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Epitaxial Growth of β-SiC Thin Films on Si(100) Substrate without a Carburized Buffer Layer

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Most of heteroepitaxial β-SiC thin films have been successfully grown on Si(100) adapting a carburizing process, by which a few atomic layers of substrate surface is chemically converted to very thin SiC layer using hydrocarbon gas sources Using an organo-silicon precursor, bis-trimethylsilylmethane (BTMSM, [$C_7H_{20}Si_2$]), heteroepitaxial β-SiC thin films were successfully grown directly on Si substrate without a carburized buffer layer. The defect density of the β-SiC thin films deposited without a carburized layer was as low as that of β-SiC films deposited on carburized buffer layer. In addition, void density was also reduced by the formation of self-buffer layer using BTMSM instead of carburized buffer layer. It seems to be mainly due to the characteristic bonding structure of BTMSM, in which Si-C was bonded alternately and tetrahedrally (SiC_4).

Key words : SiC, Thin film, Epitaxial, Self-buffer, Carburized buffer

I. Introduction

SiC is a promising candidate material for high temperature, high power, high frequency, and radiation resistive electronic devices because of its superior properties such as high saturation electron velocity, high breakdown field, high thermal conductivity, wide bandgap, and good chemical stability. Chemical vapor deposition (CVD) has been a successful and reliable method for epitaxial SiC thin film growth on Si and SiC substrates.[1-5] Usually SiC single crystalline films were deposited using gas sources such as SiH_4 (or Si_2H_6) and hydrocarbons. High deposition temperature (> 1300°C) was needed in gas source CVD. In addition, these gases are very toxic and flammable.

Recently, OMCVD (Organo-metallic Chemical Vapor Deposition) has been adapted for the epitaxial β-SiC film deposition. Many researchers have investigated alternative precursors, which contain directly bonded Si and C atoms and would be decomposed at a lower temperature, such as methyltrichlorosilane (MTS),[6] silacyclobutane (SCB),[7] hexamethyldisilane (HMDS),[8,9] methylsilane,[10,11] and bis-trimethylsilylmethane (BTMSM).[12-14] Epitaxial β-SiC thin films have been successfully grown on carburized Si(100) substrates using bis-trimethylsilylmethane (BTMSM) as an organo-silicon precursor at deposition temperatures as low as 1100°C.[12,13] The defect density of the β-SiC thin films deposited to 5 μm on carburized buffer layer using BTMSM was as low as that of the films deposited using gas sources.[14]

In heteroepitaxial growth of β-SiC on Si(100) substrates by CVD, the buffer layer techniques[1,2,15-17] were widely used, where the buffer layer was formed by carburizing Si substrates at relatively low temperature prior to high temperature deposition. Carburizing with hydrocarbon gases causes to form voids in Si substrate because the Si atoms were consumed by SiC island formation. Therefore, high density (10^6~10^8 cm^{-2}) of voids[18] were formed during carburizing procedure due to out-diffusion of Si from substrate. Many researchers have endeavored to reduce the void density with various methods.[17,19]

In this paper, we report results on the deposition and characterization of β-SiC epitaxial films without a carburized buffer layer using BTMSM $(CH_3)_3$-Si-CH_2-Si-$(CH_3)_3$, which is neither toxic nor flammable. In order to deposit epitaxial film without a carburized buffer layer, a self-buffer layer was formed using BTMSM prior to film deposition. It was observed that the void density of the films with self-buffer layer was less than that of the with a carburized buffer layer

II. Experimental Procedure

β-SiC thin films were deposited in a cold wall, horizontal-type CVD reactor, where the Si(100) substrates were heated by an rf induction heating method using a graphite susceptor. The typical substrate temperature was 1260°C, which was measured by an optical pyrometer and calibrated using the melting temperature of Si (1418°C). The source material (BTMSM), which is liquid at R.T., was contained in a pyrex bubbler and carried by H_2 gas. The input flow rate of diluent gas, H_2, was kept at 3,000 sccm and the flow rate of carrier gas, which is also H_2, was varied from 5 to 60 sccm for the formation of self-buffer layer and epitaxial film growth. The

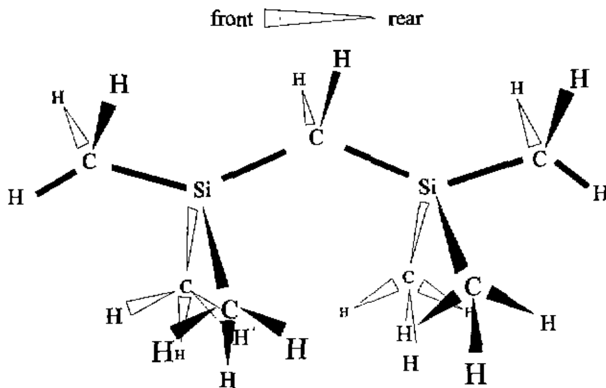

Fig. 1. Schematic diagram of source material, bis-trimethylsilylmethane.

chamber pressure was 360 torr for epitaxial film growth. A carburized buffer layer and a self-buffer layer were formed at 150 and at 360 torr, respectively, by heating Si substrate from R.T to 1260°C in the diluent H_2 flow for various periods. The observed thickness of buffer layers was varied from ~25 nm to ~60 nm. The bubbler temperature was held at R.T. The actual transport rate of the source material was not determined because its vapor sure has not been reported. The source material, BTMSM, has alternate Si-C bonds and SiC_4 tetrahedral structure, as shown in Fig. 1. This structure is the same as that of crystal SiC, which may help the epitaxial deposition of SiC thin films even at low temperatures. The substrate was cleaned using acetone and then dipped in 10% HF, and rinsed in distilled water before loading.

The crystalline quality and orientation of the deposited films were analyzed by X-ray diffraction (XRD). The film thickness and morphology were obtained by scanning electron microscopy (SEM), and transmission electron microscopy (TEM) was used to examine defects in the films such as twins, stacking faults, etc.. Optical microscopy was also used to observe voids. Spectroscopic ellipsometry was used for thickness measurement of buffer layers.

III. Results and Discussion

Figure 2 is the micrographs of film surface deposited without a carburized buffer layer at high temperature (Fig. 2(a)) and from R.T. to high temperature (Fig. 2(b)). The surface morphologies of films are much different, since nucleation probability and reaction kinetics at high temperature are much different from those at R.T. At the early stage of the low temperature deposition, excess C in BTMSM first reacts with Si substrate to form β-SiC nuclei which have the same crystalline orientation as the Si substrate. However, at high temperature deposition, the reaction between Si substrate and excess C in BTMSM occurs so rapidly that the randomly oriented islands form. Consequently, the β-SiC thin films, con-

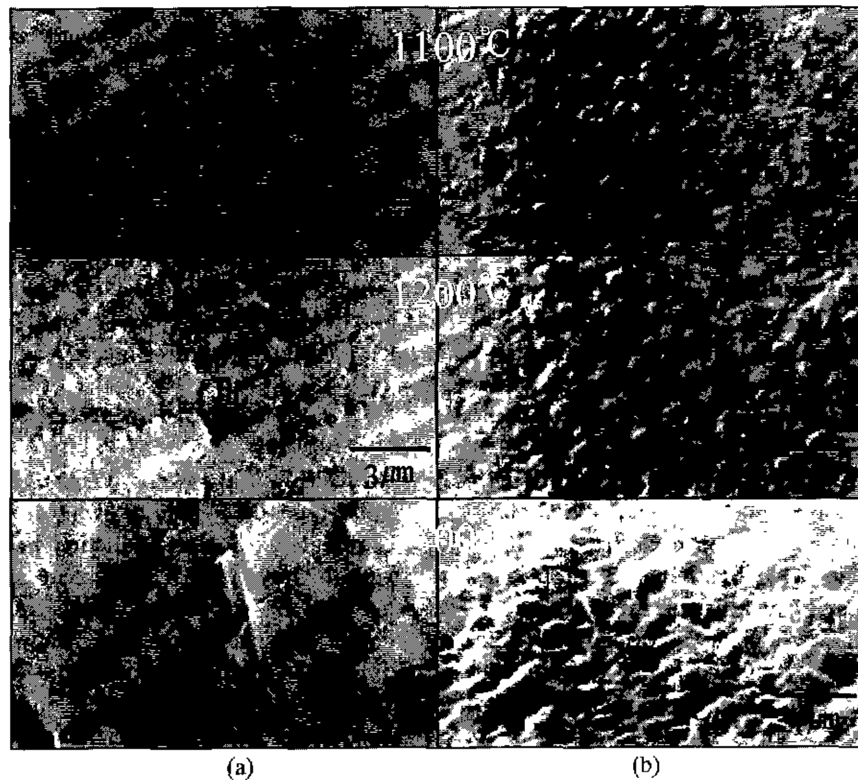

Fig. 2. Surface morphologies of the films deposited carburized buffer layer. The films are deposited at high temperature (a) and from room temperature (b).

sisting of the randomly oriented SiC grains, have higher intensity (111) peak.[14] A similar result was also reported in the deposition of β-SiC thin films using HMDS.[9]

Self-buffer layers were formed using BTMSM during the heating from R.T. to high temperature (1260°C) without carburizing procedure using hydrocarbon as Fig. 2(b). The 'self-buffer layer' was used to distinguish from the 'carburized buffer layer', which is formed by carburization procedure. The self-buffer layer makes the CVD deposited films on it have more (100) oriented alignment and smoother morphologies than the films deposited on bare Si substrates.

As the flow rate increased, the void density decrease, as shown in Fig. 3(a), which is a general result of SiC buffer layer formation.[17,19] In general, the void densities were slightly increased or saturated with increasing the carburizing time, however, the void densities were decreased as the time increased to 2 min during self-buffer formation, as shown in Figs. 3(b) and 4. It can be explained as follows; the formation of SiC islands begins about 800~900°C, therefore, for short formation time the supply of source material from gas phase was ter-

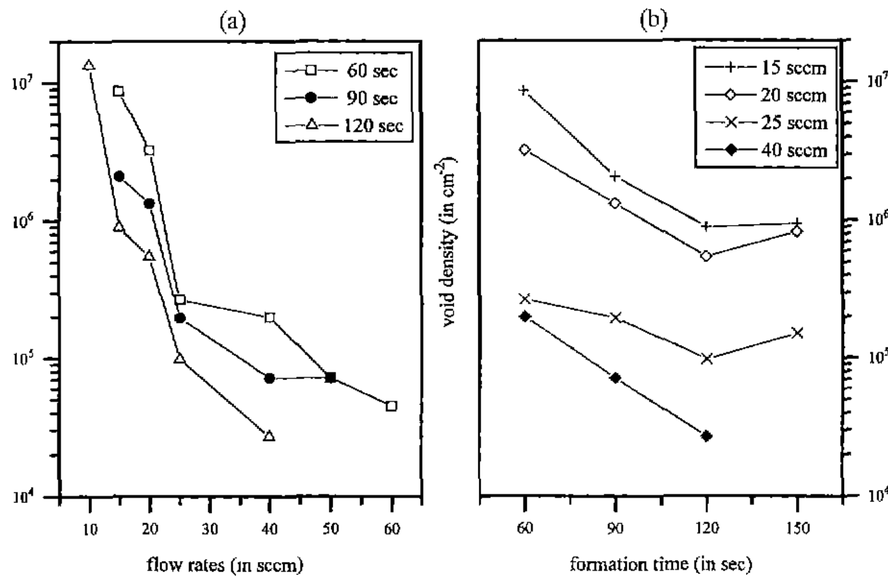

Fig. 3. Plots of void densities versus flow rate (a) and buffer formation time (b) The void density at 2 min is less than carburized buffer (10^6~10^8 cm^{-2}).

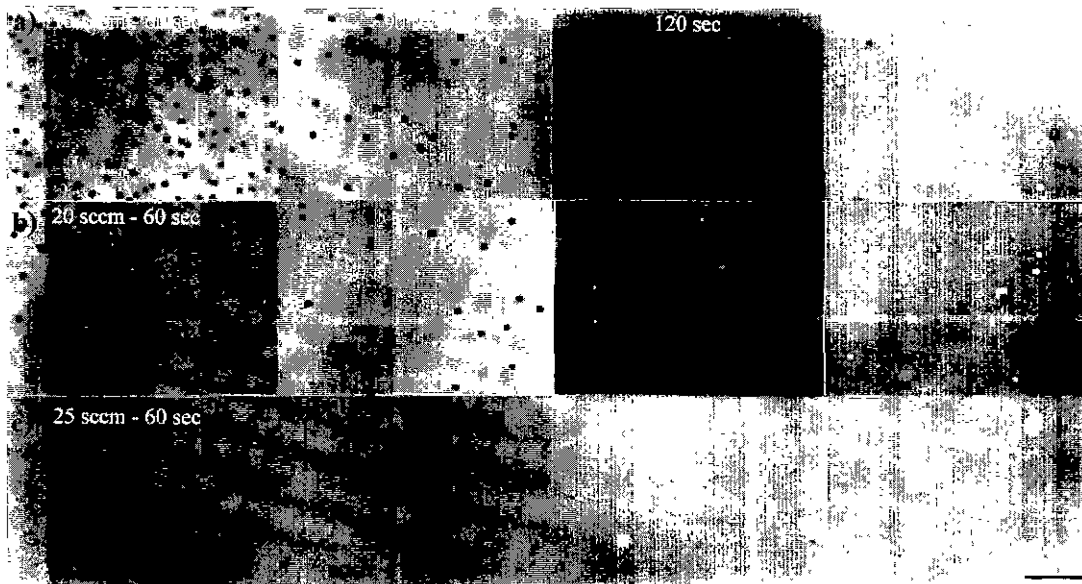

Fig. 4. Optical micrographs of voids with variation of formation time. The self-buffer layers were formed using BTMSM (a) 15 sccm, (b) 20 sccm, and (c) 25 sccm during heating up to 1260°C. From the left row, the buffer formation times were 60 sec (1st row). 90 sec (2nd row), 120 sec (3rd row) and 150 sec (4th row). It shows the decrease of void density with formation time, obviously.

minated shortly after beginning of SiC island formation, while for longer formation time the supply of the source from gas phase still be lasted during SiC island formation. During SiC island formation, Si atoms were consumed by surface migration and out-diffusion and then voids were produced in Si substrate. The termination of supplying of source material shortly after beginning of SiC island formation causes imperfect coverage of Si surface with SiC islands at that moment. And then buffer layer formation occurred by surface migration of C atoms adsorbed on SiC island surface rather than from gas phase. As a result, the required time for SiC buffer layer to fully cover Si surface is increased and then Si out-diffusion and void formation are increased. Therefore, continuous source supply during SiC island formation reduces the void formation because the supplied source materials from gas phase could effectively cover and then seal the unreacted (or uncovered) Si surface. In addition, BTMSM may promote the effect of reducing the void density, since it contains Si atoms. After 2 min, SiC buffer layers formed all over the Si surface and then Si atoms were diffused out and consumed through the misfit dislocations and/or grain boundaries in the buffer layer. And consequently the rate of void formation would be drastically decreased Therefore, the self buffer layer formed for 2 min shows lower void density than a carburized buffer layer (10^6~10^8 cm^{-2})[18].

Figure 5 shows the SADP patterns of self-buffer layer with various times and flow rates. The result indicates that the buffer layers had high epitaxial alignment at lower flow rates and had random orientation at higher flow rates. It means that very high flow rates are not advantageous to having epitaxial relationship with substrate, while carburized buffer layers were more epitaxially grown at higher flow rates[17,19]. At low flow rate (Fig. 5(a)), partially random oriented grains appear, which may due to incomplete coverage of the surface. As the flow rate increased, the grains in the buffer layer became more aligned with substrate (Fig. 5(b) and (c)). But further increase of flow rates caused randomization of grains (Fig. 5(d) and (e)). The extreme case of 60 sccm (Fig. 5(f)) showed that the buffer layer consisted of nanocrystalline SiC grains. The results indicates that there are optimum flow rates and formation times.

As a result, the epitaxial films deposited on self-buffer layer have less void density than those on carburized buffer layer do. Figure 6 compares two epitaxial films with carburized buffer layer and with self-buffer layer. It clearly shows that the film with self-buffer layer had lower void density than with carburized buffer layer. Therefore, self-buffer layer makes it possible to reduce a void density as well as to make a excellent epitaxial relationship with Si substrate, as shown in Figs. 4 and 5.

β-SiC has polar surfaces such as (100) and (111), while Si does not because the former has a zinc-blende structure and the latter has a diamond structure. Therefore, the formation of buffer layer needs a first atomic layer to be covered with C layer.[20] As shown in Fig. 7, for other sources such as $Si(CH_3)_4$ and $SiCH_3Cl_3$ the first atomic layer consists of not only C atoms but a mixture of Si and C. But BTMSM provides only C atoms to form the first C atomic layer on the whole surface of Si substrate. It is largely due to the Si-C bonding structure of BTMSM. Si and C atoms are bonded alternately and BTMSM has SiC_4 tetrahedron which is the same unit structure as SiC crystal. In addition, there is no Si-Si

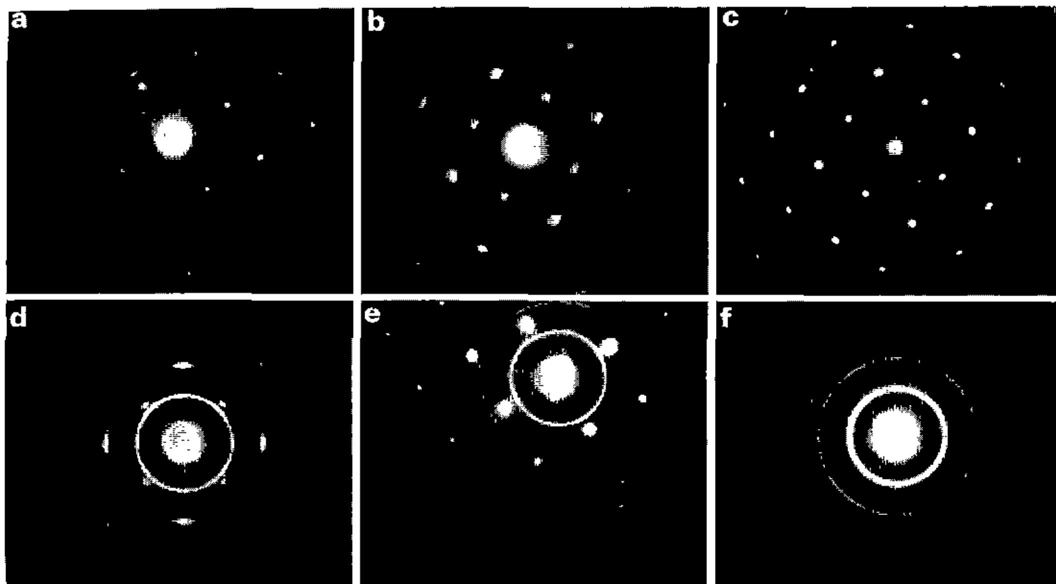

Fig. 5. Selected area diffraction patterns of 'self-buffer' layer. The films were deposited using BTMSM which carried by H_2 (a) 5 sccm for 180 sec, (b) 15 sccm 90 sec, (c) 15 sccm for 180 sec, (d) 30 sccm for 90 sec, (e) 40 sccm for 120 sec and (e) 50 sccm for 60 sec. The single crystalline spots (e) belong to Si substrate.

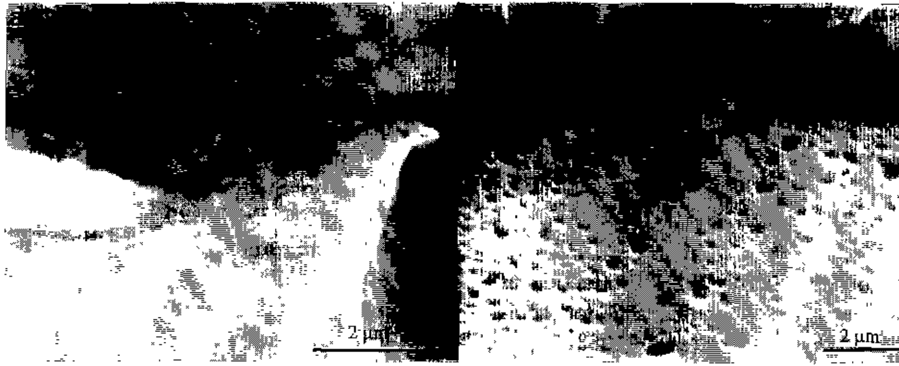

Fig. 6. Void images at Si substrates after epitaxial film deposition. The films were deposited on (a) self buffer layer and (b) carburized buffer layer.

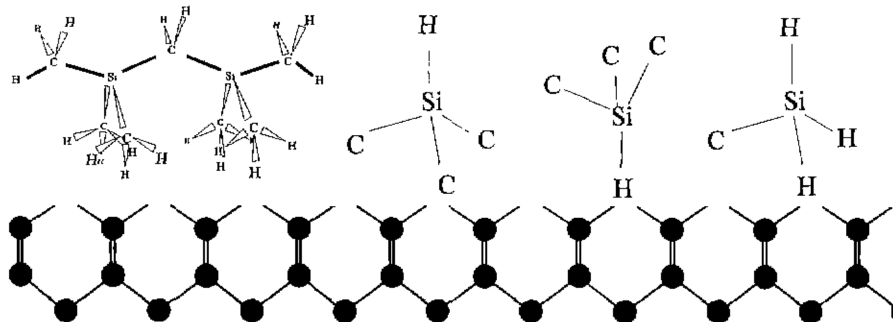

Fig. 7. Proposed model of self buffer formation mechanism with comparison of other sources.

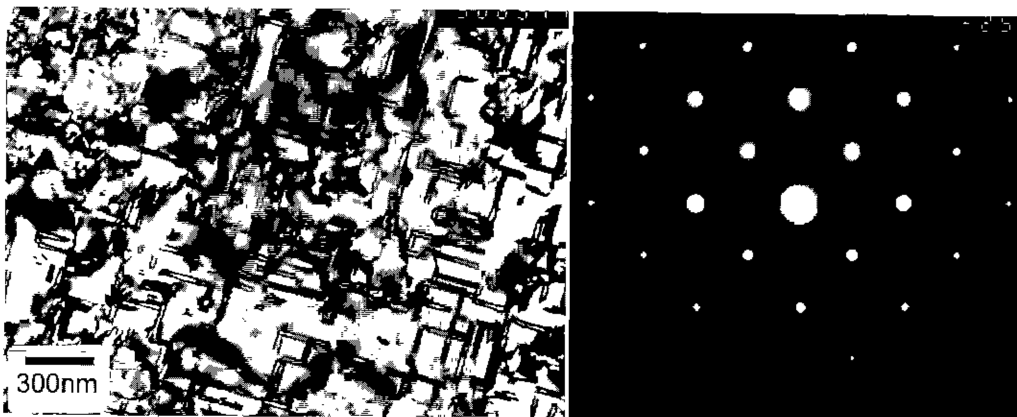

Fig. 8. TEM micrograph of epitaxially grown thin film using self buffer technique. The thickness of the epitaxial film was about 500 nm.

bond in BTMSM in contrast with HMDS,[8] which means that free Si radical or species containing Si-Si chain are rarely formed. Since these radical or species may deteriorate the alignment of the films, the sources which contain these species can not be expected to get self-buffer effect.

Figure 8 shows TEM micrograph of thin (500 nm) film grown epitaxially on self-buffer layer. It shows similar defect density to that of films deposited on carburized buffer layer. It means that the formation of self-buffer layer is a successful procedure for epitaxial SiC thin film growth as well as an effective method to reduce the void density at Si/SiC interface.

IV. Conclusion

β-SiC epitaxial films were grown on Si (100) substrate using an organo-silicon source, bis-trimethylsilylmethane (BTMSM), without a carburized buffer layer. BTMSM produced the self-buffer SiC layer on Si substrate during heating from room temperature to 1260°C. The formation of self-buffer layer was effective to reduce the voids which deteriorate the electronic properties of the epitaxial film. BTMSM seems to be a good candidate source material for epitaxial growth of high quality β-SiC thin films without a carburized buffer layer because of its alternate and tetrahedral Si-C bonding structure.

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