Local Deposition of Carbon Containing SiOₓ Synthesized Using Atmospheric Pressure Microplasma Jet

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Local deposition of carbon containing SiOₓ was studied by using a very-high-frequency (VHF) inductive coupling microplasma jet (MPJ) from a tetraethoxysilane ([(SiOC₄H₄)₄], TEOS) and argon mixture. Two distinct thickness profiles were observed in the product, i.e., the dome shaped profiles with and without a hollow at the center region. The products showed a strong white photoluminescence emission. The gas flow dependent deposition profile of products is discussed in terms of the film thickness, chemical composition, and photoluminescence characterizations.

Key words: Miroplasma jet, White light emission, SiOₓ, SiOₓ

1. INTRODUCTION

Silicon oxide films deposited from organic precursors by using various atmospheric pressure plasma jets have been extensively studied for the application as the functional coating to enhance the barrier property of polymer against gases or liquids [1-5]. Organic materials, such as TEOS ([(SiOC₄H₄)₄]Si) and hexamethydisiloxane (HMDSO, (CH₃)₃SiO(Si(CH₃)₃) are widely used as the precursors for silicon oxide film deposition [6, 7]. Most of interests have been focused on the surface cleaning and protective coating on organic and polymer materials using a low gas-temperature plasma source [8, 9]. In particular, the understanding of the determining factors of film thickness and compositional profile is a key issue to controlled deposition with the source moving relative to the substrate, since the gas flow dynamic influence the thickness profile of the product. These gas flow dependent deposition profile is also stressed in an atmospheric pressure microplasma jet (MPJ) source having a smaller tube diameter of several sub-millimeters to millimeters.

Here, we demonstrate the local static deposition of white-luminescent carbon containing SiOₓ using an atmospheric pressure thermal MPJ of a TEOS and argon mixture. The major subject is the understanding of the determining factors of the thickness profile and chemical compositional distribution in the product through the systematic deposition studies from a TEOS and Ar mixture as a function of Ar gas flow rate, Qₐr.

2. EXPERIMENTAL

2.1 Plasma jet geometry

Figure 1 shows a schematic of the deposition apparatus used in this study, which is constituted by the very-high-frequency (VHF) thermal MPJ of argon. A quartz glass tube with an inner diameter of 2 mm was used as the argon gas inlet. The VHF power of 200 W was supplied to the 3-turn coil through a matching circuit. At a distance between the working coil and the tip of the tube end of 25 mm.

Carbon containing SiOₓ was synthesized on c-Si(100) (resistance: 0.4–0.6 Ω cm) wafer with a native oxide and glass at Tₛ of 30°C and 275°C by supplying TEOS from a tube end outside independently under the steady flow of MPJ of argon. The tube-substrate distance d was 10 mm. The deposition parameters were Qₐr (1–20 standard liter per minutes (slm)) and Tₛ. The axial distribution of the MPJ of argon was monitored by optical emission spectrometer (OES). The thickness profile of the products was characterized with surface profiler and scanning electron microscope (SEM). The Fourier-transform infrared spectrometer (FT-IR) and x-ray photoelectron spectroscopy (XPS) studies were also employed to understand the chemical compositional profiles at the center and outer regions of ring-shaped products. In addition, the photoluminescence (PL) spectra in the products were measured using a 325 nm He-Cd laser of 5 mW at room temperature.

Fig. 1 Schematic of the deposition apparatus used in this study constituting of a thermal microplasma jet and the Ar plasma emission.
3. RESULTS AND DISCUSSION

3.1 Static deposition profile and film morphology

Figure 2a and b show the SEM image and static deposition profile of the products on c-Si synthesized under different \( Q_{Ar} \)s, respectively, at a \( T_s \) of 30°C. The particle was dominant at \( Q_{Ar} \) below 4 slm, which was due to extreme decomposition of TEOS molecule being enhanced and the fast radical recombination in the flow. However, the film morphology transited from the particle state to the uniform film with increasing \( Q_{Ar} \). In addition, the ring-shape products having a hollow profile at the center region were visible at \( Q_{Ar} \) below 4 slm reflecting the capillary dimension. These hollow profiles observed at the center region were more prominent at higher \( T_s \) of 270°C (Fig.3). On the other hand, the deposition profile showed almost symmetrical dome-shaped structure at \( Q_{Ar} \) above 4 slm.

![Fig. 2 SEM image and static deposition profile of products deposited at different Ar flow rates, \( Q_{Ar} \)s and a \( T_s \) of 30°C.](image)

The deposition rate obtained from the maximum values of the thickness profile showed a maximum 46 nm/s at 4 slm of Ar with a radial distribution of ~4 mm in a diameter. The maximum height of products decreased with increasing the radial distribution with \( Q_{Ar} \). The simple gas flow dynamics simulation revealed that these deposition profiles are ruled by the radical velocity profile determined by the residence time of argon and the substrate position.

![Fig. 3 Thickness profiles of the products deposited under different Ar flow rates, \( Q_{Ar} \)s at a \( T_s \) of 270°C. The distance \( d \) was 10 mm.](image)

Figure 4 shows the typical step coverage performance of the product synthesized on crystalline Si wafer with a trench structure at a \( T_s \) of 30°C. Notably, a good step coverage performance was obtained even using the atmospheric pressure TPJ, which suggested that the sticking process follow the CVD-like behavior. These findings suggest that the thickness profile is determined mostly by the parabolic velocity profile due to the laminar dynamic of the gas flow as well as the surface diffusivity of deposition precursors after coming to the growing surface.

![Fig. 4 Typical step coverage performance of the product fabricated at a \( T_s \) of 30°C.](image)

3.2 Chemical analysis of deposited films

The FT-IR spectra of the products corresponding Fig. 2 are shown in Fig. 5. The spectra analysis revealed that the dominant peaks in the spectra were derived from Si-containing molecules, the inorganic SiO\(_2\), being the most prominent compound in the ring area. The Si-O-Si related peak in the SiO\(_2\) film at 912-1265 cm\(^{-1}\) has broadened with a higher frequency shift compared those in stoichiometric SiO\(_2\) (1070 cm\(^{-1}\)) with \( Q_{Ar} \). They can be deconvoluted into four peaks, which are centered at 960, 1035, 1065, and 1140 cm\(^{-1}\) [10]. The IR peak centered at 960 cm\(^{-1}\) were attributed to Si-OH stretching mode. Peaks centered at 1035, 1065, and 1140 cm\(^{-1}\) were attributed to Si-O-Si asymmetric stretching mode, the main difference between these three peaks was the bond angle, the peak at 1140 cm\(^{-1}\) represents the Si-O-Si out-of-phase stretching mode which has a bond angle of
150°, termed as cage structure [11].

On the other hand, no marked differences were observed in the FT-IR spectra at the center and outer regions for the dome-shaped products. The degree of the diffusivity of the deposition precursor determines the chemical composition of oxygen and carbon.

3.3 Photoluminescence

The PL profile was also used to understand the radial profile of film fine structure. The typical PL spectra for carbon containing SiOₓ deposited at Tₛ of 30°C and 270°C are shown in Fig. 7a. The broad band spectra are observed at 2.1 and 2.6 eV attributed to the emissions from SiC and SiO related complexes, respectively. To date, the origin of the PL has been extensively studied by several groups. It is reported that SiOₓ films fabricated by electron cyclotron resonance (ECR) PE-CVD method exhibits intense visible PL emission centered at 2.1 eV, which attributes to carbon doped effects [12]. Similar results have been observed in Si and C ion implanted silicon dioxide films [13]. Hayashi et al. also observed a broad band PL band centered at about 2.2 eV in carbon rich silicon oxide films prepared by radio-frequency (rf) sputtering method. The PL emission intensity correlates with the carbon related vibration modes [14]. Uchino et al. have reported that nanometer sized silicon dioxide showing white light PL emission centered at 2.6 eV [15]. Noy et al. also found that the PL spectra of SiOₓ/Si nanowires samples exhibit a blue-green emission centered at 2.6 eV attributed to the carrier recombination at oxygen related defects [16].

(a)

(b)

Fig. 7 (a) PL spectra of carbon containing SiOₓ products deposited at Tₛ of 30°C and 270°C. (b) Radial profiles of PL integrated emission intensity of ring-shaped products having dome and hollow profiles at the center region. Inset shows corresponding thickness profiles of
the products. These suggest that the PL peaks centered at 2.1 and 2.6 eV are attributed to the carrier recombination at carbon and oxygen related defects, respectively, in SiOx matrix [17]. The white PL emission intensity in the products synthesized at a T of 30°C was two orders of magnitude stronger than that of 270°C, which was due to higher carbon and oxygen concentrations. The radial distribution of the PL intensity over radius was also compared for products having typical two thickness profiles with dome and hollow at the center region. Figure 7b shows the radial profiles of PL integrated emission intensity. Inset shows the thickness profiles of corresponding products. Significant differences were observed in the PL integrated emission intensity in the center and outer regions. The PL intensity was negligibly small at the center region rather than the outer despite of a thicker film thickness of 600 nm. The PL emission intensity was 600-1000 times stronger at the outer region in the circle having only 1.5 times thicker film thickness. These findings originate from the radial distribution of the chemical composition of C and O in SiOx matrix as shown in the FT-IR results. On the other hand, the radial distribution of the integrated PL emission intensity showed similar with that of film thickness in the dome shaped products. The FT-IR and XPS studies revealed that the chemical composition of carbon containing SiOx was almost identical in the radial direction. Thus, the PL intensity profile originates from those of film thickness and chemical composition, which will be available for the real time monitoring during the product growth.

4. CONCLUSION
We have demonstrated the local static deposition of carbon containing SiOx employing atmospheric pressure VHF microplasma jet of a TEOS and Ar mixture. Two distinct deposition profiles were observed in the ring-shaped products having dome and hollow profile at the center region. Lower flow of Ar and higher T, promoted preferentially the formation of inorganic SiOx with less carbon content with a parabolic profile. On the other hand, the polymeric much carbon containing SiOx was obtained at the outer region in the circle. Further increase of argon flow promoted insufficient decomposition of TEOS, which formed strong white emissive carbon containing SiOx with a symmetrical dome-shaped profile. These thickness and chemical compositional profiles are determined mostly by the parabolic velocity profile of the gas flow, the surface diffusivity of the deposition precursor at the growing surface and the position of substrate holder. These findings are a guiding principle for the local deposition of functional materials utilizing the atmospheric pressure microplasma jet.

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REFERENCES

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