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Low-energy mass-selected ion beam production of fragments from tetraethylorthosilicate for the formation of silicon dioxide film

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ABSTRACT

Fragment ions produced from tetraethylorthosilicate (TEOS) in a Freeman-type ion source were investigated using a low-energy mass-selected ion beam system and then, their mass numbers were identified. Although the chemical formulae of these fragments were not completely identified yet, the possible candidates of dominant fragment ions were C^{2+}, C^+, CH_2^+, O^+, H_2O^+, Si^+, SiC^+, SiO^+, $SiH(OH)_2^+$, $Si(OH)_3^+$, $SiH(OH)(OC_2H_5)^+$, $SiH(OCH_3)_2^+$, $Si(OH)_2(OC_2H_5)^+$, $SiH(OC_2H_5)_2^+$, $Si(OH)(OC_2H_5)_2^+$, $Si(OCH_3)_2(OC_2H_5)^+$, $Si(OCH_3)(OC_2H_5)_2^+$, and $Si(OC_2H_5)_3^+$. Among these fragment ions, $Si(OH)_3^+$ ions were mass-selected. The ion energy was approximately 50 eV. Then, the $Si(OH)_3^+$ ions were irradiated to a Si substrate and resulting deposited films were analyzed. Following the completion of the ion irradiation experiment, X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy assays of the films demonstrated the occurrence of silicon dioxide deposition. We conclude that the irradiation of the mass-selected $Si(OH)_3^+$ ions, obtained from TEOS, to substrates is useful for the secure growth of silicon dioxide films.

1. Introduction

Low-energy mass-selected ion beam deposition is a powerful technique for the film coating on substrates, e.g., the coatings of substrates with iron [1], diamond [2], and silicon carbide [3,4]. It is important, however, to determine which source materials are appropriate for a certain film coating process.

Meanwhile, silicon dioxide (SiO_2) film formation has attracted much attention in its possible application: thin silicon dioxide films have been used as an insulating layer in semiconductor technologies or a barrier coating in food packages. It seems likely that the low-energy mass-selected ion beam deposition technique can be also employed for silicon dioxide film formation. Recently, we demonstrated that irradiations of low-energy SiO^+ ions produced from hexamethyldisiloxane (HMDSO, $(CH_3)_3SiOSi(CH_3)_3$) to substrates were available for the silicon oxide film formation [5]. However, the atomic ratio of oxygen to silicon (O/Si ratio) was 1 in the SiO^+ ion. It seems likely therefore that oxygen atoms would be insufficient for the formation of SiO_2 film when SiO^+ ion beam deposition to substrates was employed.

Silicon dioxide films can be deposited on substrates by a plasma enhanced chemical vapor deposition (PECVD) technique using silane as a source material [6]. Careful treatments are, however, needed for these experiments because silane is extremely flammable. On the other hand, tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$) has also been employed as a source material, being an alternative to silane for silicon dioxide film formation with the PECVD technique [7,8], because TEOS is less flammable than silane. It has been found that the chemical stoichiometry of films produced from TEOS was closely correlated with experimental conditions. Carbon atoms were mostly incorporated into the deposited silicon dioxide films. Therefore, it is necessary for optimum experimental conditions to minimize the carbon elements to be incorporated in the film [9–12]. Voulgaris et al. [10] have investigated the effects of radio frequency (RF) power on both growth rate and chemical composition of the deposited films, and discovered that the increase of RF power enhanced the film growth rate whereas the Si-C contents in the deposited films increased with the RF power. Likewise, Abbasi-Firouzjah et al. [12] have reported that the chemical composition of films, produced from TEOS and oxygen, was dependent on TEOS/oxygen pressure ratio.

We suppose that the low-energy mass-selected ion beam technique is applicable to silicon dioxide film formations using TEOS as a source material. HMDSO has two Si atoms and a single O atom in its molecule while TEOS molecule possesses a Si atom and four O atoms. Therefore, it seems possible that using the low-energy mass-selected ion beam

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technology, we would be able to obtain TEOS-derived fragment ions possessing sufficient O/Si ratios which were effective for the formation of SiO_2 films on substrates. Although a variety of fragments produced from TEOS have so far been reported [13], no attempt has been made not only to identify fragment ions produced from TEOS in a Freeman-type ion source but also to produce the low-energy mass-selected ion beam of fragments from TEOS. In order to minimize the carbon concentration in the deposited films, furthermore, it is important to investigate which fragment ions are suitable for the silicon dioxide film deposition processes.

We previously proposed a method of characterization of fragment ions from source materials in a Freeman-type ion source [14], and actually characterized the fragment ions derived from methylsilane [14], dimethylsilane [15], and hexamethyldisilane [16]. In this paper, we identify mass numbers of fragment ions produced from TEOS. Furthermore, we propose an experimental methodology for silicon dioxide film deposition by means of irradiating fragment ions produced from TEOS to substrates.

2. Experimental setup

Experiments were carried out in a low-energy mass-selected ion beam system (Ulvac). The schematic drawing of the system has been shown previously [3]; the system consists of a Freeman-type ion source, an extractor electrode, a mass selector, a decelerator, and a process chamber. The ion source is composed of a stainless chamber, a gas feed tube, a bubbling system, a tungsten wire, a power supply for the electric current of the tungsten wire, and an ion energy power supply. TEOS was bubbled by Ne gas at room temperature and the mixed gas of TEOS and Ne was introduced into the chamber at a flow rate of 2 sccm through the gas feed tube. Fragment ions produced from TEOS in the ion source were extracted through the slit of the chamber by a high voltage of $-15 \sim 25$ kV applied to the extractor electrode. Since the initial ion beam extracted from the ion source contained several kinds of ions, a magnetic-field-based mass selector was installed to select the desired ions. High-energy neutral species may be produced by collisions of ions with residual gas. For the removal of such neutrals, the ion beam was deflected by an electrostatic deflection plate which was placed near the end of the beam line, and guided ions alone to the process chamber. The high-energy neutrals, on the other hand, went straight and were caught by a cup installed on the axis. The mass-selected ion beam was slowed down by the decelerator installed at the quite end of the ion beam line in the process chamber. The incident angle of ion beam was set to be normal to the substrate surface. The ion beam qualities could be assessed with a so-called plasma process monitor (Balzers, model: PPM-421) placed in the process chamber behind the decelerator. The degree of vacuum in the process chamber was 6×10^{-7} Pa.

The experimental procedures were as follows: Firstly, we measured the mass spectrum of ions in the ion source by altering the electric current to generate the magnetic field of the magnetic-field-based mass selector. Secondly, $Si(OH)_3^+$ ions were selected with an appropriate adjustment of the mass selector, and their energy distribution was measured. The $Si(OH)_3^+$ ion beam was irradiated to a Si untreated substrate. The Si substrate was mounted on the manipulator in the process chamber. Finally, the resulting film deposited on the substrate was examined by X-ray photoelectron spectroscopy (XPS; Kratos, model: AXIS-165×), Fourier-transform infrared spectroscopy (FTIR; Jasco, model: FT/IR-410), atomic force microscopy (AFM; Jeol, model: JSTM-4200D), and variable-angle spectroscopic ellipsometer (J. A. Woollam, model: VASE).

3. Experimental results and discussion

TEOS was supplied into the Freeman-type ion source and then broken down into fragments by the electron impact ionization. Ion mass distribution in the ion source can be analyzed by measuring ion current

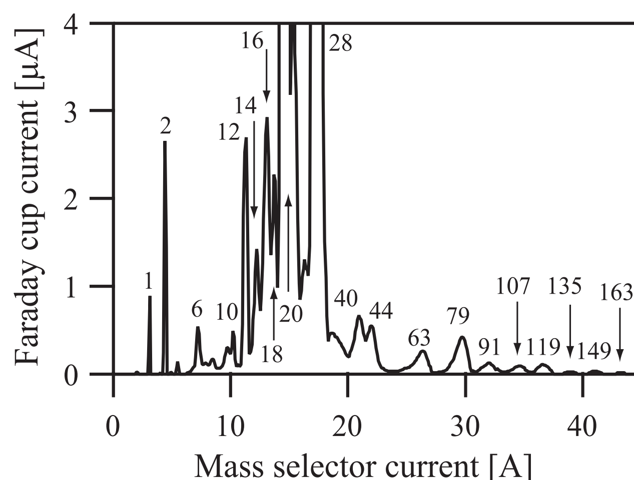

Fig. 1. Ion intensity measured by a Faraday cup for each ion species selected by a mass selector. The horizontal axis represents the current to produce the magnetic field of the mass selector. The figure above each spectrum is the mass number of corresponding ion species.

intensity changes using a Faraday cup installed just behind the mass selector during the scanning of mass selector current. Fig. 1 shows a result of scanning the mass selector current. The vertical axis represents the Faraday cup current, which is an indicator of the production rate of fragment ions during the scanning process. Twenty dominant peaks are observed in Fig. 1. PPM-421 measurements showed that the mass numbers of the first two peaks were 1 and 2 u, corresponding to H^+ and H_2^+. PPM-421 assays also showed that peaks corresponding to Ne^+ (20 u) and Ne^{2+} (10 u) existed. Mass numbers for other peaks were identified to be 6, 12, 14, 16, 18, 28, 40, 44, 63, 79, 91, 107, 119, 135, 149, and 163 u. We could not find any ions whose mass numbers were heavier than 163 u. Although the chemical formulae of these ions have not been identified yet, we tried to determine the structure of fragment ions using a quantum chemical calculation [17]. The calculation showed that the possible candidates for these ions were C^{2+}, C^+, CH_2^+, O^+, H_2O^+, Si^+, SiC^+, SiO^+, $SiH(OH)_2^+$, $Si(OH)_3^+$, $SiH(OH)(OC_2H_5)^+$ (or $SiH(OCH_3)_2^+$), $Si(OH)_2(OC_2H_5)^+$, $SiH(OC_2H_5)_2^+$, $Si(OH)(OC_2H_5)_2^+$ (or $Si(OCH_3)_2(OC_2H_5)^+$), $Si(OCH_3)(OC_2H_5)_2^+$, and $Si(OC_2H_5)_3^+$.

Fig. 1 shows that small fragments such as C^+, O^+, and Si^+ coexisted with large fragments such as $Si(OC_2H_5)_3^+$ in the ion source. In the decomposition of HMDSO in the same ion source [5], intensities of large fragments such as $Si_2OC_5H_{15}^+$ were comparable to those of small fragments (e.g., C^+ and O^+). On the other hand, Fig. 1 shows that intensities of large fragments such as $Si(OC_2H_5)_3^+$ are much smaller than those of small fragments such as C^+, O^+, and Si^+. These results suggest that the ability of HMDSO decomposition in the Freeman-type ion source is less effective and thus, large fragments such as $Si_2OC_5H_{15}^+$ are produced. On the other hand, TEOS is decomposed effectively and hence, yields of smaller fragments such as C^+, O^+, and Si^+ are significantly large.

Three fragment ions, i.e., SiO^+, $SiH(OH)_2^+$, or $Si(OH)_3^+$ which are generated from TEOS and devoid of contamination with carbon elements are considered to be useful for the deposition of silicon oxide films. We previously established that SiO^+ ion beam could be obtained from the decomposition of HMDSO [5]. However, the intensity of SiO^+ ion beam generated from TEOS was found to be less than the half of SiO^+ ion beam from HMDSO, suggesting that for the production of SiO^+ ion beam, HMDSO could be a more advantageous source material than TEOS. Thus, we did not perform any additional deposition experiments using the SiO^+ ion beam. Furthermore, we found that $SiH(OH)_2^+$ ion beam had much less intensity than $Si(OH)_3^+$ ion beam. In this study, we thus selected the $Si(OH)_3^+$ ion beam for the deposition of

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