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Silicon carbide film deposition at low temperatures using monomethylsilane gas

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ABSTRACT

A silicon carbide film is formed at low temperatures on a silicon surface by chemical vapor deposition using monomethylsilane gas along with hydrogen chloride gas in ambient hydrogen at atmospheric pressure. A 0.2-μm thick film, obtained at 1073 K and at a hydrogen chloride gas concentration greater than that of the monomethylsilane gas, possessed a specular surface having the root-mean-square microroughness of 0.7 nm. At temperatures lower than 900 K, the 0.1-μm thick silicon carbide film could be formed on the silicon surface, immediately after the surface cleaning in ambient hydrogen at 1373 K. Because the weight of the film formed at room temperature did not decrease after the etching using hydrogen chloride gas at 1073 K, the film obtained in this study is expected to be a tough coating film.

1. Introduction

A silicon carbide (SiC) thin film is expected to be a suitable coating material because it is very stable and tough even in a hazardous environment, such as the coating film of a susceptor of a silicon epitaxial reactor [1]. However, one of the problems of SiC as a coating material is the very high temperature often necessary for its film formation.

A SiC film is formed using the chemical vapor deposition (CVD) method at various substrate temperatures [2–4]. The deposition temperature is often comparable to the melting point of silicon and may induce some damage due to the difference in the thermal expansion between the SiC film and the substrate material [5]. In order to reduce these problems, the SiC film coating at lower temperatures is expected.

For the low temperature film formation, methylsilanes, such as monomethylsilane (MMS), dimethylsilane and trichloromethylsilane, are expected candidates, because these gases have a covalent bond between the silicon and carbon in their molecular structure. Many researchers have studied SiC film formation technology using monomethylsilane gas [4–13], as well as dimethylsilane [14]. The low temperature SiC film was formed on a silicon surface using MMS gas with hydrogen chloride (HCl) gas at 1073 K [15,16]. By this method, the excess silicon in the SiC film was reduced by hydrogen chloride gas, because HCl can react with SiH_x in the gas phase and Si at the surface to form gaseous product of chlorosilanes. By this method, the SiC film thickness saturated within 60 s. Here, it should be noted that the high purity HCl gas did not corrode the stainless tube and quartz chamber in the CVD reactor.

In order to develop the low-temperature SiC CVD technology, further details should be obtained, particularly about the influence of the gas composition, the surface morphology, the film formation temperature and the substrate surface cleaning condition.

The relatively low-temperature SiC film formation has been studied in the field of surface physics and surface science. Particularly, Nakazawa and Suemitsu [6] studied the thermal decomposition of MMS molecules chemisorbed on the silicon surface. In their study, MMS was chemisorbed at room temperature on the silicon surface, which was cleaned in a high vacuum environment at high temperature immediately before the chemisorption. This indicates that SiC film or its intermediate compound film can be formed at low temperatures using MMS gas at the clean silicon surface which has dangling bonds or silicon dimers.

In order to prepare an atomically clean silicon surface, the industrial silicon epitaxial growth process employs the annealing technique in ambient hydrogen. Additionally, the hydrogen-annealed silicon surface has been known to contain monohydrides with silicon dimers [17–19]. These dimers are expected to help the formation of chemical bonds between the silicon surface and precursors, such as MMS, at low temperatures. Thus, the SiC deposition from MMS gas on the silicon surface combined with the hydrogen annealing technique should be studied.

Therefore, in this study, the SiC film deposition on a silicon surface is further studied using MMS gas at 1073 K and lower temperatures, particularly about the influence of the gas composition, the surface

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morphology, the film formation temperature and the substrate surface cleaning condition. Through this study as an extension of our previous study [15,16], hydrogen chloride gas is introduced along with MMS gas, expecting the decrease of excess silicon in the SiC film.

2. Experimental

In order to obtain the SiC film by the CVD method, the horizontal cold-wall reactor shown in Fig. 1 was used. This reactor consists of a gas supply system, a quartz chamber and six infrared lamps. A 30-mm-wide × 40-mm-long (100) silicon substrate manufactured by the Czochralski method is horizontally placed on the bottom wall of the quartz chamber. The silicon substrate is heated by infrared rays from the six halogen lamps through the quartz chamber. Because quartz absorbs only a slight amount of infrared light having the wavelength of *ca.* 1 μm from the halogen lamps, the temperature of the quartz chamber wall remains low. Electric power provided to the infrared lamps is adjusted on the basis of the temperatures measured beforehand in ambient nitrogen. The gas flow channel above the substrate of this reactor has a low height and a small rectangular cross section in order to achieve a very high consumption efficiency of the reactive gases. The height and the width of the quartz chamber are 10 mm and 40 mm, respectively, similar to those in our previous studies [20–22].

The gas supply system has the function of introducing gases of hydrogen, nitrogen, MMS, hydrogen chloride and chlorine trifluoride. Hydrogen gas is used as the carrier gas as well as the cleaning gas for removing the silicon oxide film and organic contamination on the silicon surface [21]. Throughout the process, hydrogen gas is introduced into the reactor at atmospheric pressure at the flow rate of 2 slm. Water vapor in the hydrogen gas is removed by passing the hydrogen gas through a liquid nitrogen trap (77 K) at the entrance of the reactor. Chlorine trifluoride gas [23,24] is used in order to remove the SiC film, which is formed on the inner wall of the quartz chamber during the SiC CVD process.

The typical process used in this study is Steps (A), (B) and (C) shown in Fig. 2.

Step (A): cleaning of the silicon surface at 1373 K for 10 min in ambient hydrogen.
Step (B): SiC film formation using a gas mixture of MMS and hydrogen chloride, at room temperature — 1073 K after Step (A).
Step (C): etching by hydrogen chloride gas at 1073 K for 10 min.

The average thickness of the SiC film is evaluated from the increase in the substrate weight.

In our preliminary experiment, a polycrystalline 3C–SiC wafer produced by the CVD method (Admap Inc., Tokyo) was found to suffer from no etching by the 100% hydrogen chloride gas at 1273 K for over 40 min. This clearly indicates that SiC film is not etched by the hydrogen chloride gas. Thus, in order to quickly determine the formation of SiC, some of the films obtained by Steps (A) and (B) were

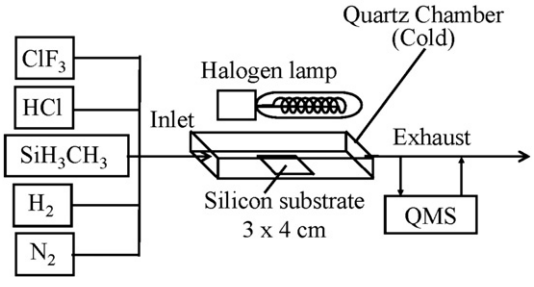

Fig. 1. Horizontal cold-wall chemical vapor deposition reactor used for SiC film deposition.

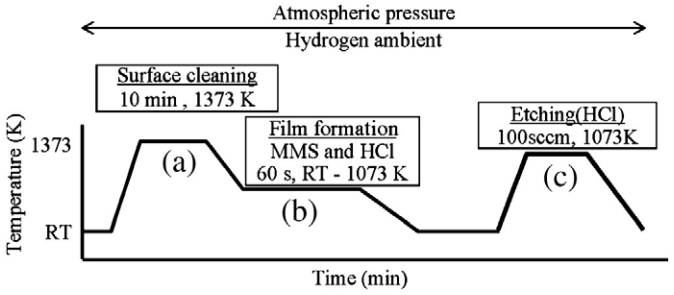

Fig. 2. Process for SiC film deposition and etching using gases of MMS, hydrogen chloride and hydrogen. Step (A): cleaning silicon surface at 1373 K, Step (B) film formation after Step (A), and Step (C): etching of film surface using hydrogen chloride gas at 1073 K.

exposed to the gas mixture of hydrogen chloride and hydrogen at the flow rate of 100 sccm and 2 slm, respectively, at 1073 K, as Step (C) in Fig. 2. Here, it may be pointed out that silicon surface suffers significant etching by hydrogen chloride gas at 1073 K [20].

After finishing the film deposition, the quartz chamber is cleaned using chlorine trifluoride gas (Kanto Denka Kogyo Co., Ltd., Tokyo, Japan) at the concentration of 10% in ambient nitrogen at 673–773 K for 1 min at atmospheric pressure. This cleaning technique is an application of the SiC etching technique using chlorine trifluoride gas [23,24].

In order to evaluate the chemical bond between silicon and carbon in the SiC film, the X-ray photoelectron spectra (XPS) were obtained using a PHI 5400MC spectrometer (Perkin-Elmer Co., Ltd., USA) which had an aluminium X-ray source. The incident angle of X-ray was 90° for the film having the thickness larger than 0.1 μm.

The surface morphology was observed using an optical microscope (USB Microscope, Scalar Corp., Tokyo), a laser microscope (VK-9500, Keyence Corp., Tokyo), a scanning electron microscope (SEM) (VE-8800, Keyence, Tokyo) and an atomic force microscope (AFM) (VN-8000, Keyence Corp., Tokyo and SPA400 and SPI3800N, Seiko Instruments Co., Ltd., Tokyo). Surface microroughness was evaluated by AFM. In order to observe the surface morphology and the film thickness, a transmission electron microscope (TEM) (HD-2700, Hitachi High-Technologies, Tokyo) was taken. The XPS and TEM measurements were *ex situ* performed at the Foundation of Promotion of Material Science and Technology of Japan (Tokyo).

3. Results and discussion

3.1. SiC film thickness

First, the SiC film thickness was evaluated at various gas compositions of MMS and hydrogen chloride for 5 min at 1073 K, as shown in Fig. 3 and as listed in Table 1. The hydrogen gas flow rate was 2 slm; the hydrogen chloride gas flow rate was 100 sccm (circle), 150 sccm (square) and 200 sccm (triangle).

In Fig. 3, the film thickness entirely decreases with the increasing hydrogen chloride gas flow rate. The square and triangle show that the SiC film thickness was very small but it gradually increased with the increasing MMS gas flow rate between 50 and 200 sccm. In contrast to this, the SiC film thickness obtained at the hydrogen chloride gas flow rate of 100 sccm, indicated by the circle, showed a significant increase at the MMS gas flow rate greater than 100 sccm. Here, the surface appearance of the film having such a significant thickness increase was dark and very rough.

Here, it should be noted that the silicon substrate surface was significantly etched by hydrogen chloride gas at its flow rate of 100 sccm for 60 s, without MMS gas. This indicates that the silicon–silicon bond present at the film surface can be removed by hydrogen chloride gas. Thus, based on the results in this study and following our