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Polycrystalline silicon carbide film deposition using monomethylsilane and hydrogen chloride gases

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Abstract

A polycrystalline silicon carbide film is formed on a silicon surface by atmospheric pressure chemical vapor deposition using a gas mixture of monomethylsilane and hydrogen chloride in ambient hydrogen. The film deposition near 1000 K stops within 1 min. However, the film thickness, obtained before the saturation of the deposition, increases by increasing the monomethylsilane gas flow rate. Because the film surface is considered to be terminated with hydrogen bonding with carbon, a further deposition is enabled by annealing step at 1273 K to remove hydrogen. By means of the high temperature annealing and by increasing the monomethylsilane gas flow rate, thick SiC film can be obtained.

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Keywords: Silicon carbide; Monomethylsilane; Hydrogen chloride; Chemical vapor deposition; Hydrogen desorption

1. Introduction

Silicon carbide (SiC) has various useful properties, such as a high thermal conductivity, high chemical stability, high mechanical hardness, and low dielectric constant [1]. However, because the SiC film is usually formed at very high temperatures, such as that higher than 1500 K [2,3], the substrate must be chosen from materials having very high melting points. For forming a SiC film on various materials having low melting point, the technology to achieve a low temperature SiC film deposition is expected.

For this purpose, monomethylsilane gas is expected to allow the low temperature SiC film formation, because it has a covalent bond between the silicon and carbon in its molecular structure. Thus, many researchers have studied SiC film formation technology using monomethylsilane gas [4–13].

In our previous study [13], a polycrystalline SiC film formation was performed near 1000 K by atmospheric pressure chemical vapor deposition (CVD) method using the gas mixture of monomethylsilane and hydrogen chloride in ambient hydrogen. The excess amount of silicon on the film surface was reduced using the hydrogen chloride gas. After the saturation of the film deposition, a further deposition was enabled using annealing step at 1273 K in ambient hydrogen.

From the viewpoint of suitable gas system, many researchers reported SiC film deposition [14–21] adding hydrogen chloride gas for obtaining various effects, such as suppressing nucleation in the gas phase and increasing the growth rate, mainly in propane–silane system. Although the SiC film growth using organic silicon carbide source gas with hydrogen chloride gas may enable the low temperature film deposition, such the study is very scarce [21].

In this study, the SiC film formation process on silicon substrate is further studied using the gas mixture of monomethylsilane and hydrogen chloride, focusing on the detail of the chemical process during the film deposition at low substrate temperatures. The method to effectively increase the film thickness is also discussed.

2. Experimental procedure

In order to obtain a SiC film using the chemical vapor deposition (CVD) technique, the atmospheric pressure horizontal cold-wall reactor, shown in Fig. 1, was used. This reactor consists of a gas supply system, a quartz chamber (40-mm wide, 10-mm high and 500-mm long) and infrared lamps. A 30-mm wide × 50-mm long (100) silicon substrate manufactured using

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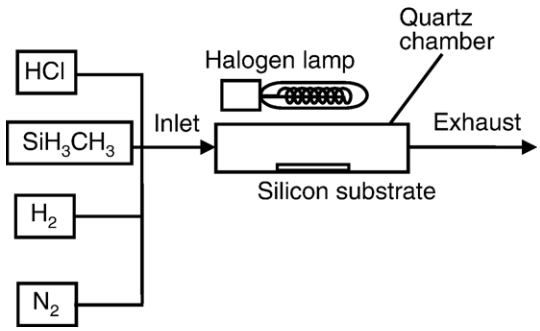

Fig. 1. Atmospheric pressure horizontal cold-wall chemical vapor deposition reactor used in this study.

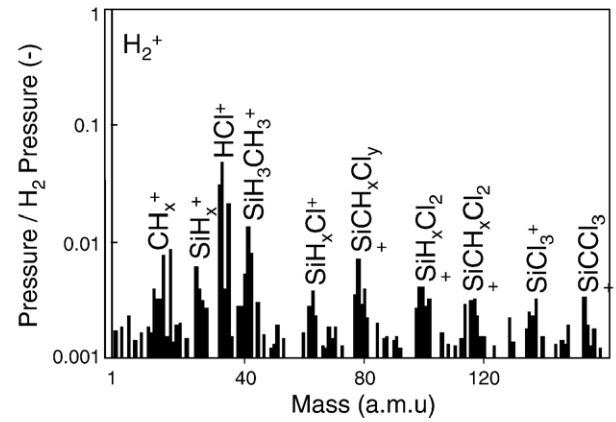

Fig. 3. Quadrupole mass spectra measured during SiC film deposition using the process in Fig. 2. The substrate temperature is 1093 K. Monomethylsilane gas concentration is 2.3%. Hydrogen chloride gas concentration is 4.7%.

the Czochralski method is horizontally placed on the bottom wall of the quartz chamber.

The gas supply system has the function of introducing gases, such as hydrogen, nitrogen, monomethylsilane and hydrogen chloride. Hydrogen gas is used as the carrier gas and is also used in order to remove the silicon oxide film and organic contamination existed on the silicon substrate surface [22] immediately before the film deposition. Hydrogen chloride gas is added to monomethylsilane gas in order to remove excess silicon in the obtained film [13]. The temperature of the gas mixture at the reactor inlet is 300 K.

The entire process used in this study is shown in Fig. 2. The SiC film deposition is performed using the following steps:

Step (a): baking at 1373 K for 10 min in ambient hydrogen for cleaning the silicon substrate surface, such as removing silicon oxide film and organic contaminants,
Step (b): SiC film deposition using the gas mixture of monomethylsilane and hydrogen chloride at 873–1373 K, and
Step (c): annealing the SiC film in ambient hydrogen at 1273 K for 10 min.

The process shown in Fig. 2 has Step (a) and then the repetition of Steps (b) and (c).

Throughout this process, hydrogen gas is introduced into the reactor at atmospheric pressure at a flow rate of 2 l min^{-1}. The average thickness of the SiC film was evaluated by the increase in the substrate weight.

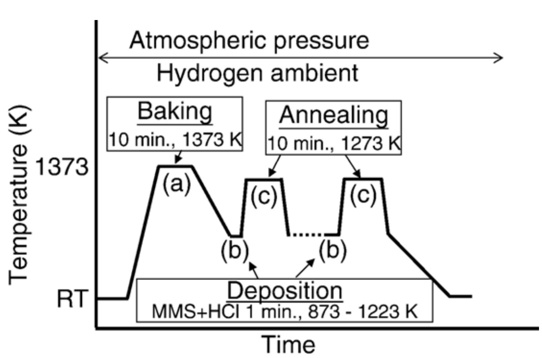

Fig. 2. Process for SiC film deposition, using gases of monomethylsilane, hydrogen chloride and hydrogen. Step (a): baking at 1373 K, Step (b): film deposition and Step (c): annealing at 1273 K.

In order to evaluate the gaseous products produced during the film deposition in the quartz chamber, a part of the exhaust gas from the reactor was fed to the quadrupole mass spectra (QMS) analyzer (Microvision, Spectra International LLC).

3. Results and discussion

3.1. Chemical reactions

Fig. 3 shows the quadrupole mass spectra measured during the SiC film deposition using the gas mixture of monomethylsilane and hydrogen chloride at the substrate temperature of 1093 K.

Fig. 3 shows the $SiH_xCH_y^+$, CH_x^+, SiH_x^+ and HCl^+ groups, which are assigned to the monomethylsilane gas, its fragments and hydrogen chloride gas. The chlorosilane groups (SiH_xCl_y) at the masses over 63 (y=1), 98 (y=2) and 133 (y=3) and the chloromethylsilanes group ($SiH_xCl_yCH_z$) at the masses over 75 (y=1), 110 (y=2) and 145 (y=3) are observed. This result indicates that the chlorination of monomethylsilane and silanes occurs.

Based on the information obtained from Fig. 3, the chemical reactions and process in the gas phase and at the substrate surface can be described as shown in Fig. 4 and as follows:

$$\text{Thermal decomposition of } SiH_3CH_3: \quad SiH_3CH_3 \rightleftarrows SiH_3 + CH_3 \tag{1}$$

$$Si_2H_6 \text{production}: 2SiH_3 \rightleftarrows Si_2H_6 \tag{2}$$

$$\text{Si production}: SiH_3 \rightleftarrows Si\downarrow + 3/2H_2 \tag{3}$$

$$\text{Si production}: Si_2H_6 \rightleftarrows 2Si\downarrow + 3H_2 \tag{4}$$

$$\text{Si etching[14]}: Si + 3HCl \rightleftarrows SiHCl_3\uparrow + H_2 \tag{5}$$

$$\text{Chlorination of } SiH_3: SiH_3 + 3HCl \rightleftarrows SiHCl_3 + 5/2H_2 \tag{6}$$