Synthesis of SiOC(–H) Films by the Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition Method*

Takanori Mori,† Taiki Masuko, Akira Shirakura, and Tetsuya Suzuki
Graduate School of Science and Technology, Keio University,
3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan
(Received 28 December 2014; Revised 2 July 2015; Accepted 26 October 2015; Published 14 November 2015)

Synthesis of SiOC(–H) films outside generation regions using afterglow plasma under atmospheric pressure have been gaining attention because it allows deposition to complex configuration substrates with large area. We synthesized SiOC(–H) films at different oxygen gas flow rates and substrate temperatures by the atmospheric pressure plasma enhanced chemical vapor deposition method from TrMS/O₂/He gases. Substrates were placed at a working distance of 10 mm between discharge electrode and substrate surface. Plasma emission is gradually weakened with an increase in oxygen gas flow rate, and excessive introduction of oxygen into the process caused the plasma to disappear. The SiOC(–H) films were composed of a number of particles; Their large size particles lead to an increasing deposition rate and the non-dense structure of the films. As the oxygen gas flow rate increased, the particle size was larger at 100 nm and related -OH peaks strongly observed. Carbon content of SiOC(–H) films decreased from 17% to only 1.8% with an increase in substrate temperature at 140°C. In this paper, we report the characterization of SiOC(–H) films synthesized under atmospheric pressure PECVD method.

[DOI: 10.1380/ejssnt.2015.445]

Keywords: Atmospheric pressure; Plasma Processing; Amorphous thin film; Chemical vapor deposition; Silicon oxides

I. INTRODUCTION

SiOC(–H) films have attracted much attention in various industrial fields such as dielectrics in semiconductor technology or mechanical application or food packaging because of prominent properties including hardmess [2], low-k [3], electronic applications [4], gas barrier properties [5] and optical transparency [6]. In recent research, silica based films which have led to improvements in the properties noted above, have also been studied for potential applications as coatings on polymeric materials. Organosilicon compounds such as hexamethyldisiloxane (HMDSO), tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) are common raw materials used in the synthesis of SiOC(–H) films [7–10]. These precursors are liquid at room temperature and contain some carbon related bonds. A carburetor or bubbling device is needed to use these precursors as a raw material. In general, SiOC(–H) films were synthesized for industrial fields. Synthesis on polymeric materials is less suitable because of high synthesis temperature. Large amounts of carbon and hydrogen into SiOC(–H) films also lead to a decline in mechanical properties. Various approaches were studied such as adding oxidizer gas, substrate heating substrate and changing reactant gases flow rates to improve the properties of the films.

The plasma-enhanced chemical vapor deposition (PECVD) method is a commonly used technique for preparing SiOC(–H) films, but it is generally performed at low pressure. The achievement of deposition at low cost with high quality and on a large area is an important issue for a wide variety of industrial applications. Use of the PECVD method under vacuum conditions has limitations because of high vacuum equipment costs and the size of deposition area. Furthermore, the PECVD method has difficulties with deposition onto a tridimensional configuration or thick substrate. This problem can be solved by employing a line type atmospheric pressure PECVD (AP-PECVD) method using a dielectric barrier discharge (DBD). This improved system is expected to become one approach to achieving the aforementioned required production performance standards. Yokoyama et al. reported that a homogeneous DBD known as atmospheric pressure glow discharge (APGD) can be obtained [11]. APGD requires the insertion of dielectric plates between metal electrodes and uses helium or neon as a dilution gas to prevent the transition from glow to arc discharge. Massines et al. have remarkably contributed to the understanding of discharges at atmospheric pressure. DBD using molecular gases such as nitrogen instead of noble gas has also been studied [12]. The discharge using nitrogen gas at atmospheric pressure is generated by using a modulated power supply to suppress or even to avoid streamers [13].

SiOC(–H) films with high hardmess of about 7 GPa were synthesized by the AP-PECVD process with optimum deposition conditions [14, 15]. Deposition on a tridimensional configuration or thick substrate using a traditional direct-type AP-PECVD method is impossible because the discharge gap is typically a few millimeters. The systems that the discharge gap was expanded or the plasma stream exiting the discharge generation region is mixed with a gas stream containing the precursor, have received attention because it enables deposition to complex configuration substrates. Synthesis of SiOC(–H) films by remote system to large area under atmospheric pressure could make it protect materials. Deposition outside discharge area was employed an atmospheric pressure plasma jet [16, 17]. Silicon dioxide has been deposited by mixing TEOS or HMDSO with atmospheric pressure plasma jet at high temperature [18, 19]. U. Lommatasch et al. reported that very high deposition rate at 750 nm/s can be obtained and the films can be used for low-adhesion applications using an atmospheric pressure plasma jet [20].

* This paper was presented at the 7th International Symposium on Surface Science, Shimane Prefectural Convention Center (Kiihikhi Messe), Matsue, Japan, November 24-6, 2014.
† Corresponding author: tmori050@gmail.com
However, the plasma jet system has proven difficult to use for deposition onto large area. Instead a line-type AP-PECVD system has been employed as it enables deposition to tridimensional and especially large areas at low temperature which are indispensable in industrial fields.

In this study, we have successfully developed a line-type plasma enhanced chemical vapor deposition method which makes it possible to deposit to tridimensional and a large area under atmospheric pressure. We synthesized SiOC(–H) films outside discharge areas using Trimethylsilane (TrMS) and oxygen gases with the application of He as a dilution gas in order to suggest a possible effect of deposition on tridimensional configuration substrates. L. Cui et al. reported that large area coatings of dense silica films on polymeric substrate is succeeded using TEOS, bis (triethoxysilyl) ethane (BTESE) and tetramethylcyclotetrasiloxane (TMCTF) with a vaporizing system for liquid precursors [21]. Generally, silica based films are synthesized using HMDSO whose volatility is very high and not harmful in industrial fields. TrMS is a gas phase material at room temperature, and thus does not require any vaporizing system before to introducing in the afterglow region. Furthermore, flow rate control of TrMS gas is easier than that of HMDSO, and it is suitable for consideration of the reaction process since the structure of TrMS is similar to that of HMDOS. The effects of oxygen flow rate and substrate temperature on the structure and the chemical composition of SiOC(–H) films were investigated in this paper.

II. EXPERIMENTAL

A. Apparatus

A schematic diagram of the remote-type atmospheric pressure PECVD apparatus is illustrated in Fig. 1. The plasma was produced and sustained between the Cu electrodes. Both electrodes were covered by a 1 mm-thick dielectric plate (Al$_2$O$_3$ : $\varepsilon = 9.5$) in order to prevent the transition from glow to arc discharge. The distance between the parallel plate electrodes for discharge area was 1 mm. Silicon wafers with thickness of 0.38 mm were set on a movable plate at a working distance of 10 mm between the electrode and the substrate surface. The produced plasma was spouted to the substrate and the substrates were placed at downstream of the electrode.

B. Synthesis conditions

A mixture of TrMS gases with the use of helium as a dilution gas and oxygen as oxidation of a raw material was introduced through the discharge area. The amount of total gas flow was fixed at 20 L/min. Oxygen gas flow was changed from 0.1 L/min to 1.0 L/min. TrMS flow rate was fixed at 1 mL/min. The deposition of the films was carried out at substrate temperatures of 60°C, 100°C and 140°C. We used the power generator (SPD1PGU1, SK Medical Electronics Co., Ltd., Japan). The pulse width and the power between electrodes were adjusted at 5 μs and 13 kV, respectively. The power of the generator was 170 W in direct proportion to pulse frequency at 20 kHz. The optical emission spectra of the plasma between the electrodes and the substrate were recorded with the Hamamatsu C7460 spectrometer with a CCD detector.

C. Characterization of SiOC(–H) films

The thickness of the SiOC(–H) films was measured by a contact-type surface profiler (Dektak3030, Veeco, USA). The measurements of the thickness were performed at 10 different points and the results were expressed as the mean of 10 replicates and the corresponding standard deviation. The cross sections of the samples were observed by scanning electron microscopy (SEM). The chemical bonding structure and the composition of the films were measured by Fourier transform infrared (FT-IR) spectroscopy (ALPHA-E, Bruker, Germany) in the range of 500–4000 cm$^{-1}$ and X-ray photoelectron spectroscopy (XPS: JPS-9002TR, JEOL Ltd., Japan). For elemental analysis, Ar ion sputtering was applied immediately before the measurement to remove surface contaminants and oxide.

III. RESULTS AND DISCUSSION

A. Deposition rate

Figure 2 shows the deposition rate of the SiOC(–H) films as a function of oxygen gas flow rate with working distance 10 mm. As the oxygen gas flow rate increased from 0.1 L/min to 0.8 L/min, the deposition rate of the films increased from 335 nm/min to 532 nm/min. Introduction of oxygen promoted the gas phase reaction, and excited oxygen atoms produced precursors of SiOC(–H) films in that reaction. When the oxygen gas flow rate was 1.0 L/min, the deposition rate hardly changed with oxygen gas flow rate. Cross-sectional SEM images of the SiOC(–H) films with 0.5 L/min and 1.0 L/min are shown...
FIG. 2. Deposition rate of SiOC(–H) films as a function of oxygen gas flow rate.

FIG. 3. Cross-sectional SEM image of SiOC(–H) films at (a) 0.5 L/min and (b) 1.0 L/min.

in Fig. 3. The films with 0.5 L/min consisted of plenty particles and fully dense structure was observed. The other sample with 0.1 L/min and 0.3 L/min also had a similar structure to the one shown in Fig. 3(a). On the other hand, the particle size with 1.0 L/min was at about 100 nm. It is known that excited molecular oxygen plays an important role in gas phase decomposition and stripping of precursors [22]. Therefore, as the reaction frequency of precursor with oxygen molecular in the plasma gradually increased, the deposition rate increased. This is the explanation why large particles are present on the substrate. Excessive introduction of oxygen gas caused corrosion of the plasma due to the quench effect [23]. The gas phase decomposition of monomer molecules to form the intermediates and the adsorption of these intermediates onto the substrate [24]. These active species reacted with each other in the gas volume, and generating precursor and increasing the molecular weight. Figure 4 shows the emission spectra of excited oxygen atoms with various oxygen flow rate. As the oxygen gas flow rate increased from 0.1 L/min to 0.7 L/min, the peak intensity was gradually increased. On the other hand, the peak intensity of excited oxygen atoms was hardly changed, when the oxygen gas flow rate was over 0.7 L/min. It is considered that there was a limit to the amount of excited oxygen in afterglow plasma, which caused the saturation of the deposition rate and increasing the polymerization of precursor molecules.

Figure 5 shows the deposition rate of SiOC(–H) films synthesized by the AP-PECVD method as a function of substrate temperature. The oxygen flow rate was fixed at 0.5 L/min.
deposition temperature increased lead to the decreases of deposition rate of the SiOC(H) films. Surface reaction is an important factor in this condition which easily proceeded the polymerization of monomer molecules in the gas phase reaction.

B. Chemical structure of the SiOC(–H) films

Figure 6 shows FT-IR spectra of the SiOC(–H) films corresponding to various oxygen gas flow rate. The spectra of each sample were very similar features. The strong peaks of Si–O–Si, –OH and methyl groups were observed from all samples. A broad absorption around at 3500 cm$^{-1}$ was assigned to the –OH stretching vibration of isolated SiOH groups [26]. Si–OH stretching vibrations can be observed at 920 cm$^{-1}$ and peaks with methyl group attributed to 840 cm$^{-1}$, 1280 cm$^{-1}$ and 2980 cm$^{-1}$. Peaks attributed to Si–O–Si symmetric stretching vibrations and bending mode was observed around 1100 cm$^{-1}$ and 800 cm$^{-1}$, respectively [27, 28]. In the case of SiOC(–H) films, the intense band between 1020 cm$^{-1}$ and 1250 cm$^{-1}$ is related to Si–O–Si and Si–O–C asymmetric stretch modes [29]. The Si–O–Si bond angle is flexible and varies within a wide range from 120° to 180° depending on film microstructure. The spectra in the range from around 1100 cm$^{-1}$ were decomposed into three peaks at 1120, 1070, 1030 cm$^{-1}$ related of cage structure, network structure and suboxide structure (angle < 130°) [6, 30, 31]. The network structure associates a quartz-like structure as SiO$_2$ and that angle is 140°. The bonding modes near 1104 and 1180 cm$^{-1}$ are due to Si–O–C asymmetric stretching modes [32], which are strongly overlapped by the Si–O–Si cage structure (Si–O–Si angle > 150°) contribution. Concerning suboxide structure, the Si–O–Si angle is close to 120°when Si–O–Si is submitted to repulsion forces from electron pairs (in bonds of H or methyl groups attached to Si in Si–O$_2$–X$_2$ (X = H or CH$_3$)) as in siloxane structures [33]. Hence, in the case of SiOC(–H) films, the observation of peaks such as suboxide and cage structures might indicate a strong contribution of carbon related bonds.

The FT-IR spectrum of the SiOC(–H) films prepared at various substrate temperatures is shown in Fig. 8. Peaks at around 3500 cm$^{-1}$ and 940 cm$^{-1}$ and the shape of Si–O–Si bonds were strongly dependent on the incorporation amount of oxygen. The fact that the intensity of relative –OH bond at 3500 cm$^{-1}$ and 920 cm$^{-1}$ increased with an increase of oxygen gas flow rate indicated the introduced oxygen gas mostly formed not Si–O–Si bonds but relative –OH bonds. When excessive oxygen gas was introduced in process gases, the polymerization of the trimethylsilane molecules occurred and generated large number of particles in the gas phase reaction. Larger particle size by the gas phase reaction occurred an increasing of intensity with –OH related bonds. The shape of Si–O–Si bonds gradually changed from broad to sharp shape but the position of the peak hardly changed at 1060 cm$^{-1}$, when the oxygen gas flow rate changed. Hence, an increase in the oxygen gas flow rate led to a decrease of peak intensity with contribution of carbon related bonds such as the Si–O–Si cage structure or Si–O–C asymmetric stretching modes or suboxide structure of the films. When the oxygen flow rate increased, the amount of excited oxygen atoms near the surface increased. They decomposed organic of the films at surface by excited oxygen atoms. Figure 7 shows elemental content ratio of the SiOC(–H) films as a function of oxygen gas flow rate. Carbon content ratio of the films obviously decreased as the oxygen flow rate increased, while oxygen content ratio increased. The conversion of elemental composition confirmed that when oxygen gas flow rate increased, the intensity of related to –OH peaks increase and the shape of Si–O–Si broad bands was changed to sharp.

The intensity of hydroxyl group at around 3500 cm$^{-1}$ and 940 cm$^{-1}$ and the shape of Si–O–Si bonds were strongly dependent on the incorporation amount of oxygen. The fact that the intensity of relative –OH bond at 3500 cm$^{-1}$ and 920 cm$^{-1}$ increased with an increase of oxygen gas flow rate indicated the introduced oxygen gas mostly formed not Si–O–Si bonds but relative –OH bonds. When excessive oxygen gas was introduced in process gases, the polymerization of the trimethylsilane molecules occurred and generated large number of particles in the gas phase reaction. Larger particle size by the gas phase reaction occurred an increasing of intensity with –OH related bonds. The shape of Si–O–Si bonds gradually changed from broad to sharp shape but the position of the peak hardly changed at 1060 cm$^{-1}$, when the oxygen gas flow rate changed. Hence, an increase in the oxygen gas flow rate led to a decrease of peak intensity with contribution of carbon related bonds such as the Si–O–Si cage structure or Si–O–C asymmetric stretching modes or suboxide structure of the films. When the oxygen flow rate increased, the amount of excited oxygen atoms near the surface increased. They decomposed organic of the films at surface by excited oxygen atoms. Figure 7 shows elemental content ratio of the SiOC(–H) films as a function of oxygen gas flow rate. Carbon content ratio of the films obviously decreased as the oxygen flow rate increased, while oxygen content ratio increased. The conversion of elemental composition confirmed that when oxygen gas flow rate increased, the intensity of related to –OH peaks increase and the shape of Si–O–Si broad bands was changed to sharp.

The FT-IR spectrum of the SiOC(–H) films prepared at various substrate temperatures is shown in Fig. 8. Peaks at around 3500 cm$^{-1}$ and 920 cm$^{-1}$ were attributed to OH stretching vibration of the isolated Si–OH and Si–OH stretching vibrations, respectively. Both bands diminished in intensity by a dehydration reaction by increasing the substrate temperature. Furthermore, peak intensity of methyl groups around at 840 cm$^{-1}$, 1270 cm$^{-1}$ and 2980 cm$^{-1}$ decreased with the increase of deposition temperature. In Fig. 6, the changing oxygen gas flow rate hardly had relevance to the intensity of the methyl bond.
In the forming of inorganic films, an increase of temperature dominantly persuades the byproducts desorption. Increasing of deposition temperature, the position of Si–O–Si asymmetric stretching mode gradually shifted to higher wavenumber at 1065 cm\(^{-1}\) and the intensity of Si–O–Si cage structure or Si–O–C asymmetric stretching mode decreased. This result indicate that the carbon relate bonds were decomposed by increasing the substrate temperature. As noted previously, the gas phase reaction in this study had more effects on the polymerization or the forming particles compared to a conventional AP-PECVD method. Therefore, it is considered that the surface reaction is dominant reaction in silica like coatings. Figure 9 shows the chemical composition of the films as a function of substrate temperature. The XPS spectra of the SiOC(–H) films obtained was performed using the Mg K\(\alpha\)-line. As the substrate temperature increased, oxygen content increased from 52.1% to 65.7% and the silicon content hardly changed at around 32%. At a high substrate temperature, carbon content of the films was only 1.8%. It is founded that oxygen was composited as Si–O bond because the intensity of Si–OH bond decreased, as shown in FT-IR spectra. Increase in the deposition temperature leads to gas phase temperature causing the gas phase reaction is more active. The decomposition of trimethylsilane molecular or absorbed species was enhanced by oxygen atoms and the methyl bond derived from the precursor of the SiOC(–H) films. Figure 10 shows the XPS spectra in the Si 2p region of the SiOC(–H) films prepared with varying substrate temperatures. As shown in Fig. 10, it is obvious that the position of the Si 2p peaks was slightly shifted to a higher bonding energy with increased substrate temperature. It is known that there are four component peaks which were Si(–O)\(_x\) within the Si 2p envelope \[34\]. The top of the peaks in Si 2p shifts to a higher binding energy when the “\(x\)” has a large value. This result shows that the ratio of oxygen bonded to silicon element gradually increased as the substrate temperature increased from 60\(\,^\circ\)C to 100\(\,^\circ\)C. There were similar tendencies in the relationship between carbon content ratio of the films and changing substrate temperature. Substrate temperature influence does not only the adsorption and desorption reactions associated with the deposition rate, but also the form high density Si–O–Si bonds by the dihydrogen condensation reaction between two silanol groups. These results indicate that a porosity structure of the films decreases with substrate temperature.

**IV. CONCLUSION**

In this study, we designed and set up a plasma enhanced chemical vapor deposition apparatus and synthesized SiOC(–H) films under atmospheric pressure outside of 10 mm from the discharge generation region. Deposition of the SiOC(–H) films on a tridimensional figuration or thick substrate could be substantialized by this deposition system. From SEM observation, the SiOC(–H) films consisted of a particles and exhibited high deposition rate. From FT-IR analysis, activation of gas phase reaction with introduction of oxygen gas led to more increasing high dense structure such as silica-like structure,
because this deposition system has fairly long distance of gas phase reaction. We also found that the key reaction of SiOC(–H) film formation is a surface reaction because organic films easily produced by inducing the polymerization and forming particles in the gas phase reaction. In order to apply this deposition system to industrial application, investigations of the films synthesized on polymeric material are needed.