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CHARACTERIZATION OF THE SIO_2FILM DEPOSITED BY USING PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION (PECVD) WITH TEOS/N_2/O_2

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Abstract

The purpose of this study was to examine how certain parameters like temperature, pressure, and gas composition affect the characteristics of SiO_2 film by Plasma Enhanced Chemical Vapor Deposition (PECVD). We used of low temperature and 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 standard cubic centimeters per minute (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 350V 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. It was found that the SiO_2 deposited by PECVD with TEOS/N_2/O_2 exhibited properties typical of SiO_2 deposited applying thermal CVD and evaporation. The surface roughness of the 100 nm-thick SiO_2 deposited by PECVD was similar to that of the substrate.

Key word: Silicon dioxide, PECVD, Surface, Deposition, Thin films, TEOS.

Introduction

Silicon-oxide thin films are is extensively studied for its various applications as thin gate dielectrics and passivation layers in microelectronic circuits because they have a higher dielectric constant and more effective barrier property for boron diffusion than

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SiO_2 thin films. In addition to the electronic and optical applications [1-4], many methods have been developed to deposit SiO_2 film. However, to deposit SiO_2 on organic-based materials, 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 800^0C. 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 known to have 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 turbo pumps, were eliminated because the use of high vacuum is not a productive method for next-generation large-area flexible substrates due to their out gassing. A brief summary of our results follows.

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 the 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 13.56MHz RF power source. TEOS and the gas line to the chamber were heated to 40 ^{0}C and 80 ^{0}C, respectively, and N_2 was used as the carrier gas. The bubbled N_2/TEOS gas was introduced to the substrate 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 40,100 and 500 standard cubic centimeters per minute (sccm), 500 W, and 350V, respectively.

The deposited film thickness was measured by using an alpha-step device (Alpha step-500, Tenco). The roughness of the deposited SiO_2thin films was measured by using an atomic force microscope (AFM) (CP Research, Thermo-Microscopes) in the non-contact mode, and there fractive index of the films was measured by an ellipsometer (L-117, Gaertner) working with 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).

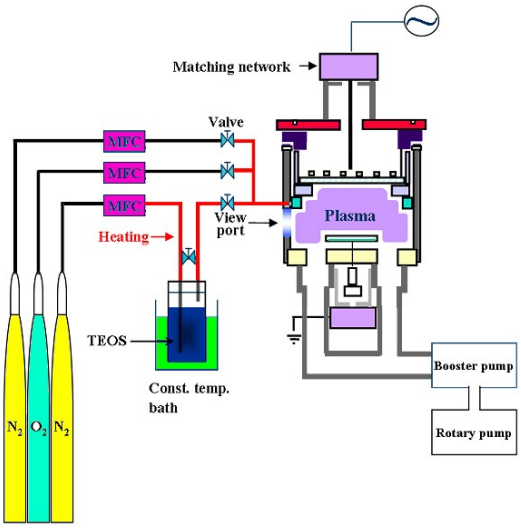

Fig. 1. Schematic diagram of the SiO_2PECVD apparatus used in the experiment.

Table 1. PECVD process parameters used in the SiO_2deposition.

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	40^0C
Delivery line temperature	$80\ ^0C$
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

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 [6, 7]. 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 and350 V, respectively. As shown in Fig. 2, 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 N2 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 could be easily scratched 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 increase 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 40sccm, we added various amounts of 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, during air exposure the deposited SiO_2 changed ~~of~~ color with time 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 slightly increased the refractive index. However, it remained within the range of 1.46 ± 0.1, close to that of pure SiO_2.

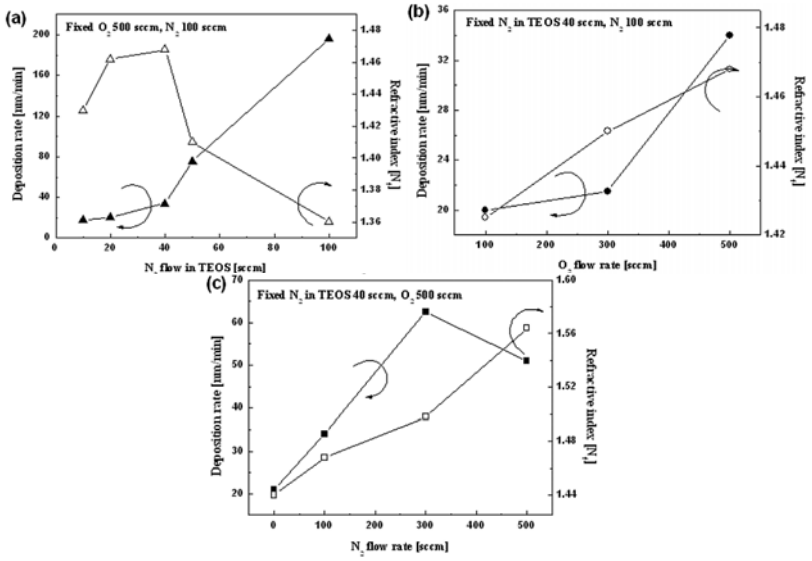

Fig. 2. Deposition rate and refractive index of the deposited SiO_2 films as functions of (a) the N_2 flow rate in TEOS, (b) the O_2 flow rate, and (c) the N_2 flow rate at an RF power of 500 W and a dc bias voltage of 350 V.

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 FT-IR, we investigated the binding states of the SiO_2films deposited with the above optimized condition, and the result is shown in Fig. 3.The FT-IR 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 shown in Fig. 3, 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 N2 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 with100 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 [6-8], originating from the hydrocarbons from incompletely dissociated TEOS, were observed to be increased. The composition of SiO_2deposited 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 from250 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 electron-beam evaporation were in investigated for comparison [9]. The film was sputter-cleaned in the XPS chamber prior to XPS analysis. All of the films measured by the XPS showed peaks related to only Si, O and C; no peaks related to N could be observed for the SiO_2deposited in our experimental condition. Therefore, no noticeable nitrogen-containing SiO_2or 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 PECVD showed similar atomic percent's of Si and O, and the atomic percent of C was close to that for air contamination.

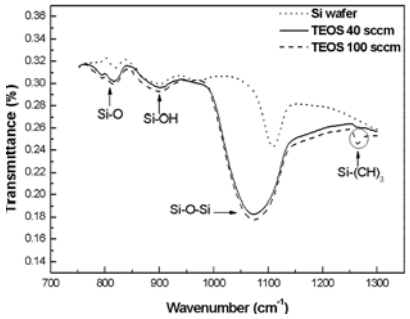

Fig. 3. FT-IR spectra of Si wafers and SiO_2films deposited by using PECVD (condition: N2 in TEOS at 40 sccm or 100 sccm, O_2 flow rate = 500 sccm, N_2 flow rate = 100 sccm, RF power = 500 W, and dc bias voltage = 350 V)

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.

Composition		***Si_{2p}***	***C_{1s}***	***O_{1s}***
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 %
PECVD 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 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 applying an XPS narrow scan for the SiO_2 films deposited by using PECVD with the optimized condition and for those deposited by 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 [10-12].

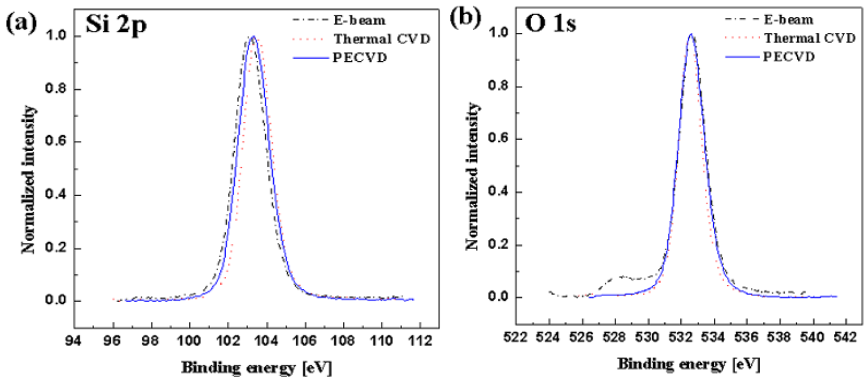

Fig. 4. XPS narrow scan spectra of (a) Si_{2p} and (b) O1s of the films deposited by using e-beam, thermal CVD, and PECVD at the optimized condition. (N2 in TEOS at 40sccm, O_2 flow rate = 500 sccm, N_2 flow rate = 100 sccm, RF power = 500 W, and dc bias voltage = 350V).

As Fig. 4 shows 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 O1s 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 performing PECVD with TEOS mixed with N_2 and O_2.

The surface roughness of the 100-nm-thick SiO_2thinfilms deposited by PECVD with the optimized condition, thermal CVD, and e-beam evaporation were measured with an AFM, and results are shown in Table 3.

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

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

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 roughness~~'s~~ of SiO_2 deposited with thermal CVD

and PECVD was similar to that of the silicon wafer, indicating no increase in the surface roughness.

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 the next generation of 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_2at a 500 W RF power and a 350V 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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