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Development of magnetic-field and pulsed-plasma-enhanced chemical vapor deposition method to fabricate amorphous silicon carbonitride diaphragm for environmental-cell transmission electron microscope

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ABSTRACT

A magnetic-field and pulsed-plasma-enhanced chemical vapor deposition (MPECVD) was developed to fabricate amorphous silicon carbonitride (a-SiCN) diaphragm for environmental-cell transmission electron microscope (E-TEM). The films were prepared by using gaseous hexamethyldisilazane (HMDSN), N_2 and Ar with pulse voltages varied between 300 V and 600 V. The deposition rate was increased by enhancement of magnetic-field in comparison with a conventional PECVD. The diaphragms were applied to Si (100) and a Cu grid with 100-μm-diameter holes. Fourier transform infrared spectra and X-ray photoelectron spectra revealed that an elimination of organic compounds and a formation of Si–N and C–N bonds in diaphragms can be promoted with increasing pulse voltage and N_2 flow rate and decreasing ambient pressure. The diaphragms were amorphous and transparent at 200 kV electrons and no charge-up was observed by E-TEM. Durability to electron beams and reaction gases in the E-cell was improved when diaphragm was deposited with high pulse voltage.

1. Introduction

An environmental-cell transmission electron microscope (E-TEM) system has been developed to investigate for a catalytic behavior between catalyst and reaction gases and for biological living specimens. TEM is useful for analyzing structures at the atomic level. However, as specimens are generally placed in a high vacuum, it is difficult to directly examine their behaviors since the latter requires observing a specimen under ambient pressure.

The E-TEM system developed by Ueda et al. includes a specimen holder with a small chamber that employs a diaphragm to isolate the vacuum for TEM observations from the reaction gas about the specimen [1]. The diaphragm is the most important component of the E-TEM system because it both maintains the pressure difference between the vacuum and the reaction gas and allows an electron beam to pass through it. Diaphragms made from amorphous carbon thin films have been used to observe CO oxidation catalyzed by gold nanoparticles. Using a carbon thin film (thickness: 8 nm) has several advantages including high hardness, no electron diffraction contrast, and low electron scattering. However, extended observation is not possible as the electron beam and the oxygen in the E-cell damage the film. A high-hardness, chemically inert diaphragm made from an amorphous material consisting of a light element is required to minimize electron scattering and diffraction contrast. There is thus a pressing need to develop such a diaphragm.

The present study investigates the suitability of amorphous silicon carbonitride (a-SiCN) films for the diaphragm of the E-TEM. We previously reported diaphragms for the E-cell made from boron oxide, boron carbonitride and silicon carbonitride using by pulsed-plasma-enhanced chemical vapor deposition method (PECVD) [2,3]. Those films are well known as hard coating materials [4–8]. In here, to obtain a high deposition rate and a dense a-SiCN (pinhole-free), PECVD with magnet on electrode (magnetic-field and pulsed-plasma-enhanced chemical vapor deposition: MPECVD) using a precursor of hexamethyldisilazane [HMDSN; $(CH_3)_3Si–NH–Si(CH_3)_3$] has been developed. HMDSN is a safe liquid and has a high vapor pressure (1.8 kPa at 300 K) making it easier to handle than silane and methane of firedamp. The films were prepared on a Cu grid that was used as a TEM specimen holder

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and were characterized by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR) optical microscopy (OM) and TEM. The durability of films to electron beam was measured by using the developed diaphragm in the E-TEM system.

2. Experimental procedure

The procedure used to fabricate the diaphragm is described below. First, a 150-nm-thick triacetyl cellulose (TAC) film was formed on a glass slide by dipping the slide into a TAC solution (TAC: 0.595 mg; dichloroethane: 100 ml; methanol: 19 ml). The TAC film was peeled off from the glass slide and placed on a Cu grid (diameter: 3.5 mm; thickness: 1 mm; hole diameter: 100 μm). A silicon carbonitride film was deposited on the TAC film by MPECVD. Finally, the TAC film was etched with acetone. To investigate surface morphology and chemical component, a p-type Si (100) which was rinsed in a diluted hydrogen fluoride of 46% to remove native oxide was also used as a substrate.

Fig. 1 shows a schematic diagram of the experimental setup for MPECVD and the experimental conditions described in Table 1. The precursor gases were introduced into the MPECVD chamber using HMDSN, N_2, and Ar. HMDSN and Ar gas flow rates of fixed 20 and 420 ml/min, respectively. Flow rate of nitrogen gas was changed in the range of 500–1000 ml/min. Deposition pressures in the range of 30–150 Pa were realized by using a rotary pump. A pulse power supply developed in our laboratory was used to generate plasma with voltages in the range of 300–600 V. The pulse width and the frequency were set at 500 μs and 1 kHz, respectively. A cylindrical neodymium magnet of 450 mT with 59 mm outer diameter, 19 mm inner diameter and 10 mm thickness was applied on the plasma electrode.

The chemical bonding structure of prepared films on Si was characterized by FT-IR (IR Prestige-21, SHIMADZU). The IR transmittance spectra of the prepared films were obtained by subtracting the Si substrate contribution. The developed diaphragms for E-TEM were characterized by XPS (Axis-Nova, Kratos Analytical). The monochromatic Al-kα line was generated by using an emission current of 10 mA and an acceleration voltage of 15 kV and it was used to excite photoelectrons. Measurements were performed at a pressure of 10^{-7} Pa. Contamination on the sample surface was removed by Ar ion etching for 60 s (voltage: 2 kV; current: 20 mA).

The capacity of resist pressure of the developed diaphragm on a Cu grid was measured. First, both sides of the diaphragm were sealed in a gasket at atmospheric pressure. One side of the diaphragm was then evacuated by a dry pump. After measuring its resist pressure, the diaphragm was introduced to the E-TEM. The E-TEM, which is based on a conventional TEM (H-8000, Hitachi) and was developed by one of the authors at Nagoya University, was used to characterize the diaphragm and to measure an electron beam durability in CO and O_2 atmospheres. The acceleration

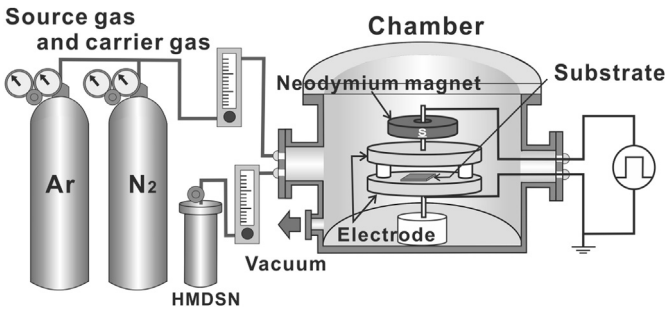

Fig. 1. Schematic diagram of MPECVD method.

Table 1
Experimental conditions of a-SiCN diaphragm fabricated by MPECVD method.

HMDSN: $(CH_3)_3SiNHSi(CH_3)_3$	20 ml/min
N_2	500–1000 ml/min
Ar	420 ml/min
Pressure at depositions	30–150 Pa
Distance of electrode	30 mm
Deposition time	5 min
Plasma voltage	300–600 V
Pulse width	500 μs
Frequency	1 kHz
Magnetic-field	450 mT

voltage and emission current of the electron beam were 200 keV and 20 μA, respectively. The pressure of the reaction gas (CO (1%), O_2 (21%), and N_2 (78%)) in the E-cell holder was set in the range $1–10^4$ Pa. The column pressure around the E-cell holder was 2×10^{-4} Pa.

3. Results and discussion

Fig. 2 shows photographs of plasma generated by a conventional PECVD (without the magnetic-field) (a) and by using the magnet on electrode (MPECVD) (b). The conditions are HMDSN, N_2 and Ar flow

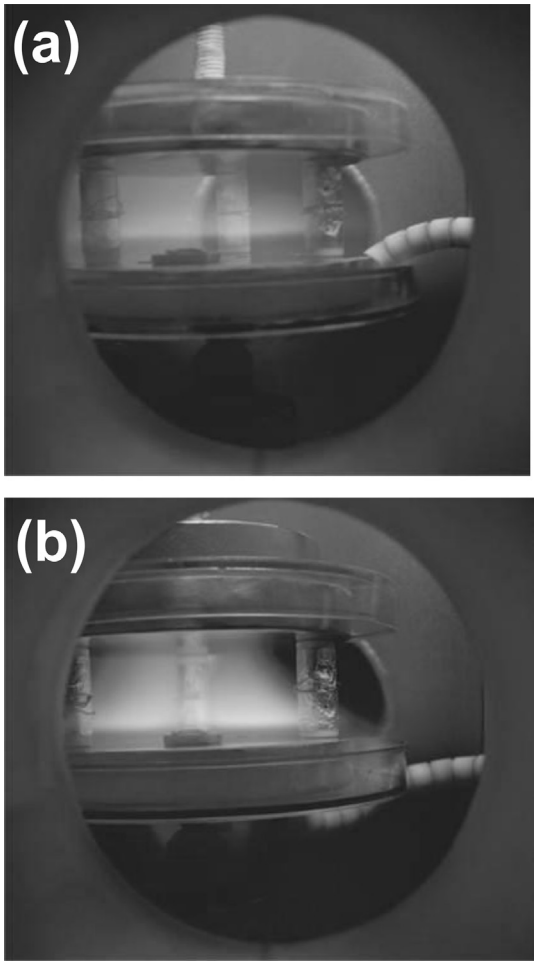

Fig. 2. Photographs of plasmas generated by a conventional PECVD (without magnetic-field) (a) and by using magnet on plasma electrode (MPECVD) (b). The conditions are HMDSN, N_2 and Ar flow rates are set at 20, 500 and 420 ml/min at a pressure of 30 Pa and the pulse voltage is 400 V.