsubscript{2} and the SiO\textsubscript{x}N\textsubscript{y} films de-
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Fig. 3. SEM images of the films deposited on Si(100) substrates at various nitrogen flow rate: (a) as-grown SiO$_2$ film, (b) SiO$_2$ film annealed at 900 °C SiO$_x$N$_y$ film, (c) as-grown SiO$_x$N$_y$ film and (d) SiO$_x$N$_y$ film annealed at 900 °C.

visible range exceeds 80 % for all samples regardless of nitrogen doping and annealing. As Figure 4(b) shows the dominant single-phase Si-N and Si-O stretching bands of the films were observed in the FT-IR spectrum. The positions of the peak were at 800 for silicon nitride and at 1070 cm$^{-1}$ for silicon oxide. The wave number of the main FT-IR transmittance peak is clearly correlated to the composition of the films. Good agreement in the composition values is reached for samples with the same peak wave number after annealing in an O$_2$ ambient.

The leakage current characteristics of the Al/SiO$_2$/Si and Al/SiO$_x$N$_y$/Si structures annealed in an O$_2$ ambient are shown in Figure 5. The leakage current densities of the films increased after annealing in an O$_2$ ambient. The leakage current densities of the SiO$_x$N$_y$ and the SiO$_2$ films were about $8.5 \times 10^{-10}$ and $6.6 \times 10^{-9}$ A/cm$^2$, respectively, at −1 V. Also, the leakage current density of the SiO$_2$ annealed in O$_2$ at 900 °C was about $1.5 \times 10^{-7}$ A/cm$^2$ at −1 V. However, the leakage current density of the SiO$_x$N$_y$ heat treated in O$_2$ at 900 °C was improved, about $4.0 \times 10^{-8}$ A/cm$^2$ at an applied voltage of −1 V. Consequently, the leakage current increased after the as-deposited thin film had been treated by annealing. This result was attributed to two main causes. The first is the high increase in the leakage current for SiO$_2$ than for SiO$_x$N$_y$ being due to the increased crystallization of these thin films. Second is the decrease in the Si-O concentration in the interfacial layer for SiO$_x$N$_y$ as compared with SiO$_2$ because nitrogen blocked the oxygen diffusion to this region.

IV. CONCLUSIONS

We prepared SiO$_2$ and SiO$_x$N$_y$ films by using the PECVD method with a tetraethylorthosilicate (TEOS) single precursor within the Si-O-N ternary system and a nitrogen flow rate. It means that the SiO$_x$N$_y$ and SiO$_2$
films were formed with/without nitrogen gas. All samples were prepared with a constant Ar flux at 100 sccm and a substrate temperature at 300 °C. The optimum r.f. plasma power was 500 W, and a pressure of 130 Pa was used for 0.5 hr for quite smooth surfaces with no cracks a SiO\textsubscript{x}N\textsubscript{y} film using N\textsubscript{2} gas. The effect of the deposition parameters, such as the nitrogen flow rate, on the film structure, crystallinity and on the optical and the electrical properties were mainly studied in this work. AFM and SEM data showed quite smooth crack-free surface. In order to better understand the differences between the sample prepared with and without nitrogen gas in terms of surface parameters, we undertook characterizations by using UV/Vis. and FT-IR spectroscopy. The leakage current densities of the SiO\textsubscript{x}N\textsubscript{y} and the SiO\textsubscript{2} films annealed at 900 °C in O\textsubscript{2} were about 4.0 × 10\textsuperscript{−8} and 1.5 × 10\textsuperscript{−7} A/cm\textsuperscript{2}, respectively, at −1 V.

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