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A study of growth properties of SiC whiskers at various temperatures and input gas ratios on different Si substrates

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In this study, SiC whiskers and films were grown on Si substrates with a carbon buffer layer. No metallic catalyst was used that might act as an impurity or a barrier on the tip of the whisker. The deposition temperature was varied between 1000ºC and 1100ºC, and the input gas ratio, α [H_2/MTS] was set at 30, 40, and 50. We used bare Si and surface polished Si (SiC abrasive paper) as substrates to simulate different surface conditions. Growth properties that were examined by SEM and TEM depended on the temperature and the input gas ratio. The chemical compositions of deposits were investigated using XPS.

Key words: silicon carbide, SiC whisker, CVD, Si substrate.

Introduction

Due to its covalent bonding, silicon carbide (SiC) possesses a low density, a low thermal expansion coefficient, a high melting point, and high strength and hardness. Thus, it is now one of the most important structural ceramic materials [1]. It also has unique electronic properties, making it suitable as a semiconductor material that can be used at high power and high frequency in severe high temperature environments [2]. Also, owing to the excellent physicochemical properties of SiC micro- and nano-size structures, many researchers have recently investigated the synthesis of various SiC nanomaterials such as nanorods, nanowhiskers, nanowires, and nanopowders [3].

The applications of SiC whiskers are expanding due to their high aspect ratios and high theoretical strength [4]. SiC whiskers have been grown using several techniques [5-7]. However, there have been several problems because previous techniques used metallic catalysts. Therefore, we have developed a non-metallic catalyst process and successfully grown silicon carbide whiskers.

Generally, it is well known that the deposition of silicon carbide on Si single crystals is very difficult due to the differences of lattice parameter and thermal expansion coefficient between Si and SiC [8]. For these reasons, it is necessary to deposit a buffer layer [9]. In this study we deposited a carbon buffer layer.

Due to the wide application fields of silicon, whiskers grown on silicon substrates may also be applied in many modern industrial fields such as in field emission displays. In this study, SiC whiskers were grown on silicon substrates, which had different surface conditions at various deposition temperatures and input gas ratios, α.

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Experimental procedures

Details of the deposition system were described in a previous report [10]. We used methyltrichlorosilane, (CH_3SiCl_3, MTS) (Acros Organics Co., U.S.A) as source gas and high purity H_2 as carrier and dilution gas. A p-type Si (100) wafer was used as substrate material.

The various substrate conditions used are given in Table 1.

The heating process was performed under an H_2 atmosphere. After reaching the deposition temperature, the deposition was carried out with flowing carrier and dilution gases with α ratios of 30, 40 and 50. The pressure was stabilized as the pressure of the bubbler. The deposition temperatures were set at 1000ºC, 1050ºC and 1100ºC.

The carbon buffer layer was used to improve the adhesive property and growth of the SiC. The carbonization process on the Si was performed using 3% C_2H_2

Table 1. Substrates preparation conditions

Definitions	Samples
SP1	Bare Si
SP2	Polished Si with grit #2000 SiC abrasive paper
SP3	Polished Si with grit #1000 SiC abrasive paper
SH1/SH2/SH3	SP1/SP2/SP3 followed by heating process to 1000ºC with H_2 flow
SD1/SD2/SD3	SP1/SP2/SP3 deposited with carbon layer at 1000ºC for 1hr

in H_2 ambient at 1000ºC for 1hr. The microstructures and surface morphologies were examined by scanning electron microscopy (SEM, Hitachi S-2700/FESEM) and transmission electron microscopy (TEM, Hitachi H-600).

Results and Discussion

Figure 1 shows SEM images of SD1 after the SiC deposition process at the temperatures of 1000ºC, 1050ºC, 1100ºC and input gas ratio, α, of 30 for 2 hours.

In Fig. 1(a), long and thin whiskers are shown. However, as shown in Fig. 1(c), thick films were also found. The difference in growth properties is related to growth rate and direction. It appeared that axial growth predominated at 1000ºC, while radial growth predominated at 1100ºC. These two distinct growth mechanisms were apparently competing at 1050ºC. The overall growth properties at different input gas ratios, α, were similar to α=30. However, the mean diameter of the whisker decreased as the input gas ratio α increased at 1000ºC while thick whiskers (0.7 μm~) appeared at 1100ºC. To investigate the relationship between growth rates and deposition temperature, we calculated and plotted the growth rates vs. deposition temperatures as shown in Fig. 2. We can see that the deposition rate increased greatly above 1050ºC. The growth rate is related to the surface morphology of deposits [11]. At a temperature below 1050ºC, the growth rate changes only slightly with temperature variation; however, above 1050ºC, the growth rate changes greatly in spite of the small temperature changes. Thus, the types of deposits are not fixed to one form above 1050ºC, and this temperature is considered to be the point at which the growth properties change.

The surface energy can be increased due to surface defects, and nucleation and growth proceeds at these sites to lower the surface energy [12]. Therefore, the Si substrate was polished with grit #2000, #1000 SiC abrasive papers before the SiC deposition to produce surface defects. Figure 3 shows the SEM images of SD3 after the SiC deposition process under the same conditions. Overall, the growth of the deposits compared well to that on SD1. The mean diameter of the whiskers decreased and the density of whiskers increased. The temperature and α dependency of growth behavior was similar to that of SD1. Total results of the growth rates are shown in Fig. 4. Some selected observations using TEM are shown in Fig. 5. Up to 1050ºC, the crystal structure of deposits was amorphous. However, at

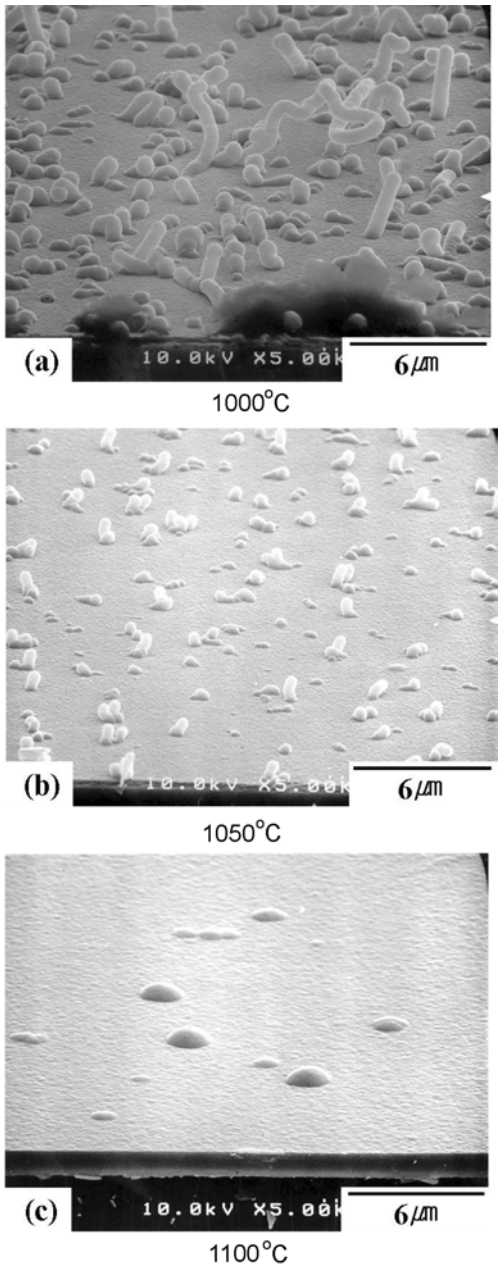

Fig. 1. SEM images of SD1 after the SiC deposition process (2 hours) at different temperatures and input gas ratios α=30. (a) 1000ºC (b) 1050ºC (c) 1100ºC

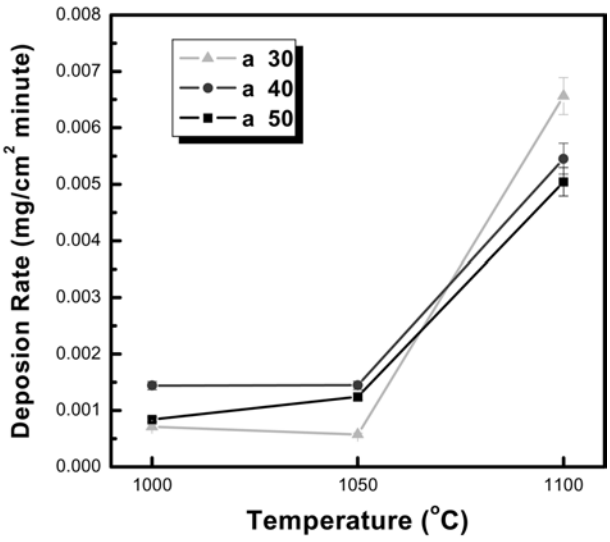

Fig. 2. Temperature dependency of the growth rate on the input gas ratio. (α=30, 40, 50)

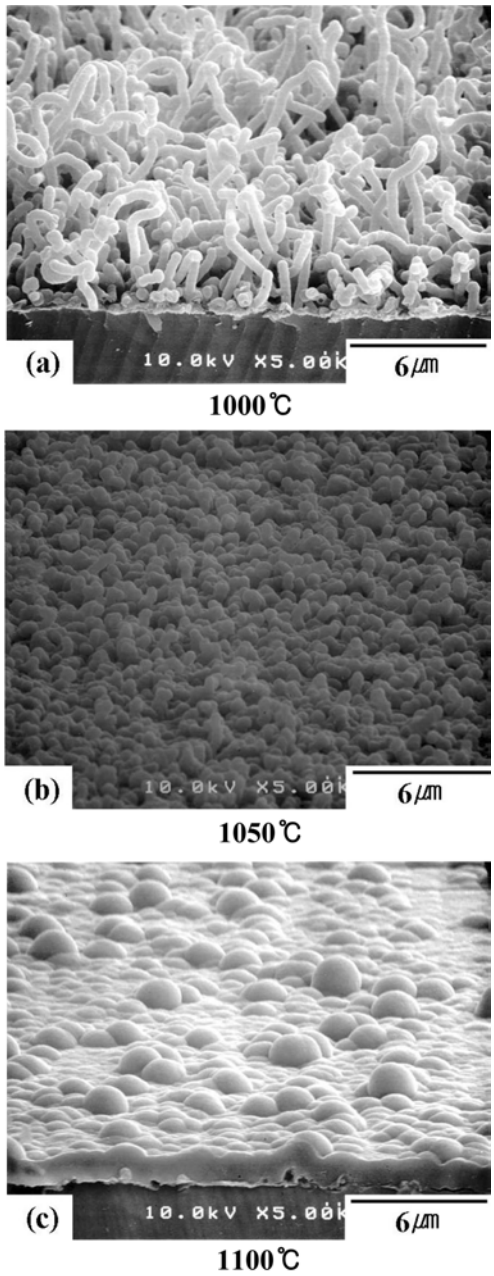

Fig. 3. SEM images of SD3 after the SiC deposition process (2 hours) at different temperatures and input gas ratios α=30. (a) 1000°C (b) 1050°C (c) 1100°C

1100°C, single crystals were formed. Thermal energy is considered to be sufficient for single crystal growth at 1100°C.

XPS narrow scan spectra of Si_{2p} and C_{1s} for the chemical composition of the deposits are shown in Fig. 6. Deconvolution of the Si_{2p} and C_{1s} peaks, by a Gaussian-Lorentzian type distribution, showed Si-C and C-Si peaks that have binding energies of 101.2 and 283.5, respectively [13, 14]. When the normalized areas that were calculated from the peak area per atomic sensitivity factor were compared [15], the ratio of relative composition of C/Si was 1.54. The excess carbon produced in their process is considered to be the cause.

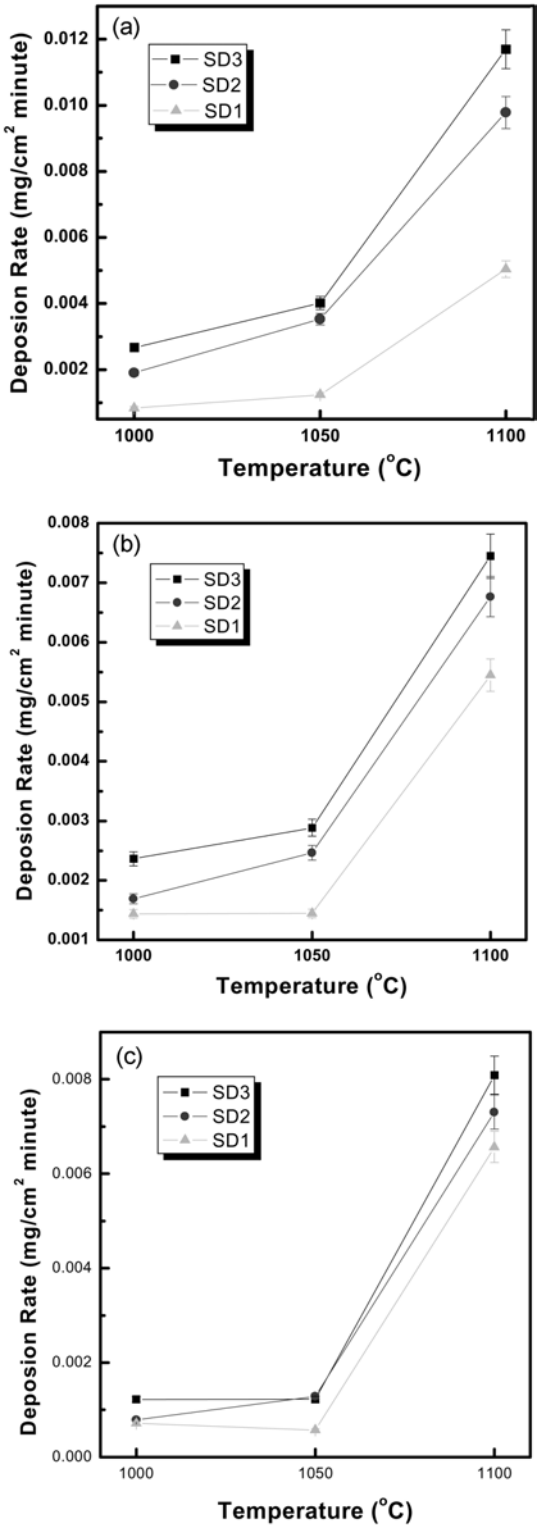

Fig. 4. Growth rate changes at different input gas ratios of SD1, SD2, and SD3 with a variation of the temperatures. (a) α=50 (b) α=40 (c) α=30

In the case of Si_{2p}, the Si-O bonding existed with higher intensity. The most likely reason is that most of the oxygen from the air bonded with Si more than C in the deposits.

The growth of the deposits on SD2 was almost the

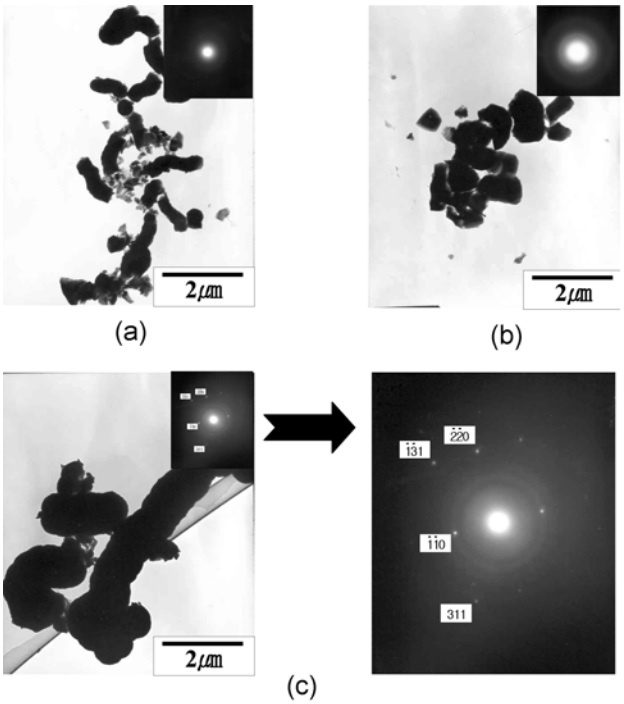

Fig. 5. TEM images and SAD patterns of deposits of SD3 at different deposition temperatures (α=40). (a) 1000ºC (b) 1050ºC (c) 1100ºC

same, but the whiskers grown on SD3 were slightly thinner and denser. To discover why, we examined the initial surface morphologies of silicon substrates and surface morphologies of silicon substrates only after the heating process to 1000ºC.

As a result, there was found to be no change between bare Si (SP1) and the post-heating state (SH1). However, the surface morphologies of polished Si with grit #2000 (SP2) and #1000 (SP3) SiC abrasive paper were changed. In its initial state, SP2 possesses thin and shallow scratches of 8.9×10^5 scratches/mm^2 and SP3

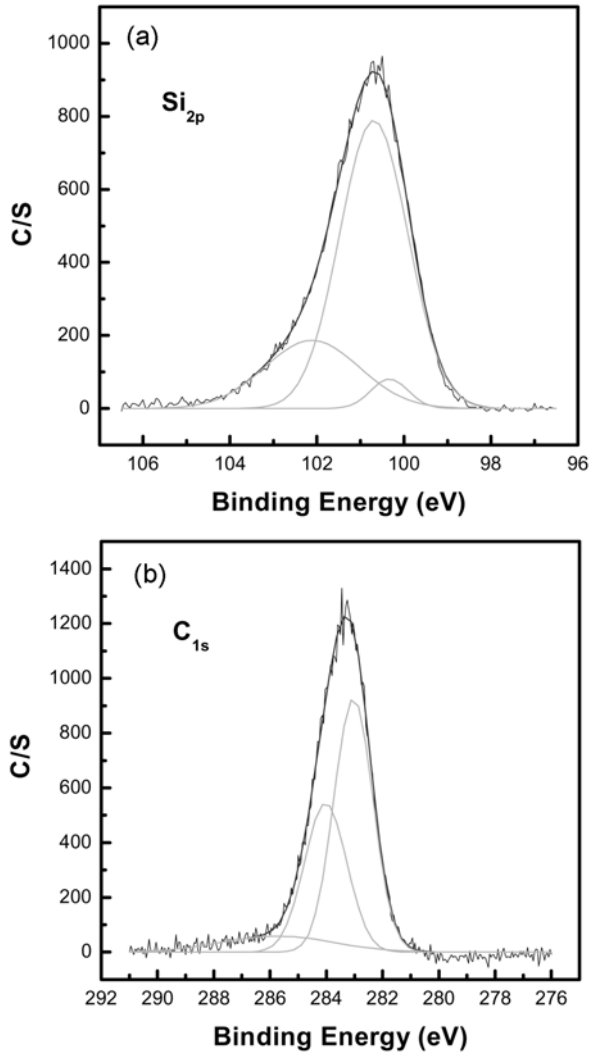

Fig. 6. XPS deconvolution of narrow scan spectra of SiC deposits on SD3 for α=30, 1100ºC. (a) Si_{2p} (b) C_{1s}

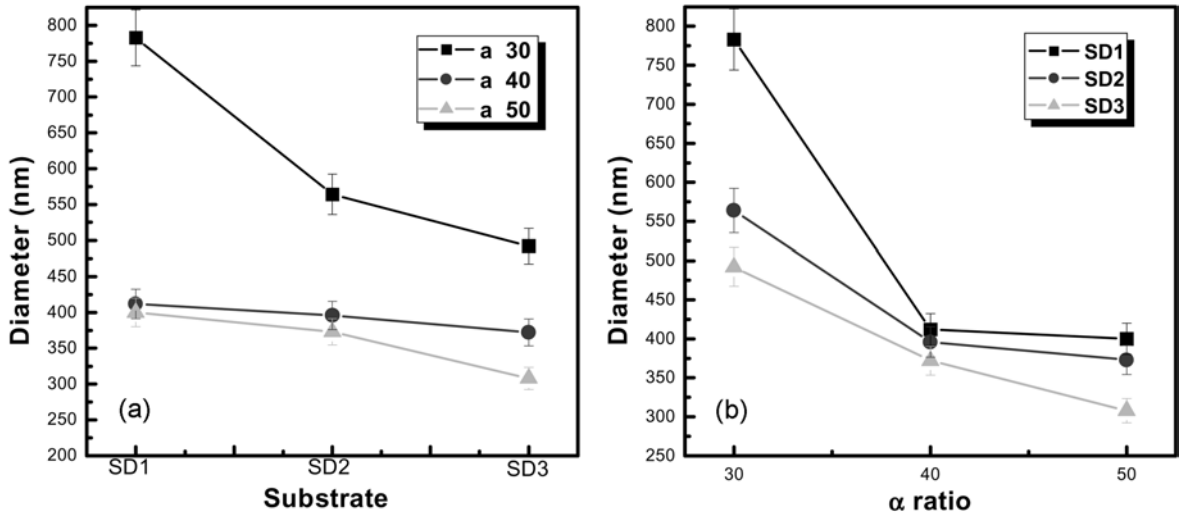

Fig. 7. Dependency of the mean whisker diameter on the various substrates and input gas ratios at 1000ºC. (a) Substrate vs. mean whisker diameter (b) Input gas ratio vs. mean whisker diameter

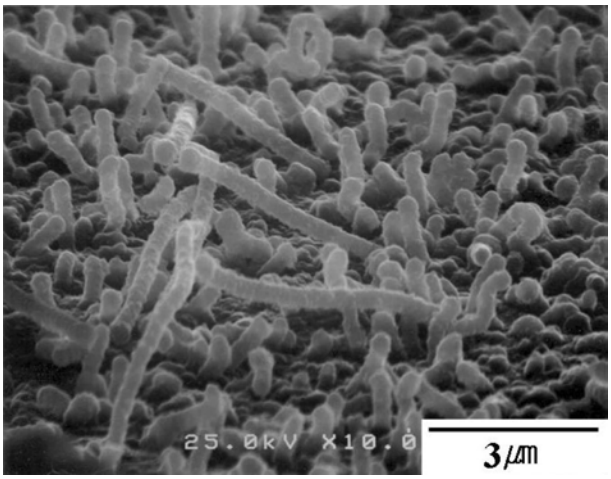

Fig. 8. SEM image of SD3 after the SiC deposition process (2 hours) at 1000°C, α=50.

has 4.4×10^5 scratches/mm^2. After heating to 1000°C, SH2 has 1.4×10^5 scratches/mm^2 and SH3 has 2.5×10^5 scratches/mm^2. It is considered that the heating process can reduce the density of surface defects. Thus, SH3 can have more high-active sites than SH2. For this reason, the whiskers grown on SD3 could be thinner, longer, and denser than those on SD2.

Finally, we express the overall result in Fig. 7. Figure 7 shows the dependency of mean whisker diameter on the substrate and input gas ratio at 1000°C. As a result, it is believed that the SD3 substrate at 1000°C and an input gas ratio 50 is suitable for the growth of thin whiskers, and the SEM image of this sample is shown in Fig. 8.

Conclusions

SiC whiskers on Si substrates were grown through a carbonization process without using metallic catalysts. Below 1050°C, the growth rates were relatively low and the crystal structure of deposits was amorphous, and axial growth was predominant. Above 1050°C, however, the growth rates increased steeply, the deposits were single crystals, and radial growth was predominant.

Also, we confirmed that surface defects can activate the growth of whiskers and with an increase of input gas ratio, the mean whisker diameter decreased. As a result, whiskers grown on SD3 substrate at 1000°C and with an input gas ratio of 50 for 2 hours have the smallest mean whisker diameter of 300 nm.

Acknowledgment

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