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Development of amorphous boron carbon oxynitride film for transmission electron microscope with environmental-cell system[†]

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KEY WORDS: (Plasma chemical vapor deposition) (Amorphous boron carbon oxynitride) (Diaphragm) (Environmental cell) (Transmission electron microscope)

1. Introduction

It is an unquestionable fact that bulk gold is chemically inert. Recently however, it was reported that gold particles of less than 10 nm in diameter exhibit unique catalytic properties [1]. The level of catalytic activity is particularly high in the oxidation of carbon monoxide (CO) and similar substances when the particles are bound tightly to specific metal oxides, such as TiO₂ [2]. To determine the reaction mechanism of this gold nanoparticle catalyst, which is unclear, requires investigation of the gold nanoparticle surface and interface atomic structures. Transmission electron microscopy (TEM) is useful for analyzing structures at the atomic level, but as specimens are normally placed under a strong vacuum, it is difficult to examine directly the relationship between the observed structures and catalytic behavior, which requires instead observation of the catalyst under reaction gas conditions.

The environmental-cell (E-cell) TEM system developed by Ueda *et al.* includes a specimen holder with a small

chamber to isolate the vacuum around the TEM from the reaction gas atmosphere around the specimen by means of a diaphragm [3]. The diaphragm is the most important part of the E-cell TEM system because it not only maintains the pressure difference between the vacuum and the reaction gas but also transmits the electron beam. Amorphous carbon thin films have so far been used as the diaphragm to allow observation of the oxidation of CO using the gold nanoparticle catalyst. The carbon thin film (thickness 8 nm) has advantages such as high hardness, no electron diffraction contrast and low electron scattering. However, extended observation is not possible as the film suffers damage from the electron beam and the oxygen in the E-cell. The diaphragm must consist of a light element, chemically inert, of high hardness, and amorphous. The development of a diaphragm is therefore a pressing need.

The present paper turns attention to the use of boron carbon oxynitride films in the diaphragm of the E-cell TEM. The films for the diaphragm were prepared using plasma enhanced chemical vapor deposition (p-CVD) with precursor of trimethyl borate (B(OCH₃)₃: TMB) and mixture gases of nitrogen (N₂) and argon (Ar). This method has the advantage of greater film step coverage than other coating methods. The prepared films on a Cu mesh for a specimen holder of TEM were characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

2. Experimental Procedure

Figure 1 shows the procedure for diaphragm formation. First, a triacetyl cellulose (TAC) film was formed on a slide glass. The TAC film peeled off from slide glass was put on a Cu mesh (diameter ϕ 3.5 mm, thickness 1 mm, hole diameter ϕ 100 μ m). A boron carbon oxynitride film was deposited on it by p-CVD. Finally, the TAC film was etched with acetone.

Figure 2 shows a schematic diagram of p-CVD method experimental equipment. The gas canister and the chamber were connected with stainless pipes. The source gas and carrier gas were adjusted using a flow meter between chamber and gas canisters. The electrodes were isolated with glass. The inter electrode distance was 13 mm.

The boron carbon oxynitride films were deposited on

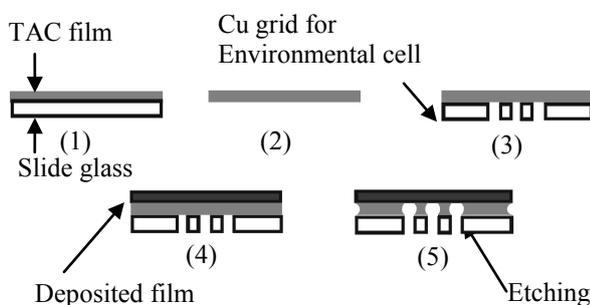


Fig.1 Procedure for diaphragm formation.

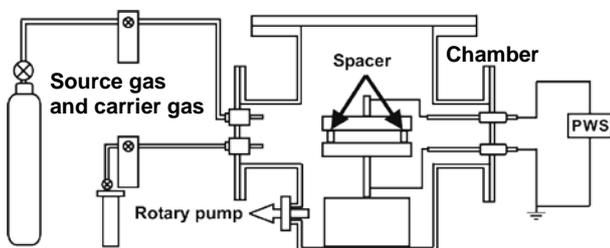


Fig. 2 Schematic diagram of p-CVD method.

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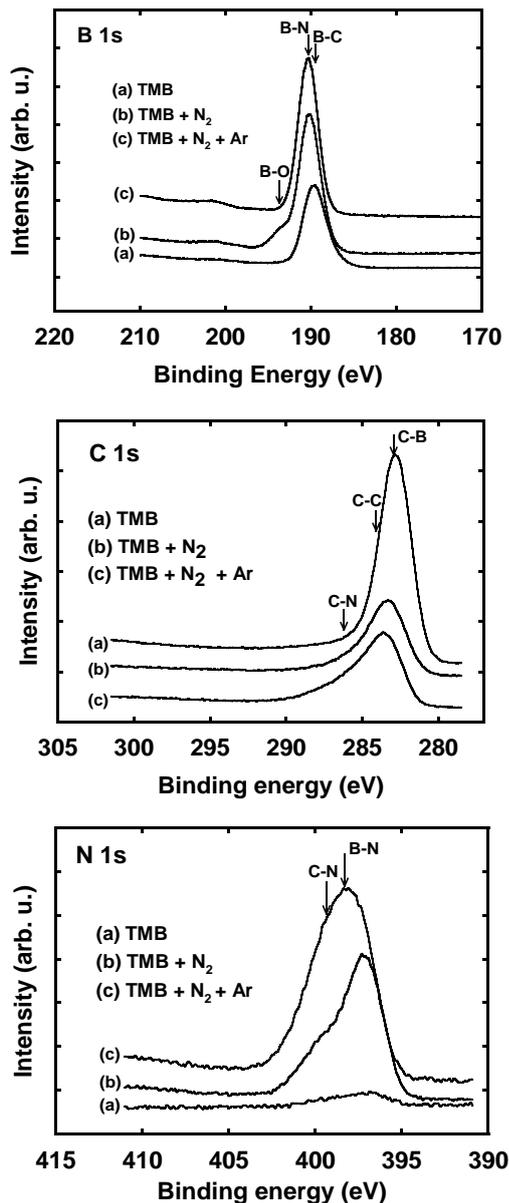


Fig. 3 XPS spectra of B 1s, C 1s and N 1s for boron carbon oxynitride films deposited on Cu substrate under various gas conditions.

Cu mesh and Cu substrate by p-CVD. TMB and N₂ were used as source gases and Ar as carrier gas. The gas flow rate of TMB, N₂ and Ar ranged from 5 to 50 ml/min., 50 to 500 ml/min., and 0 to 450 ml/min., respectively. A direct current (D.C.) power supply was used to generate plasma with voltage 250 V. The pressure at deposition was 5-20 Pa.

3. Results and discussion

Boron carbon oxynitride films deposited by p-CVD with source gases of TMB and N₂ were investigated by XPS. It is well known that including nitrogen in films made of boron-carbon produces high hardness [4]. **Figure 3** shows XPS spectra of B 1s (upper), C 1s (middle) and N 1s (lower) for deposited films. Sample (a) as a control was deposited at a TMB gas flow rate of 50 ml/min. Sample (b) was deposited under mixed gas flow of TMB (50 ml/min)

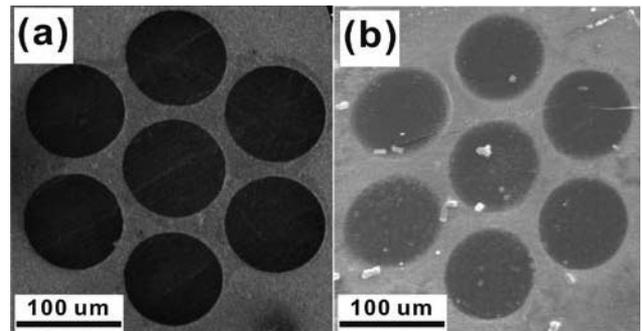


Fig. 4 SEM photographs of boron carbon oxynitride film applied to holes of Cu mesh; before (a) and after deposition (b).

and N₂ (300 ml/min). Sample (c) was deposited with Ar gas (100 ml/min.) added to the gas flow for sample (b). In the B 1s spectrum of sample (a), main peak was 189.6 eV corresponding to B-C bonding and the spectrum did not include a peak at 192-193 eV corresponding to B-O bonding [5, 6]. The C 1s spectrum of sample (a) included peaks at 288.5 eV and 283 eV corresponding to C-O and C-B bonding, respectively. The atomic ratio of sample (a) was about B:C = 1:2. TMB is composed of the chemical bonding of B-(O-CH₃)₃ and the atomic ratio of TMB is B:C = 1:3. It is therefore thought that oxygen desorption in the TMB gas was promoted by the generation of TMB plasma and that film with B-C bonding was deposited by recombination of B-C or displacement of TMB.

In the B 1s spectrum of sample (b), main peak was 190.2 eV corresponding to B-N bonding and the spectrum also had a shoulder corresponding to B-O bonding (192-193 eV) and B-C bonding [7]. In the N 1s spectrum of sample (b), main peak was at 398.5 eV corresponding to B-N bonding and there was also a shoulder corresponding to C-N bonding (399 eV). Although the deposited film was nitrified by incorporation of N₂ gas in TMB, TMB decomposition of TMB was less than in sample (a) because of the inclusion of B-O bonding in sample (b). The atomic ratio in sample (b) was B:C = 1:0.48 indicating a lower carbon content than sample (a). It is thought that decomposition of O-CH₃ bonding to a level lower than the bonding energy of B-O in TMB was mainly promoted. In the B 1s spectrum of sample (c), the main peak was the same as in sample (b) but the spectrum did not include a peak for B-O bonding. In the C 1s and N 1s spectra of sample (c), C-N bonding and the atomic ratio of nitrogen were higher than in sample (b). This suggests that inclusion of Ar in the source gas enhances the dissociation of TMB and the reaction of boron, carbon, and nitrogen.

Figure 4 is a SEM photograph of the boron carbon oxynitride film applied to the holes of Cu mesh. Photograph (a) is before deposition on the Cu mesh and the photograph (b) after deposition. A film was formed on the holes of Cu mesh. There is no contrast variation, indicating that the film was extremely smooth.

4. Conclusions

For use as a diaphragm in the environmental cell, boron carbon oxynitride films were prepared on Cu mesh by

plasma enhanced CVD with TMB and were characterized by XPS. The films were composed of B-C, B-N and C-N bonding and inclusion of Ar in the source gas enhanced the dissociation of TMB and the reaction of boron, carbon and nitrogen. The boron carbon oxynitride films were successfully applied to a Cu mesh with holes of ϕ 100 μm .

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