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Characteristic of SiO_2 Films Deposited by Using Low-Temperature PECVD with TEOS/N_2/O_2

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In this study, SiO_2 thin films were deposited at room temperature by using plasma enhanced chemical vapor deposition (PECVD) driven by an inductively coupled plasma (ICP) for various with gas mixtures of TEOS/N_2/O_2 at a given rf power and dc bias voltage. For the gas mixture with 40 sccm of N_2 in TEOS, 100 sccm of N_2, and 500 sccm of O_2, transparent and scratch-resistant SiO_2 could be deposited with a deposition rate of 30 nm/min when rf power of 500 W and a dc-bias voltage of − 350 V were applied. The characteristics of the deposited SiO_2, such as the composition, the binding energy, *etc.*, were compared with the SiO_2 deposited by using thermal CVD and evaporation. We found that the SiO_2 deposited using by PECVD with TEOS/N_2/O_2 exhibited properties typical of SiO_2 deposited by using thermal CVD and evaporation. The surface roughness of the 100-nm-thick SiO_2 deposited by using PECVD was similar to that of the substrate.

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I. INTRODUCTION

SiO_2 films are the most widely used dielectric materials in the solid-state electronic and optoelectronic devices such as insulators, waveguides, defect passivations, *etc.* [1,2]. In addition to the electronic applications, SiO_2 can be used as a diffusion barrier on various plastic packaging materials [3]. SiO_2 films can be deposited in various ways. However, to deposit SiO_2 on organic-based materials, a low-temperature deposition methods, such as sputter deposition and e-beam evaporation, are required so that the SiO_2 can be deposited at temperatures lower than plastic softening temperature. However, the step coverage of the SiO_2 deposited by these methods is not sufficient. Therefore, not all of the surface area may be covered when these methods are used, and leakage paths can be introduced. Chemical vapor deposition is known to provide excellent step coverage, but the growth temperature is generally higher than 800 °C. Therefore, plasma-enhanced chemical vapor deposition (PECVD) should be used to decrease the deposition temperature without significantly decreasing the step coverage and deposition rate. For the deposition precursors, various gas combinations containing silicon and oxygen can be used. Among the various silicon-containing precursors, tetraethylorthosilicate (TEOS) is know to have a good step coverage in addition to chemical stability and safety. Also, it is easy to handle as a liquid at room temperature [4,5].

In this paper, the properties of SiO_2 thin films deposited at room temperature by using TEOS PECVD and for applications as transparent thin-film diffusion barriers for next generation organic light-emitting diodes (OLEDs) and flexible thin-film transistor liquid-crystal displays (TFT-LCDs) are studied. In the PECVD system used in this experiment, high-vacuum tools, such as turbopumps, were eliminated because the use of high vacuum is not a productive method for next-generation large-area flexible substrates due to their outgassing. A brief summary of our results follows.

II. EXPERIMENT

Fig. 1 shows the PECVD system used in this study for the deposition of SiO_2 at room temperature. The plasma source for the PECVD system was an inductively coupled plasma source (ICP) having a 3.5-turn copper coil on top of the dielectric window of the reactor chamber with 100 to 900 W of 13.56-MHz rf power applied to the coil to generate inductively coupled plasmas. To improve the properties of SiO_2 deposited at room temperature, we varied the bias on the substrate from − 150 to − 350 V by using a separate 13.56-MHz rf power source. TEOS and the gas line to the chamber were heated to 40 °C and 80 °C, respectively, and N_2 was used as the carrier gas. The bubbled N_2/TEOS gas was introduced to the substrate

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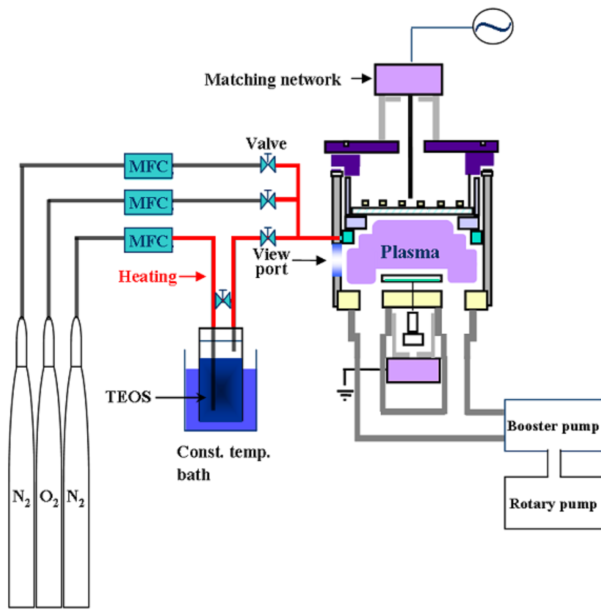

Fig. 1. Schematic diagram of the SiO_2 PECVD apparatus used in the experiment.

Table 1. PECVD process parameters used in the SiO_2 deposition.

Substrate	Si Wafer
Gas chemistry	$TEOS/N_2 + O_2$, $TEOS/N_2 + O_2 + N_2$
Deposition temperature	Room temperature
RF power	300 ~ 700 W
Bias voltage	– 150 ~ – 450 V
Bubbler temperature	40 °C
Delivery line temperature	80 °C
Flow rate of N_2 in TEOS	10 – 100 sccm
Flow rate of N_2	0 – 500 sccm
Flow rate of O_2	100 – 55 sccm

surface with a N_2/O_2 mixture by using a gas ring located on the top of the reactor. The SiO_2 deposition conditions used in the experiment are shown in Table 1. While the other parameters were varied, the N_2/TEOS flow rate, the O_2 flow rate, the N_2 flow rate, the rf power to the source, and the dc-bias voltage were maintained at 40 sccm, 500 sccm, 100 sccm, 500 W, and – 350 V, respectively.

The deposited film thickness was measured by using an alpha-step device (Alpha step-500, Tenco). The roughness of the deposited SiO_2 thin films was measured by using an atomic force microscope (AFM) (CP Research, Thermo-Microscopes) in the non-contact mode, and the refractive index of the films was measured by an ellipsometer (L-117, Gaertner) that used a 633-nm a He-Ne laser as the light source. The chemical bonding status of the films was determined by a Fourier transform infrared spectrometer (FT-IR) (Bruker IFS-66/S, Bruker). The chemical structure and the composition of the films were estimated by using an X-ray photoelectron spectrometer (XPS) (ESCA2000, VGmicrotech), with a monochromic Al-kα line.

III. RESULTS AND DISCUSSION

The deposition of SiO_2 by PECVD is generally carried out using SiH_4-based gas mixtures due to the high deposition rate at low temperatures. However, SiH_4 is explosive and toxic, and the SiO_2 deposited when using SiH_4-based gas mixtures does not show good step coverage [4,6]. Therefore, in this study, instead of SiH_4-based gas mixtures, TEOS carried by N_2 was used as the precursor for the SiO_2 deposition, and various N_2/O_2 mixtures were added to remove carbon and hydrogen in the TEOS and to form more stoichiometric SiO_2. The deposition rate and the measured refractive index of the SiO_2 deposited by using the PECVD are shown in Fig. 2 as functions of the flow rates of N_2, O_2, and N_2 in TEOS. The ICP source power and the dc bias voltage were maintained at 500 W and – 350 V, respectively. Also, when one gas flow rate was varied, other gas flow rates were maintained at 40 sccm, 100 sccm, and 500 sccm for N_2 in TEOS, N_2, and O_2, respectively. As shown in the figure, when N_2 in TEOS was increased from 10 to 100 sccm, the deposition rate increased almost linearly from 40 sccm, and at a flow of 100 sccm of N_2 in TEOS, a 200-nm/min deposition rate could be obtained. However, when the quality of the deposited SiO_2 was examined for the film deposited with 100 sccm of N_2 in TEOS, the deposited SiO_2 scratched easily with tweezers even though the deposited film was transparent. The refractive index measured by using an ellipsometer increased initially from 1.43 to 1.46 for increasing flow rate to 40 sccm, but further increases to 100 sccm decreased the refractive index to 1.36. Therefore, the SiO_2 film deposited at high gas flow rates of N_2 in TEOS appears to contain hydrocarbons.

By maintaining the gas flow rate of N_2 in TEOS at 40 sccm, we added of various amounts N_2 or O_2. As Fig. 2 shows, increasing the N_2 or the O_2 from 0 to 500 sccm did not change the deposition rate significantly; however, when O_2 was increased from 100 to 500 sccm, the deposition rate increased from about 20 to 30 nm/min. When the oxygen flow rate was lower than 100 sccm, the deposited SiO_2 changed of color with time during air exposure due to the TEOS being deposited without complete dissociation. The addition of N_2 to 300 sccm also increased the deposition rate of SiO_2 to 60 nm/min; however, a further increase in the N_2 flow rate decreased the deposition rate. Also, when the N_2 flow rate was higher than 100 sccm, a rough SiO_2 surface was obtained. In addition, increasing the N_2 or the O_2 to 500 sccm increased the refractive index slightly. However, it remained within

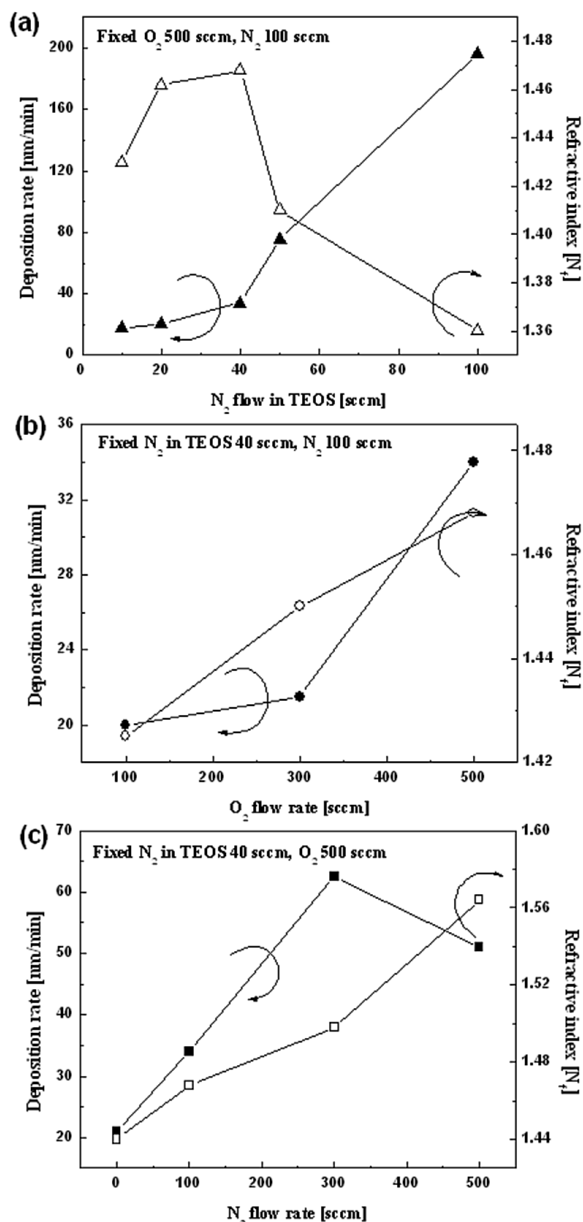

Fig. 2. . Deposition rate and refractive index of the deposited SiO_2 films as functions of (a) the N_2 flow rate in TEOS, (b) the O_2 flow rate, and (c) the N_2 flow rate at an rf power of 500 W and a dc bias voltage of – 350 V.

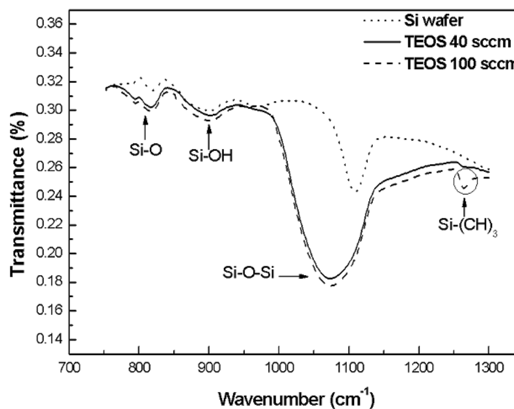

Fig. 3. FT-IR spectra of Si wafers and SiO_2 films deposited by using PECVD (condition: N_2 in TEOS at 40 sccm or 100 sccm, O_2 flow rate = 500 sccm, N_2 flow rate = 100 sccm, rf power = 500 W, and dc bias voltage = – 350 V)

Table 2. Atomic percentages of SiO_2 films measured by XPS for different deposition methods. For PECVD, the rf power and the dc bias voltage were varied at the optimized condition.

Method \ Composition			Si2p	Cls	O1s
Thermal CVD			38.3 %	0.4 %	61.3 %
E-beam			3.7. %	0.8 %	62.6 %
PECVD	Source power	300 W	37.6 %	0.3 %	62 %
		500 W	37.7 %	0.37 %	62 %
		700 W	37.6 %	1.1 %	61.4 %
	DC bias voltage	– 250 V	38.1 %	0.2 %	61.7 %
		– 350 V	37.7 %	0.37 %	62 %
		– 450 V	38 %	0.3 %	61.7 %

the range of 1.46 ± 0.1, close to that of pure SiO_2.

From the above experiment, the optimized gas flow condition for obtaining transparent and scratch-resistant SiO_2 films was determined to be 40 sccm of N_2 in TEOS, 100 sccm of N_2, and 500 sccm of O_2 at an rf power of 500 W and a dc-bias voltage of – 350 V. Using FTIR, we investigated the binding states of the SiO_2 films deposited with the above optimized condition, and the result is shown in Fig. 3 the FTIR peaks from the silicon wafer and the SiO_2 deposited with 100 sccm N_2 in TEOS are also shown as references. The thickness of the deposited films was about 100 nm. As the figure shown, peaks related to Si-O-Si (1098 cm^{-1}), Si-O (808 cm^{-1}), Si-OH (900 cm^{-1}), and Si-(CH)$_3$ (1263 cm^{-1}) were observed, and for the SiO_2 deposited with 40 sccm of N_2 in TEOS, the peak heights due to Si-O-Si and Si-O were significant compared to those from the Si wafer, indicating the formation of SiO_2. In the case of the SiO_2 deposited with 100 sccm of N_2 in TEOS, in addition to the Si-O and Si-O-Si peaks from SiO_2, the Si-CH_3 and the Si-OH [5,7, 8], originating from the hydrocarbons from incompletely dissociated TEOS, were observed to be increased.

The composition of SiO_2 deposited with the optimized gas flow rate condition of 40 sccm of N_2 in TEOS, 100 sccm of N_2, and 500 sccm of O_2 was investigated using XPS, and the result is shown in Table 2. As references, the rf power and the dc bias voltage were varied around the optimized condition from 300 to 700 W and from – 250 to – 450 V, respectively, and corresponding compositions were investigated. In addition, the compositions of SiO_2 deposited by using thermal chemical vapor deposition (CVD) and by using e-beam evaporation were in-

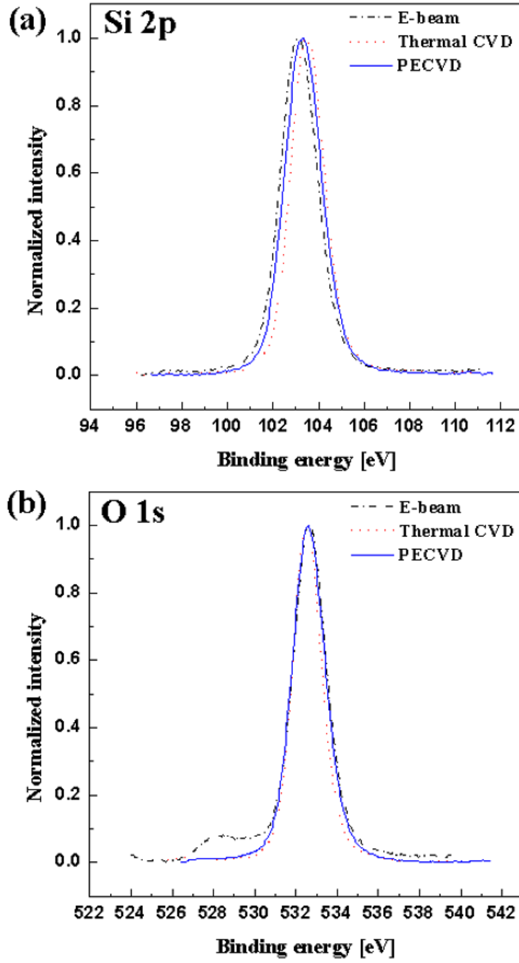

Fig. 4. XPS narrow scan spectra of (a) Si_{2p} and (b) O_{1s} of the films deposited by using e-beam, thermal CVD, and PECVD at the optimized condition. (N_2 in TEOS at 40 sccm, O_2 flow rate = 500 sccm, N_2 flow rate = 100 sccm, rf power = 500 W, and dc bias voltage = – 350 V).

vestigated for comparison. The films was sputter-cleaned in the XPS chamber prior to XPS analysis. All of the films measured by using the XPS showed peaks related to only Si, O and C; no peaks related to N could be observed for the SiO_2 deposited in our experimental condition. Therefore, no noticeable nitrogen-containing SiO_2 or oxynitride was formed for the PECVD film deposited with the optimized condition in our experiment due to the N_2 in the plasma. Also, all of the films deposited by using PECVD showed similar atomic percents of Si and O, and the atomic percent of C was close to that for air contamination. The atomic compositions of the SiO_2 film deposited by using PECVD were similar to those of SiO_2 deposited by using thermal CVD and evaporation. Fig. 4 shows the binding energies of Si and O measured by using an XPS narrow scan for the SiO_2 films deposited by using PECVD with the optimized condition and for those deposited by using thermal CVD and evaporation. The Si_{2p} peak and the O_{1s} peak of SiO_2 are located at binding energies of 103.3 eV (or 103.6 eV) and 532.5 eV (or, 533.3, 534.3 eV), respectively [8, 9]. As the figure, show all of the SiO_2 films deposited by using thermal CVD, evaporation, and PECVD at the optimized condition have Si_{2p} peaks near 103.3 eV and O_{1s} peaks near 532.5 eV. Therefore, in our experiment, SiO_2 having chemical properties similar to those of SiO_2 deposited by using thermal CVD or evaporation could be successfully deposited at room temperature by using PECVD with TEOS mixed with N_2 and O_2.

Table 3. AFM root-mean-square (RMS) values of the SiO_2 films deposited by different deposition methods.

Metods of SiO_2 film deposition	RMS (nm)
Reference silicon wafer	0.4585
Thermal CVD	0.449
E-beam	2.155
PECVD	0.4183

The surface roughness of the 100-nm-thick SiO_2 thin films deposited by using PECVD with the optimized condition, thermal CVD, and e-beam evaporation were measured with an AFM, and results are shown in Table 3. As a reference, the surface roughness of the silicon wafer used to deposit SiO_2 by PECVD, thermal CVD, and evaporation in our experiment is also shown as the base roughness. As the figure shows, the roughnesses of SiO_2 deposited with thermal CVD and PECVD were similar to that of the silicon wafer, indicating no increase in the surface roughness.

IV. CONCLUSION

In this study, SiO_2 was deposited at room temperature by using PECVD driven by an ICP as functions of the gas flow rates of TEOS/N_2, N_2, and O_2 at a given rf power and dc bias voltage, and the optimized SiO_2 characteristics were investigated for applications to next generation diffusion barriers for OLEDs and flexible TFT-LCDs. By optimizing the gas mixtures, we could successfully deposit transparent and scratch-resistant SiO_2 thin films at a deposition rate of 30 nm/min by using 40 sccm of N_2 in TEOS, 100 sccm of N_2, and 500 sccm of O_2 at a 500-W rf power and a – 350-V dc-bias voltage. The hydrocarbons contained in the SiO_2 film due to incomplete dissociation of TEOS were negligible at the optimized condition. The binding status and the atomic composition of the optimized SiO_2 investigated by using XPS were similar to those of the SiO_2 deposited by using thermal CVD and e-beam evaporation. No increase in surface roughness was observed for the SiO_2 deposited by using PECVD.

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