

Characterization of Polycrystalline SiC Films Grown by HW-CVD using Silicon Tetrafluoride

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Abstract

SiC films were synthesized by hot-wire chemical vapor deposition using a tungsten filament and a gas mixture of SiF₄ and CH₄. The etching of the substrate instead of the film growth occurred on the samples prepared using only source gases without H₂ dilution. The atomic or molecular hydrogen was believed to control the density of radicals containing F in a gas phase or on a growth surface. Polycrystalline 3C-SiC(111) films were successfully obtained at substrate temperatures lower than 500°C by using H₂ dilution. The growth mode limited by source-gas supply was found to be important to obtain polycrystalline SiC films. The SiC film grown at higher deposition pressure was amorphous and contained no Si-H_x bonds but 6% fluorine. In SiF₄/CH₄/H₂ system, the radicals containing F are considered to play very important roles in the reactions both on a growth surface and in a gas-phase.

Keywords

Hot-wire, CVD, 3C-SiC, SiF₄, H₂ dilution

1. Introduction

Silicon Carbide (SiC) is a promising wide gap semiconductor material utilized in a wide variety of applications. Its superior physical and chemical properties make it attractive for power electronic and optoelectronic device applications. The crystalline SiC growth is generally carried out at very high temperatures higher than 1200°C. This high growth temperature prevents the flexible design of the electronic devices.

Hydrogenated amorphous or microcrystalline SiC alloy films are also expected to be material for thin film solar cells. The a-SiC and μ c-SiC films could be prepared at the substrate temperatures lower than 300°C by plasma enhanced chemical vapor deposition (PECVD) and hot-wire (HW) CVD. Recently the low temperature epitaxial growth of 3C-SiC was also reported [1]. In the SiC growth by PECVD, various Si sources, such as SiH₄ [2], methylsilanes [3] and silicon halide [4], are used. SiH₄ and methylsilanes are also applied to HW-CVD [5-6]. However, the SiC film growth by HW-CVD using silicon halide sources has not been reported.

In this work, the polycrystalline SiC films were grown at low temperature (300-500°C) by HW-CVD using silicon tetrafluoride (SiF₄), and their structural properties were characterized.

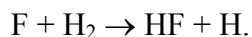
2. Experimental procedure

The Si and SiC films were deposited on Si(001) and Si(111) substrates by a HW-CVD system using a “Z” shaped tungsten filament. The filament diameter and length were 0.5mm and 150mm,

respectively. The filament temperature and filament-substrate distance were maintained at 1750°C and 45 mm, respectively. The substrates were cleaned using an ultrasonic treatment in acetone, etched by a 5% hydrogen fluoride solution and rinsed in deionized water prior to loading into the CVD system. The growth chamber was evacuated to 2×10^{-6} Torr by a turbo molecular pump. The source gases were SiF₄ (>99.999%) and CH₄ (>99.999%), and their flow rate was maintained at 5 sccm by mass flow controllers. H₂ (>99.99999%) was used as a diluent gas. For Si growth, the films were deposited with varying H₂ flow rate from 0 to 150 sccm. For SiC growth, it was maintained at 100 sccm. The substrate temperature and growth pressure was varied from 300 to 500°C and from 0.5 to 4.5 Torr, respectively. The structural property and bonding configuration of the SiC films were characterized using X-ray diffractometry (XRD), Fourier transfer infrared absorption spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS).

3. Results and Discussion

The Si films were grown using SiF₄ and H₂ at the substrate temperature of 400°C and the growth pressure of 1.5 Torr. Etching of the substrate surface was observed on the samples prepared using only SiF₄ without H₂ dilution. Similar results were reported in other works about Si film growth by plasma enhanced CVD using SiF₄ [4,7]. The results indicate a strong etching reaction of radicals containing fluorine atoms generated by the decomposition of SiF₄. In addition, it is suggested that the atomic or molecular hydrogen controls the density of radicals containing F in a gas phase. An example of the possible gas phase reactions is as follows [8]:



The SiC films were obtained using H₂ dilution at the substrate temperatures of 300-500°C. Figure 1 shows the dependence of XRD patterns on the substrate temperature. The films were deposited at the growth pressure of 1.5 Torr. A diffraction peak at 28° originates in Si(111) substrate. A peak originating in 3C-SiC(111) was measured at 36° in the films grown at the temperature higher than 400°C. Thus the polycrystalline 3C-SiC films were obtained at the temperature lower than 500°C. In addition, the similar results were obtained in the XRD patterns of the films grown on the Si(001) substrate. It is implied that the SiC films are grown in the 3D island growth mode instead of the epitaxial like growth, because of no dependence of XRD pattern on the substrate difference.

The dependence of IR spectra on the substrate temperature is indicated in Fig. 2. A remarkable absorption peak at 800cm⁻¹ originating in Si-C stretching mode was detected. The sharp Si-C peak of the film grown at 300°C suggests the crystallization of the film [9].

In our samples, no Si-H_x peak at around 2000cm⁻¹ was detected. It is widely known that the H concentration in the Si films grown by HW-CVD is comparative low value of 1-10% [10-11]. However, the H concentration in our samples was almost 0%. The result suggests that the radicals containing F remove the H atoms on the growth surface. Another possible reason is the temperature of the growth surface. In this work, the substrate temperature was measured by a thermocouple located at the heater block under the substrate holder. Thus it is probable that the surface temperature increases up to higher than 500°C, which is the temperature of H thermal desorption from the Si surface, by thermal radiation of the hot wire.

Figure 3 shows the dependence of growth rate on the deposition pressure. The films were deposited at 400°C. The growth rate increased with increasing pressure up to 1.5 Torr, and saturated at the pressure higher than 3.0 Torr. Thus, the growth reaction is limited by source-gas supply at the pressure lower than 1.5 Torr, and limited by surface reactions at the pressure higher than 3.0 Torr.

XRD patterns of the SiC films grown on Si(111) at various growth pressures are shown in Fig. 4. The 3C-SiC(111) peak was measured in the patterns of the films grown at 1.0 and 1.5 Torr. It was confirmed by FTIR measurements that the structure of the films grown at pressure higher than 3.0 Torr was amorphous. The results indicated that the growth mode limited by source-gas supply is required to obtain the SiC films with high crystallinity. In the growth limited by surface reactions, the precursors bond at unstable sites on the growth surface because of insufficient surface diffusion length, resulting in amorphous film growth.

Generally, atomic hydrogen has many very important roles, such as removing weak bonds and passivating dangling bonds on the growth surface, in the low temperature CVD of Si films [12-13]. In SiF₄/CH₄/H₂ system, the radicals containing F also seemed to play important roles in the growth mechanism. Figure 5 indicates XPS spectra of the SiC films grown at 1.5 and 4.5 Torr. The substrate temperature was maintained at 400°C. No fluorine peak was observed in the XPS spectrum of the polycrystalline SiC film grown at 1.5 Torr. On the other hands, apparent fluorine peaks were detected in the amorphous SiC film grown at 4.5 Torr. The concentration of fluorine was estimated to be 6% from the peak area of the spectrum. The results suggest that crystallinity of the SiC film is strongly affected by the radicals containing F both in the gas-phase and on the growth surface. In order to improve the film crystallinity, the effects of the radicals containing F must be examined and followed by careful discussions of growth kinetics.

4. Conclusion

The polycrystalline 3C-SiC(111) films were successfully obtained at substrate temperatures lower than 500°C by HW-CVD using H₂ dilution of SiF₄ and CH₄. No film growth occurred without H₂ dilution because of the strong etching reaction of radicals containing F generated by decomposition of SiF₄. The growth mode limited by source-gas supply was required to obtain the polycrystalline SiC films. It was found that the amorphous SiC film grown at higher growth pressure contained no Si-H_x bonds but 6% fluorine. The results suggested that the radicals containing F played very important roles both in gas-phase and on growth surface.

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Fig. 1. The dependence of XRD patterns of SiC films on the substrate temperature. The films were grown at the growth pressure of 1.5 Torr.

Fig. 2. The dependence of IR spectra of SiC films on the substrate temperature. The films were grown at the growth pressure of 1.5 Torr.

Fig. 3. The dependence of growth rate on the growth pressure. The films were grown at the substrate temperature of 400°C.

Fig. 4. XRD patterns of SiC films grown at various growth pressures. The films were grown at the substrate temperature of 400°C.

Fig. 5. XPS spectra of SiC films grown at growth pressure of 1.5 and 4.5 Torr. The substrate temperature was maintained at 400°C.

Fig. 1

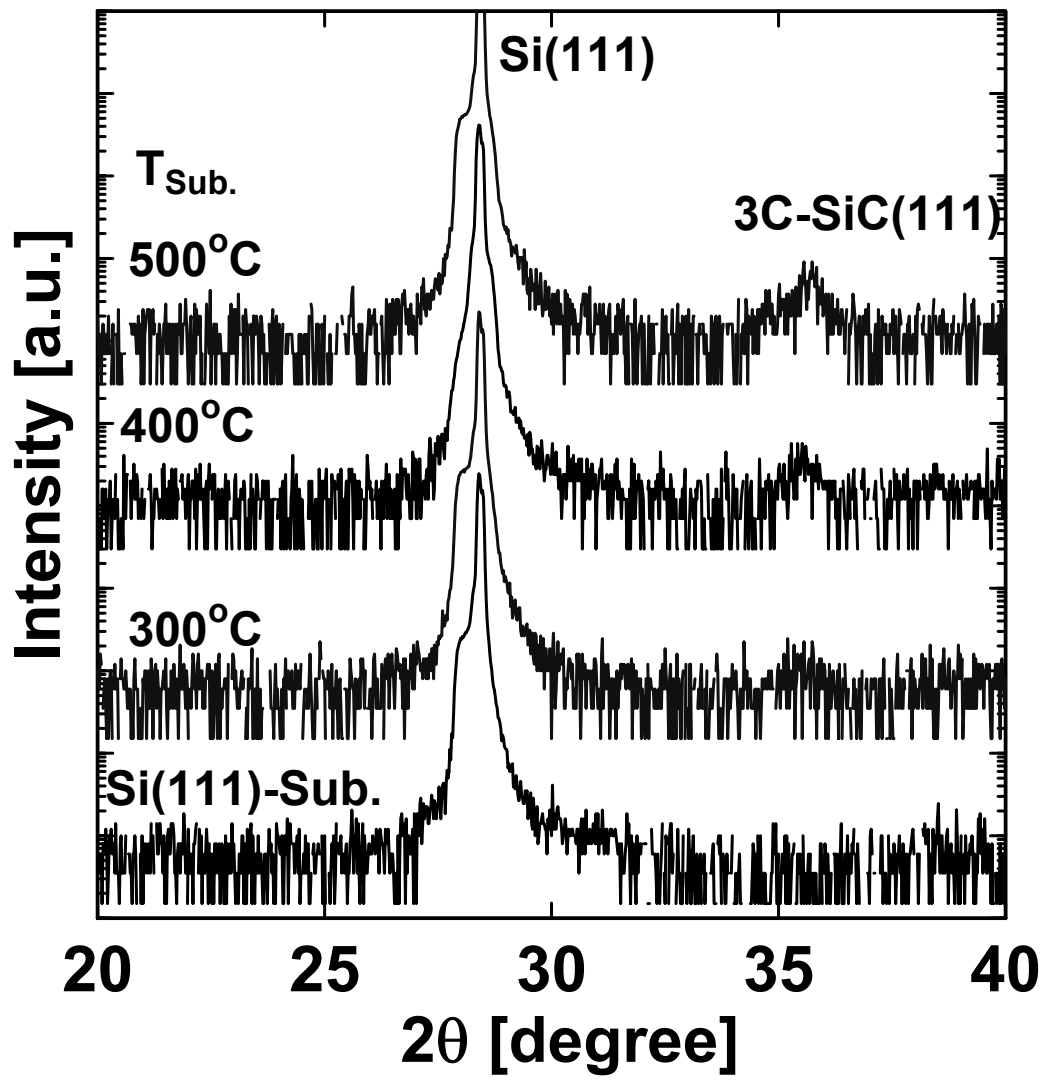


Fig. 2

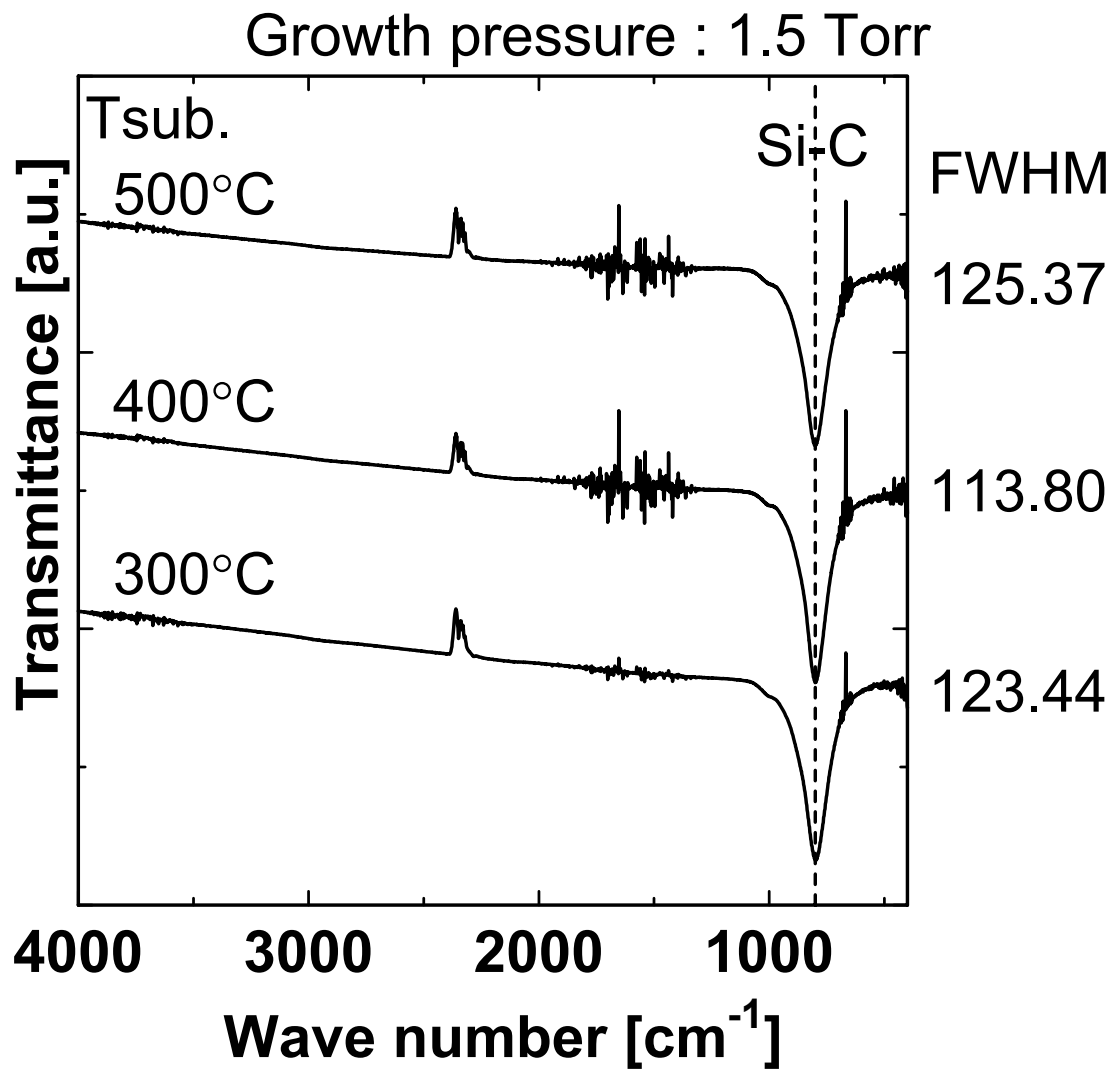


Fig. 3

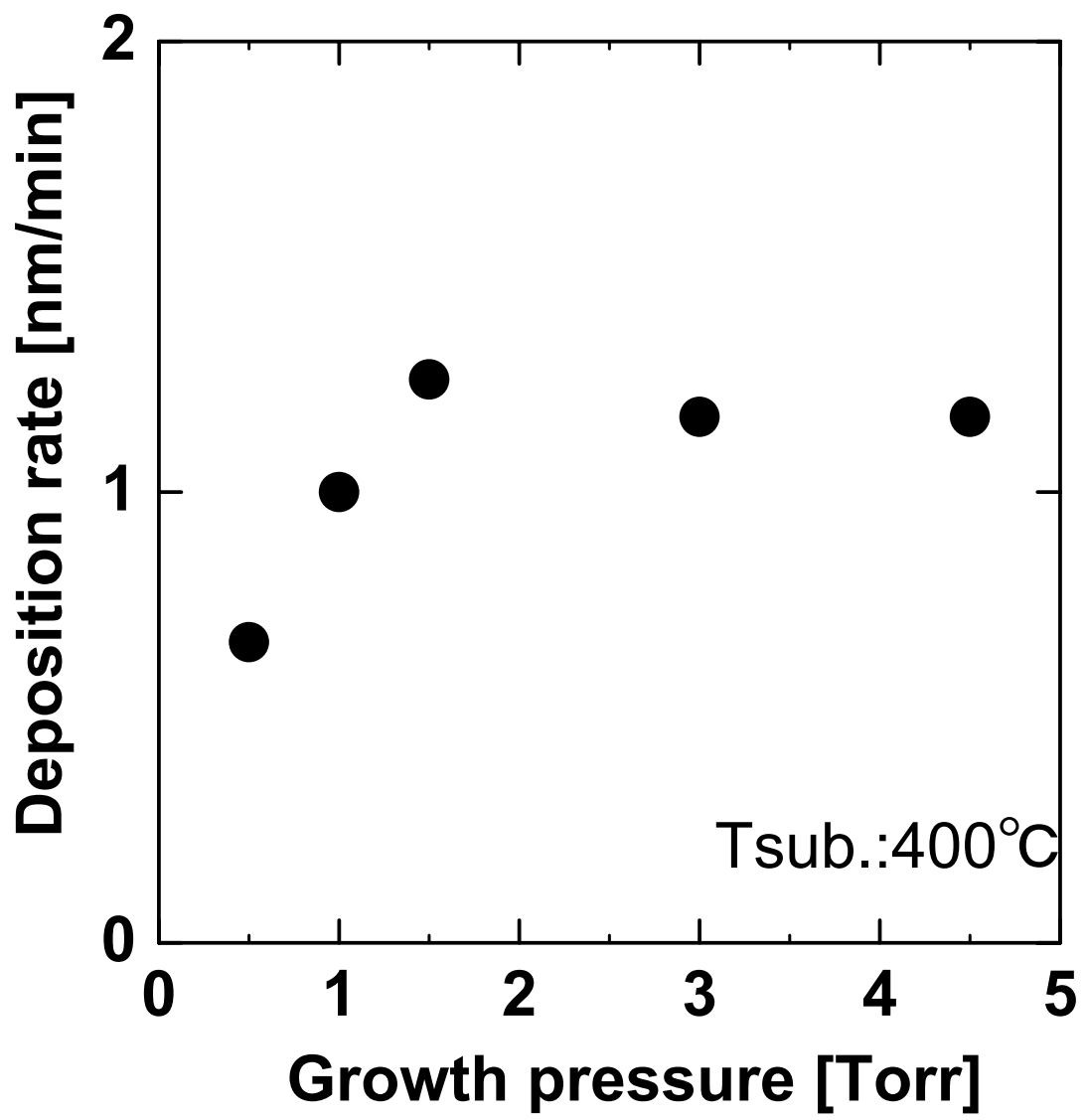


Fig. 4

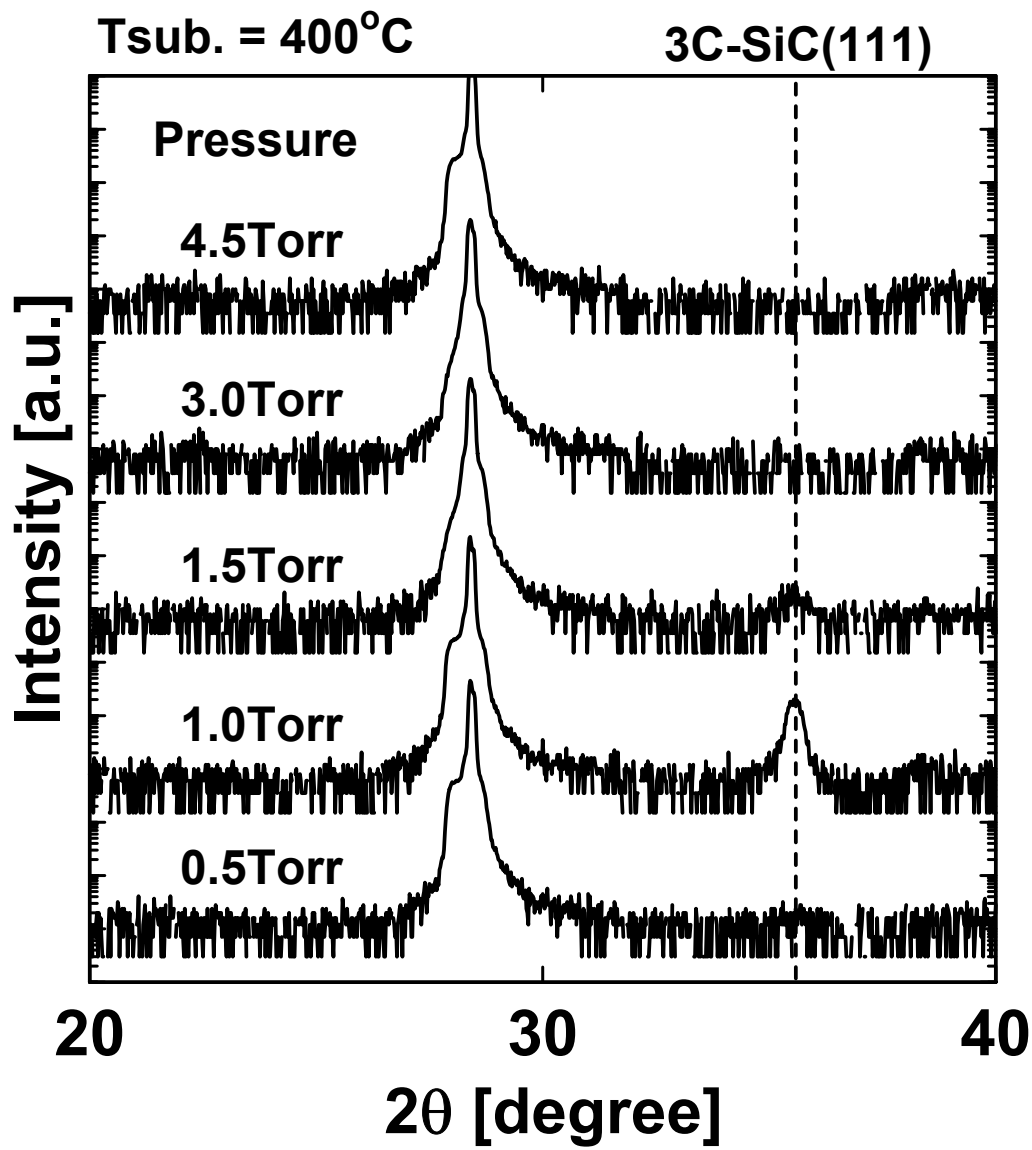


Fig. 5

