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LOW TEMPERATURE DEPOSITION OFSIOx FILMS BY PLASMA-ENHANCED CVD USING 100 kHz GENERATOR

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ABSTRACT

Silicon oxide thin films are prepared by plasma-enhanced CVD (PECVD) using 100kHz and 13.56MHz generators. Source gases are two sorts of mixture, tetramethoxysilane (TMOS) and oxygen, and tetramethylsilane (TMS) and oxygen. We investigate the effect of frequency on film properties of deposited films including mechanical properties. 100kHz PECVD process can deposit silicon oxide films at 23℃ at the power of 20W. X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR) and ellipsometric measurements reveal that the structural quality of the films prepared both by 100kHz process and by 13.56MHz process are very like silicon dioxide. The 100kHz process is adequate for low temperature deposition of SiOx films.

INTRODUCTION

Recently preparation of SiOx thin films by PECVD have been investigated using a 13.56MHz generator and organosilicon compounds such as tetraethoxysilane (TEOS), tetramethyldisiloxane (TMDSO), methyltrimethoxysilane (MTMOS), TMOS and TMS as source gases at low substrate temperature below 100℃[1-5]. High quality SiOx films have been prepared by PECVD using a 50 Hz discharge, and SiH_4-N_2O and TEOS-O_2 mixtures as source gases on unheated substrates[6]. Using low frequency generator, high quality Si_3N_4, a-Si:H and a-C:H films were also deposited[7-9]. Low frequency PECVD system needs less expensive power supply and less power consumption.

To decrease the substrate temperature much more and to investigate the effect of frequency on the film properties, we used a 100kHz generator in this study. For comparison, we also used a 13.56MHz generator. This paper reports on the preparation of SiOx thin films on glass, silicon and polycarbonate (PC) substrates by PECVD using 100kHz and 13.56 MHz generators and TMOS and oxygen, and TMS and oxygen mixtures as source gases. We stress the investigation of difference in properties between films prepared by 100kHz process and those prepared by 13.56MHz. This paper also reports on the optical and mechanical properties of the films.

EXPERIMENTAL PROCEDURE

Figure 1 shows a schematic diagram of the PECVD apparatus. The discharge tube con-

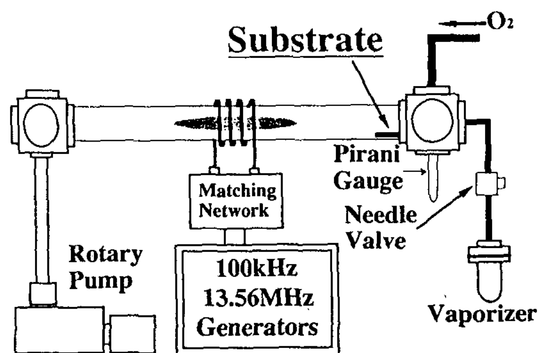

Fig. 1 Schematic diagram of the PECVD apparatus.

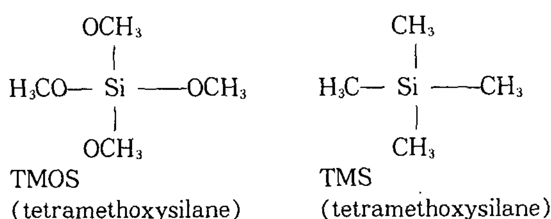

Fig. 2 Structural formulas of TMOS and TMS.

sisted of a high purity quartz glass cylinder of length 1000mm and inside diameter 35mm. Stainless steel holders supported this tube at both ends. Plasma was induced by 100kHz and 13.56MHz generators with an impedance -matching network terminating in a 5.5turn inductively coupled coil of copper tubing 6mm in diameter.

The coil was water-cooled and placed at the center of the discharge tube. The power used was 20W for 100kHz and 200W for 13.56MHz. Reactants used in the deposition were TMOS (Shinetsu LS-540) and oxygen (99.99%), and TMS (Shinetsu LS-470) and oxygen mixtures. Total gas pressure was maintained constant at 25Pa and oxygen mixing ratio was varied from 0 to 80%. The gas composition was varied by controlling the partial pressures of an organosilicon compound and oxygen. The organosilicon compound was vaporized at room temperature and flow rate was controlled with a needle valve. Glasss, silicon and PC substrates were set on a substrate holder located 50cm from the center of the inductively coupled coil.

Glass substrates were cleaned with acetone and silicon and PC substrates were cleaned with ethanol using an ultrasonic cleaner. The reactor was pumped by a rotary pump. Pressure was measured with a Pirani gauge. Before the deposition, all the substrates were pretreated with oxygen plasma during 10 minutes. Substrate temperature was measured with an alumel-chromel thermocouple. Deposition time was 5 to 120 minutes. Chemical bonding states of the deposited films were studied using Fourier transform infrared spectrometer (JASCO FT-IR 5300) and XPS system (Shimadzu Axis). Refractive index was determined by ellipsometer (PLAS MOS SD2300) at a wavelength of 632.8nm. Spectroscopic measurements were carried out by using a double-beam spectrometer (Shimadzu UV-3101PC). The hardness of a film was measured with a dynamic ultra-microhardness tester (Shimadzu DUH-200) at the load of 0.5 gf. The adhesion between a film and a substrate was evaluated with a scratch tester (RHESCA CSR-02). Thickness of the films was measured with a surface profilometer (Mitutoyo Surftest SV-600).

RESULTS AND DISCUSSION

Deposition temperature and deposition rate

At the O_2 mixing ratio of 20%, the substrate temperature during deposition was 35 ℃ for 100kHz process. With increasing O_2 mixing ratio to 60%, the substrate tempera-

ture decreased to 23℃. In 13.56 MHz process, the substrate temperature was about 85 ℃ during deposition. Films were, therefore, prepared at room temperature for 100kHz process because of low power used. Deposition rate decreased with increasing O_2 mixing ratio and the deposition rate for TMS-O_2 mixtures was higher than that for TMOS-O_2 mixtures in both 100kHz and 13.56 MHz processes because of higher vapor pressure of TMS. The maximum deposition rate 383 nm/min was obtained with TMS-O_2 mixtures in 13.56 MHz process at O_2 mixing ratio 0%. In 100kHz process, the maximum deposition rate was 18 nm/min with TMS-O_2 mixtures at O_2 mixing ratio 20%. Higher deposition rate was obtained by 13.56 MHz process than 100kHz process. The difference in power used affected the deposition rates.

FT-IR and XPS measurements

Figures 3 and 4 show the FT-IR spectra of the films deposited with TMOS-O_2 and TMS-O_2 mixtures as a function of oxygen mixing ratio.

[TMOS-O_2 mixture system] Si-O-Si stretching, bending and rocking vibration peaks are observed around at 1070, 800 and 450cm^{-1}, respectively. These peaks indicate that silicon oxide films are prepared. Si-CH_3 peaks are observed around 1270 and 835cm^{-1} and Si-OCH_3 peaks appear at 1195 and 835cm^{-1} only when O_2 mixing ratio was 0%. In 13.56MHz process, Si-OCH_3 peak at 1195cm^{-1} is not observed. It seems that TMOS is not fully decomposed without oxygen especially in 100 kHz process. Si-OH peak is observed around at 930cm^{-1} [10-14]. Si-OH peak height increases

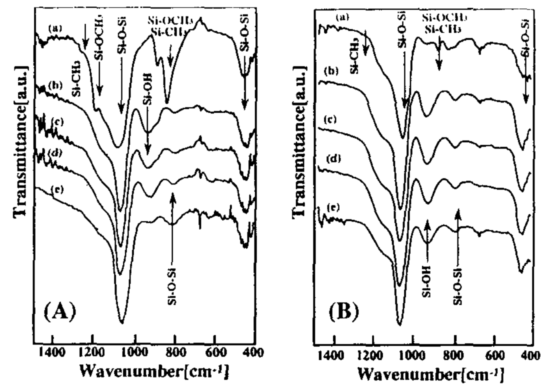

Fig. 3 IR spectra of silicon oxide films prepared with TMOS-O_2 mixtures by 100kHz and 13.56MHz processes. (A) 100kHz, (B) 13.56MHz, (a), (b), (c), (d) and (e) denote O_2 mixing ratio 0%, 20%, 40%, 60% and 80%.

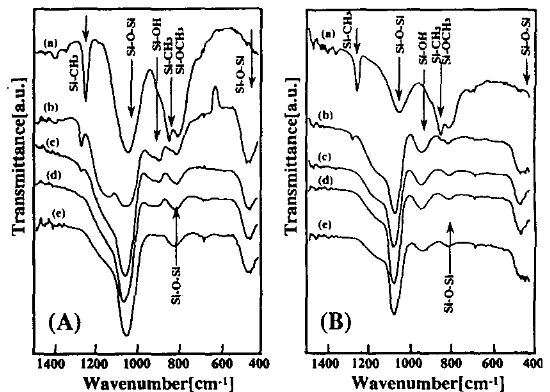

Fig. 4 IR spectra of silicon oxide films prepared with TMS-O_2 mixtures by 100kHz and 13.56MHz processes. (A) 100kHz, (B) 13.56MHz, (a), (b), (c), (d) and (e) denote O_2 mixing ratio 0%, 20%, 40%, 60% and 80%.

when O_2 mixing ratio increases from 0 to 20% and becomes constant above 20%. When O_2 mixing ratio is above 20%, no major difference is noticed in two processes.

[TMS-O_2 mixture system] Si-O-Si stretching, bending and rocking vibration peaks are observed at 1060, 800 and 440cm^{-1} and Si-CH_3 peaks are observed at 1270 and 835cm^{-1}

as well as TMOS-O_2 mixture system. Si-OH peak appears around at 930cm^{-1}. At the O_2 mixing ratio 0%, Si-CH_3 peak at 835cm^{-1} is higher than Si-O-Si peaks at 1043 and 796cm^{-1}. Si-CH_3 peak height decreases with increasing O_2 mixing ratio. TMS contains no oxygen atoms in itself, and then TMS is less decomposed only in the TMS plasma and forms the polymerized film. By introducing oxygen into the reactor, oxygen affects the oxidation process, and Si-O and Si-OH bonds form mainly and Si-CH_3 peak disappears in the IR spectra. Si-CH_3 peaks at 1270cm^{-1} and Si-CH_3 and Si-OCH_3 peaks at 837cm^{-1} for TMS-O_2 mixture system are higher than those for TMOS-O_2 mixture system. Silicon oxide films prepared with TMS-O_2 mixtures have slightly lower Si-OH peak height than those prepared with TMOS-O_2 mixtures.

To investigate the stoichiometry of the films, XPS measurement was carried out and Si, O and C are detected. At the O_2 mixing ratio 0%, carbon concentration in the films prepared with TMOS-O_2 mixtures is 11-14 at.%, and for the films prepared with TMS-O_2 mixtures, carbon concentration is 49-57 at.%. Carbon concentration decreases dramatically to 2-6 at.% when O_2 mixing ratio increases from 0 to 40% and the composition approaches to SiO_2. If the O_2 mixing ratio is above 40%, carbon concentration in the films is constant below 6 at.%. This reduction of carbon concentration in the films is attributed to the decomposition of organosilicon compounds by introducing oxygen and is consistent with the results of FT-IR measurement. No difference is observed on this tendency between 100kHz and 13.56MHz processes.

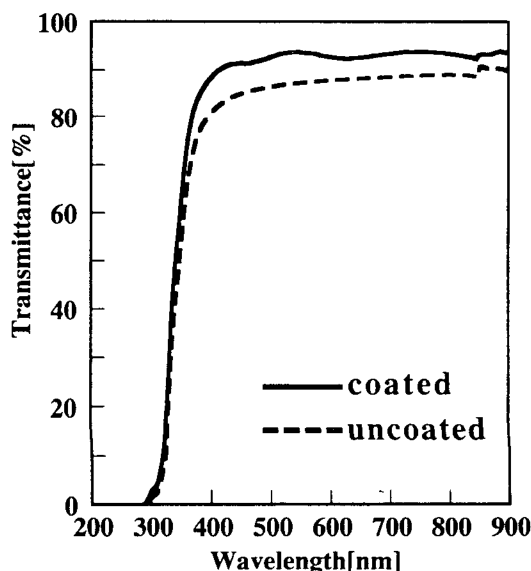

Fig. 5 Optical transmission spectra for a polycarbonate substrate before(broken line) and after(solid line) deposition.

Optical transmission spectra and refractive index

The optical transmission spectra for a PC substrate before and after deposition are shown in Figure 5. The optical transmittance of the films on glass and PC substrates was more than 90% in the range between 400 and 900 nm, and the films were colorless and transparent. The transmittance of the glass and PC substrates increased after coating. Hence the films are also useful to avoid reflection. The refractive index was about 1.44 at a wavelength of 632.8 nm, and was similar to the index of silicon dioxide. Therefore, the deposited films are very like silicon dioxide.

Hardness and adhesion

Figure 6 shows the hardness of the films prepared with TMS-O_2 mixtures as a func-

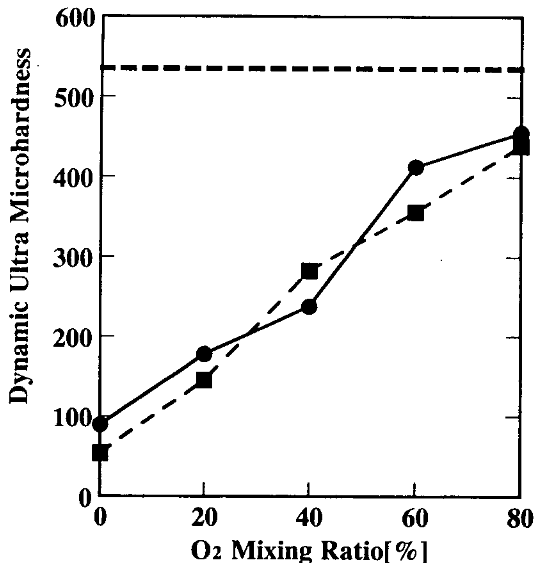

Fig. 6 Relationship between dynamic ultra microhardness of silicon oxide films prepared with $TMS\text{-}O_2$ mixtures as a function of O_2 mixing ratio.
● : 13.56MHz, ■ : 100kHz,··· : Si substrate.

tion of oxygen mixing ratio. Thickness used is 200nm. Hardness increases gradually with O_2 mixing ratio. This tendency corresponds to the decrease in $Si\text{-}CH_3$ and $Si\text{-}OCH_3$ bonds with increasing O_2 mixing ratio in the FT-IR measurement. If the $Si\text{-}CH_3$ bonds exist in silicon oxide films, the film becomes elastic[15]

With increasing O_2 mixing ratio to 80%, the oxidation proceeds, the film becomes hard and its chemical composition approaches to SiO_2. The maximum value of dynamic microhard-ness of the films is 455, whereas the hardness of the silicon substrate is about 535. The knoop hardness of Si is about 1400. Therefore hard silicon oxide films can be deposited by the present PECVD. Hardness of the films deposited with $TMS\text{-}O_2$ mixtures was higher than that with $TMOS\text{-}O_2$ mixtures. This hardness measurement gives good agreement with the result of Chen et al.[16]. Higher hardness for the films prepared with $TMS\text{-}O_2$ mixtures than those for $TMOS\text{-}O_2$ mixtures was due to the lower peak height of the Si-OH peak in FT-IR spectra.

Critical loads of adhesion between the films and glass substrates were measured by a scratch tester. Critical loads of the films prepared with $TMOS\text{-}O_2$ mixtures were roughly constant at 15-25mN on glass and 16-33mN on silicon. The value of critical loads of the films prepared with $TMS\text{-}O_2$ mixtures both on glass and silicon increased gradually when O_2 mixing ratio was varied from 0 to 80%. The maximum value was 54mN on glass and 61mN on silicon. The films adhere strongly to the substrates.

CONCLUSIONS

Silicon oxide thin films were prepared by PECVD using 100kHz and 13.56MHz generators and mixtures of organosilicon compounds and oxygen as source gases. 100kHz PECVD process can deposit silicon oxide films at 23℃. The quality of the films prepared both by 100kHz and 13.56MHz processes were very like silicon dioxide. As the oxidation proceeded, the film became hard and its chemical composition approached to SiO_2. The refractive index was 1.44 and the films were transparent. These 100kHz and 13.56MHz PECVD processes are suitable for the deposition of silicon dioxide films on less heat-resistant substrates such as plastics.

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