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Growth of nanocrystalline 3C-SiC a on Si substrate by Plasma-enhanced Chemical Vapor Deposition

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3C-SiC films were deposited on a silicon (100) substrate by a plasma-enhanced chemical vapor deposition (PECVD) technique using a gas mixture of $SiCl_4/CH_4/H_2/Ar$ in the temperature range between 1170°C and 1335°C. The Crystallinity of deposited films was investigated by varying the deposition temperature, input gas ratio, R_x [$=CH_4/(CH_4+H_2)$], and r.f. power. The PECVD method effectively enhanced the deposition rate compared with TCVD (thermal chemical vapor deposition). The highest preferred orientation of deposited 3C-SiC layers was found to be the (111) plane. The crystallinity of 3C-SiC on the Si substrate was significantly influenced by the R_x value and improved with decreasing R_x. The free silicon was co-deposited with 3C-SiC. The content of free silicon was decreased with increasing the deposition temperature and decreasing the R_x value. 3C-SiC films which had a relatively good crystallinity were obtained at a deposition temperature of 1270°C, an input gas ratio of R_x=0.04, and an r.f. power of 60 Watt.

Key words: 3C-SiC films, PECVD, Free silicon, Nanocrystalline.

Introduction

Silicon carbide is considered to be a useful material for structural and electronic applications because it has excellent physical and electronic properties such as high temperature stability, extreme hardness, excellent resistance to chemical attack, wide energy band gap, high electron mobility, *etc*. [1-5]. Crystalline SiC films have been grown by many investigators using the chemical vapor deposition (CVD) method [6-8]. CVD silicon carbide coatings on substrates (graphite, silicon, silicon carbide, *etc*.) are very interesting for many industrial applications such as for protecting substrates from oxidation at high temperature and for growing silicon carbide crystals as semiconductor materials. Although it is common to grow 3C-SiC films on Si substrates by CVD, the deposition temperature is normally higher than 1350°C, which may cause serious problems in the 3C-SiC/Si structure due to the difference of thermal expansion coefficients (~8%) and lattice parameters (~20%) between the two layers [9]. Therefore, different methods [10-12] have been explored to obtain the best crystal quality as well as to lower the growth temperature.

In the present study, the 3C-SiC films were deposited on Si substrates by a plasma-enhanced chemical vapor deposition (PECVD) technique to investigate the effect of r.f. power on the film growth. In this PECVD method the effect of the experimental conditions such as the r.f. power, the input gas ratio, and deposition temperature on the crystallinity and morphology of the deposited 3C-SiC films was examined.

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Experimental Procedures

Deposition of 3C-SiC films

3C-SiC films were deposited on (100) Si substrate by a PECVD technique using a $SiCl_4/CH_4/H_2/Ar$ gaseous mixture. The PECVD system consisted of a quartz reaction tube with a SiC-coated graphite susceptor. The Si substrate was etched in HF for 5 minutes to remove any native oxide film from its surface and then rinsed in distilled water. It was then washed in acetone and ethyl alcohol, dried, and finally loaded on the susceptor in the center of the reactor. The susceptor was heated by r.f. induction. The temperature was measured by observing the radiation from the Si substrate with an optical pyrometer. The precursors, $SiCl_4$ and CH_4, were used as silicon and carbon sources, respectively. A high purity gas mixture of Ar and H_2 was used as the carrier gas. Flow rates of these gases were individually controlled with a mass flow controller. The bubbler for $SiCl_4$ was maintained at −21°C to get the correct vapor pressures.

The experimental conditions used for the deposition of 3C-SiC films on Si substrates are listed in Table 1. After the SiC films were deposited onto the substrates,

Table 1. Typical deposition conditions for the SiC-PECVD

Precursors	$SiCl_4$	CH_4
	1.17 ml/min	2~20 ml/min
Substrate	Si (100) wafer	
Carrier gas	Ar (10 ml/min)	
Atmosphere gas	H_2 (30~48 ml/min)	
R. F. power	0~75 Watt	
Deposition Temp.	1100~1335°C	
Working	1 torr (133.3 Pa)	
Deposition time	1 h	

the samples were furnace-cooled to room temperatures in flowing H_2.

Film Characterizations

The deposition rate was determined by measuring the thickness of films with a stylus (α-STEP) instrument and scanning electron microscope (SEM, Hitachi S-4200). The crystallinity of the films was analyzed primarily by X-ray diffraction (Rigaku D/Max-2400 diffractometer) with CuK_α radiation. The surface morphology of the films was observed with SEM. Some samples were analyzed using transmission electron microscopy (TEM, Jeol 2010) operating at 200 kV. For this purpose the samples were thinned by polishing and dimpling to 20 μm thickness, followed by ion milling.

Results and Discussion

With a gas mixture of $SiCl_4/CH_4/H_2/Ar$, SiC films were prepared using two different methods, TCVD and PECVD. As shown in Fig. 1, the deposition rate of films increased with increase of deposition temperature. This indicated that the deposition process was controlled by thermal activation. However, the deposition rate by PECVD was faster than that by TCVD. It would be expected that the additional plasma energy is to dissociates the source gas very efficiently an enough to supply sufficient Si atoms to the surface [10,11].

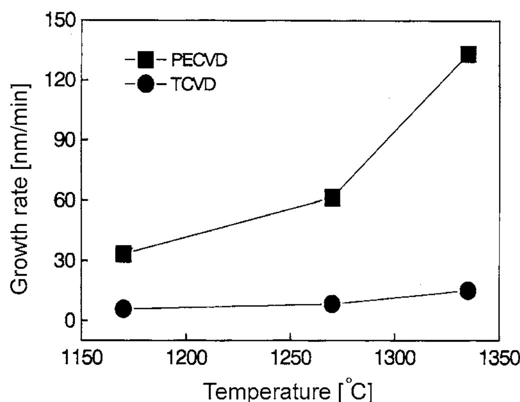

Fig. 1. Growth rate of 3C-SiC deposits as a function of temperature.

XRD patterns indicating the effects of the r.f. power, input gas ratio (R_x), and deposition temperature on the crystallinity of the deposit are shown in Figs. 2, 3, and 4, respectively. Figure 2 shows XRD patterns of the depo-sited films at various r.f.powers under conditions such that the input gas ratio and deposition temperature were kept at R_x=0.04 and at 1170°C. When the r.f. power was not applied, the growth of SiC films was weak, and this result suggested that the deposited SiC films were nearly amorphous. However, an increase of

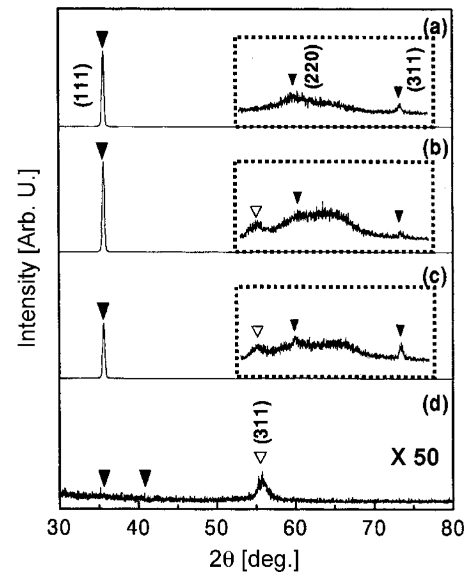

Fig. 2. XRD patterns as a function of r.f. power; (a) 75 Watt (b) 45 Watt (c) 30 Watt (d) 0 Watt. The input gas ratio and deposition temperature were kept at Rx: 0.04 and 1170°C, respectively. [▼ : Sic ▽ : S]

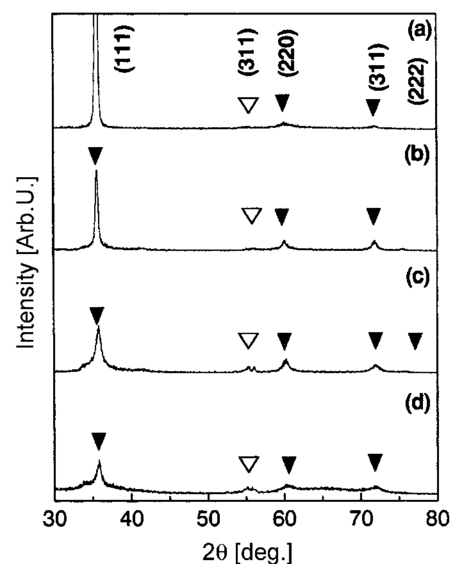

Fig. 3. XRD pattern for 3C-SiC films deposited at various input gas ratios; (a) R_x=0.04 (b) R_x=0.08 (c) R_x=0.2 (d) R_x=0.4. The r.f. power and deposition temperature were kept at 60 Watt and 1170°C, respectivly. [▼ : SiC ▽ : Si]

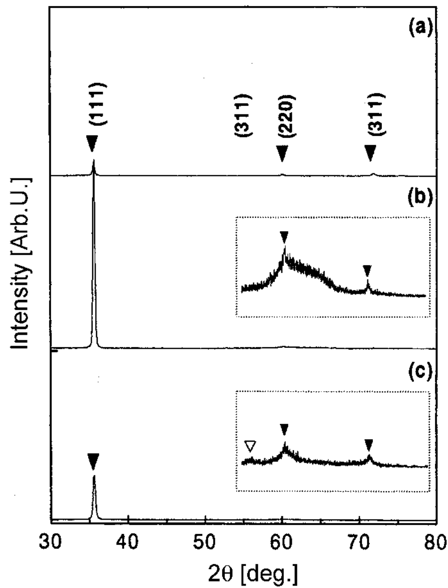

Fig. 4. XRD pattern as a function of deposition temperature; (a) 1335°C (b) 1270°C (c) 1170°C. The r.f. power and deposition temperature were kept at 60 Watt and 1170°C, respectivly. [▼ : SiC ▽ : Si]

r.f. power caused the crystallization of films in a polycrystalline form of the cubic structure of SiC with a highly (111) preferred orientation. But its peak intensity was increased with increased r.f. power up to 45 watt. Free silicon, which is frequently obtained during the deposition of SiC films [8], was observed at lower r.f. power. The content of free silicon decreased with increase in the r.f. power. The effects of input gas ratio and deposition temperature on the crystallinity of the deposit have been studied.

Figure 3 shows the variation of X-ray peak intensities with a variation of input gas ratio (at different R_x values). It is to be noted that the crystallization of the deposited films was with the cubic structure of SiC with a highly (111) preferred orientation. Also the free silicon was co-deposited as shown in Fig. 3, but its peak intensity decreased with a decrease in the R_x value. Furthermore, the peak intensity of the preferred orientation of the (111) plane increased with a decrease in the R_x value. This behavior could be explained by the reaction of $SiCl_4$ and CH_4 predominanting to form SiC rather than Si and CH_4 due to the H_2 dilution effect at a constant deposition temperature [13].

On the other hand, Fig. 4 shows the variation of X-ray peak intensities with a variation of deposition temperature. Some differences in crystallographic orientation of the deposited films with changing R_x value are noted as indicated by the changes in the relative peak intensity. A free silicon peak was observed in the layers deposited at 1170°C, and the peak corresponding to free silicon disappeared with increasing deposition temperature. The monolithic 3C-SiC phase without the free silicon appeared at both 1270°C and 1335°C.

The texture of 3C-SiC layers obtained by the PECVD process was strongly dependent on the reaction conditions, especially the deposition temperature. The preferred orientation of a certain crystal plane (*hkl*) in polycrystalline deposits is described by the texture coefficient using the Harris method [14]. The result of calculating the texture coefficients of the films deposited at different deposition temperatures showed that the 3C-SiC (111) texture grows favorably at low temperature (1270°C) and 3C-SiC (200) texture is preferred at higher temperature (above 1335°C), at which the surface-adsorbed atoms have sufficient energy to migrate to the stable sites. This tendency in the change of preferred orienta-

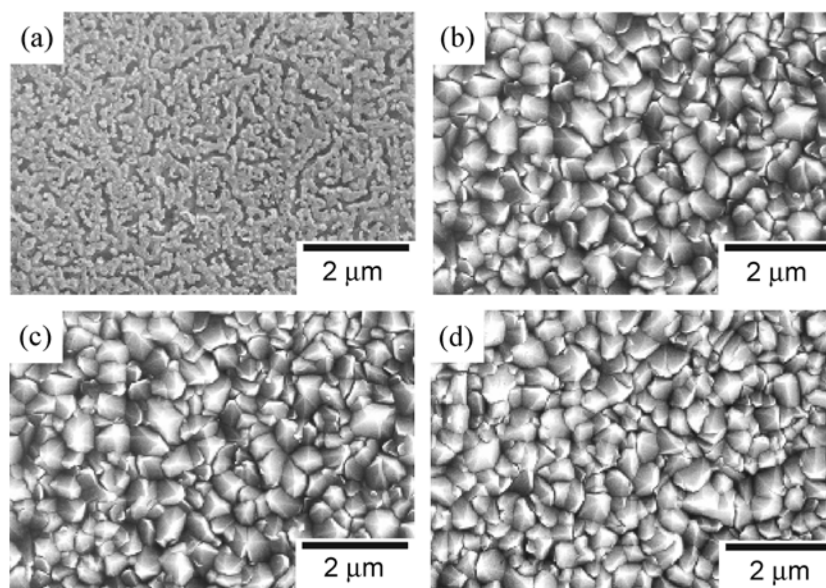

Fig. 5. Plan view SEM images of 3C-SiC layers at various r.f. powers; (a) 0 Watt, (b) 30 Watt, (c) 45 Watt, and (d) 75 Watt. The input gas ratio and deposition temperature were kept at R_x = 0.04 and 1170°C, respectively.

tion at higher temperature was consistent with other reports for the deposition of 3C-SiC films [8].

The microstructures of the deposited films were observed by SEM as shown in Fig. 5 and 6, respectively. Figure 5 represents the surface morphologies of the 3C-SiC films by TCVD and PECVD. A porous structure was shown in the films deposited by TCVD, however, the films prepared by PECVD consisted of faceted grain structures. In the TCVD method the porous structure could have arisen because the substrate temperature was not enough higher to dissociate the CH_4 gas. However, in the PECVD method, the faceted grain structure can be assumed to be due to the addition of plasma energy. This plasma energy would be expected to dissociate the source gas very efficiently and enough to supply sufficient atoms to the surface [11]. Figure 6 shows the microstructure and surface morphology of 3C-SiC films deposited at different input gas ratios (R_x) at a constant deposition temperature and r.f. power. The faceted grain crystallites in the deposits were changed with varying the R_x value. It would generally be considered that the surface morphology of deposited films is related with the surface thermal energy and mass diffusion of constituent elements. As shown in Fig. 6 at lower R_x values, the 3C-SiC films had strongly faceted grain structures.

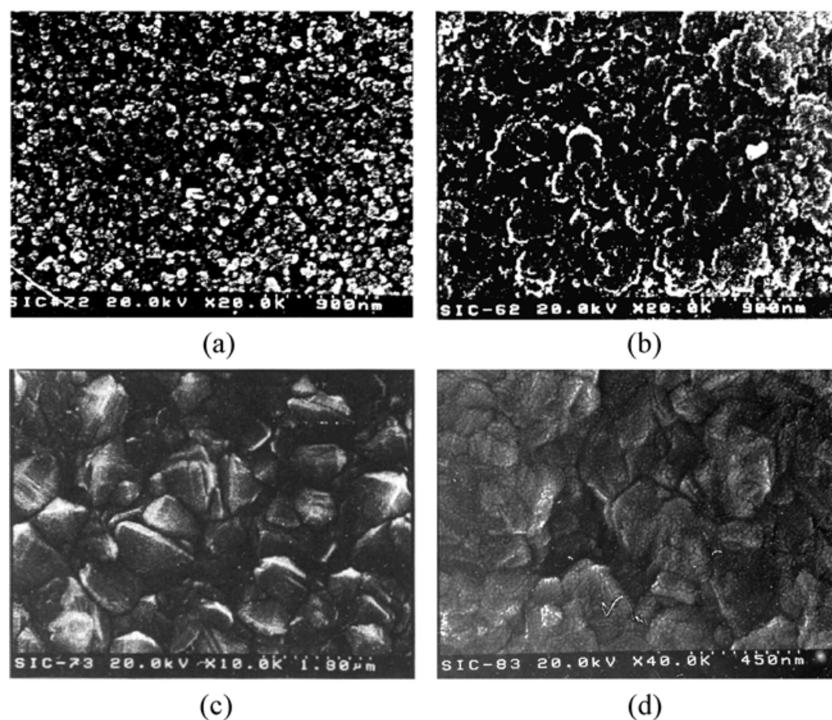

Fig. 6. Plan-view SEM micrographs of 3C-SiC films at various R_x values; (a) R_x=0.4, (b) R_x=0.2, (c) R_x=0.08, and (d) R_x=0.04. The r.f. power and deposition temperature were kept at 60 Watt and 1270°C, respectively.

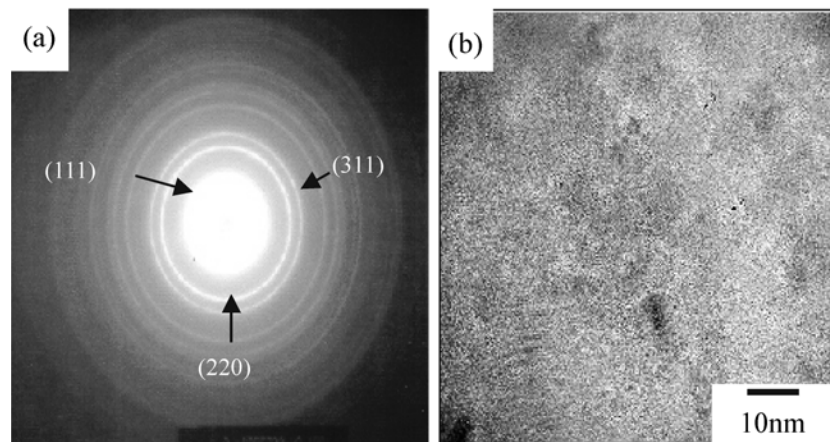

Fig. 7. TEM micrographs of 3C-SiC films at r.f. power 75 watt, R_x: 0.4, and 1170°C; (a) electron diffraction pattern (b) plane-view (S: Crystalline Structure and A: Amorphous).

This may be ascribed to the high surface mobility of constituent elements due to the higher H_2 dilution effect [8]. As a result, the degree of multiple faceted grain structures increased with a decrease in input gas ratio.

In order to reveal the microscopic qualities of the films, some samples were characterized by TEM. Figure 7 shows a selected area diffraction (SAD) pattern and bright-field (BF) micrograph of a SiC film grown at a deposition temperature of 1170°C, an r.f. power 60 watt, and an input gas ratio (R_x = 0.4). This observation confirmed the result of XRD that the deposited films obtained by PECVD, were polycrystalline and had a SiC cubic structure. Therefore, the deposition is polycrystalline with an almost uniform grain size of about a few nm. On the other hand, an amorphous phase in the deposited films is also observed. This could be due to the existence of free silicon.

Conclusions

3C-SiC films were deposited on a silicon (100) substrate by a plasma-enhanced chemical vapor deposition (PECVD) technique using a gas mixture of $SiCl_4$/CH_4/H_2/Ar and the following results were obtained. (1) The PECVD method effectively enhanced the deposition rate and the crystallinity of 3C-SiC in deposited films compared with TCVD. (2) The highest preferred orientation of deposited 3C-SiC layers was found to be the (111) plane. (3) The crystallinity of 3C-SiC on Si substrates was influenced by the R_x value and improved with decreasing R_x. (4) The free silicon was co-deposited with 3C-SiC, however, the content of free silicon was decreased by increasing the deposition temperature. (5) The deposited films were polycrystalline with an almost uniform grain size of about a few nm. (6) 3C-SiC films which had a relatively good crystallinity were obtained at a deposition temperature of 1270°C, an input gas ratio of R_x=0.04, and an r.f. power of 60Watt.

References

1. R. J. Price, Ceram. Bull. 48 (1969) 859-.
2. R. C. Marshall, J. W. Faust, and Jr. C. E. Ryan (Eds), “Silicon carbide” (University of South Carolina Press, Columbia, SC, 1973) p. 668.
3. K. Sasaki, E. Sakuma, S. Misawa, S. Yoshida, and S. Gonda, Appl. Phys. Lett. 45 (1984) 72.
4. E. A. Bergemeister, W. von Muchen, E. Pettenpaul, J. Appl. Phys. 50 (1979) 5790.
5. W. von Muench, I. Pfaffender, J. Appl. Phys. 48 (1977) 4831.
6. K. Teker, C. Jacob, J. Chung, and M. H. Hong, Thin Solid Films 371 (2000) 53-60.
7. N. Nordell, S. Nishino, J. W. Yang, C. Jacob, and P. Pirouz, J. Electrochem. Soc. 142[2] (1995) 565-571.
8. T. T. Lin and M. H. Hon, J. Mater. Sci. 30 (1995) 2675-2681.
9. S. Nishino, J. A. Powell, and H. Will, Appl. Phys. Lett. 42 (1983) 460.
10. H. Shimizu, K. Naito, S. Ishio, in: C. Y. Yang, M. M. Rahman, and G. L. Harris (Eds.), Amorphous and Crystalline Silicon Carbide IV, Springer-Verlag, Berlin, (1992) p. 119.
11. H. S. Kim, Y. J. Park, I. H. Choi, and Y. J. Baik, Thin Solids Films 341 (1999) 42-46.
12. M. J. Thwaites and H. S. Reehal, Phys. Stat. Sol. (a), 153 (1996) 459.
13. Y. G. Jung, S. W. Park, and S. C. Choi, Materials Letters, 30 (1997) 339-345.
14. C. Barret and T. B. Massalski, “Structure of Metals”, Pergamon, Oxford, (1980) p. 204.