

CHEMICALLY-FORMED BUFFER LAYERS FOR GROWTH OF CUBIC SILICON CARBIDE ON SILICON SINGLE CRYSTALS*

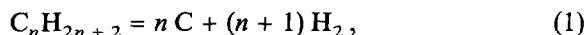
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Buffer layers of cubic silicon carbide were formed by reaction of (100) Si substrates with propane in hydrogen at 1380-1400°C. Reaction times ranged from 5 to 600 s. Reproducibility was improved by wet etching of substrates. Even for buffer-layer thicknesses of less than 10 nm, their reflectance spectra were identical to that of SiC. Crystal layers of cubic SiC were deposited on buffers by reaction of silane and propane in hydrogen at 1400°C for 15 min. Reflectance spectra of these crystal layers suggest that short buffer-layer-formation times favor crystal layer perfection.

1. Introduction

Single-crystal layers of cubic silicon carbide (β -SiC) can be prepared on silicon substrates by chemical vapor deposition (CVD) if a thin intermediate layer ("buffer layer") is formed beforehand on the substrate [1-5]. Buffer layers have been prepared by sputtering of SiC [1,2] and by reaction of the substrate with a gaseous hydrocarbon [3-6]. The latter method may be represented schematically:



If the substrate temperature is 1350°C or higher, reactively-formed buffer layers are single crystals [5,6]. Silane may be added to the hydrocarbon for CVD of SiC, directly on the as-grown buffer layer:



High buffer-layer-formation (BLF) temperatures tend to improve crystal quality. However, the risk of producing regions of hexagonal, 2H SiC in the buffer layer increases as the melting point of silicon (1414 \pm 3°C) [7] is approached. X-ray analyses of some of our samples, prepared at 1410°C, have indeed shown regions containing 2H SiC [8].

Protracted BLF times can lead to deposition of graphite on the surface [6]. Apparently, increasing

impairment of Si diffusion with increasing thickness of the buffer layer limits the supply of Si for reaction (2). Any free carbon on the buffer layer interferes with epitaxy of the CVD SiC. Our first goal was to obviate free-carbon deposition by using the shortest effective BLF times.

Short BLF times at temperatures near 1400°C should favor good quality of CVD SiC. For BLF, Nishino and co-workers [4] heated Si substrates to 1400°C in dilute propane-hydrogen mixtures, maintained the maximum temperature for about a minute, and quenched. Thus, their buffer layer formation took place throughout the thermodynamically-feasible range of temperatures between about 1000 and 1400°C. Our second goal was to narrow the temperature range of BLF to between 1380° and 1400°C.

2. Experimental

Both BLF and CVD took place in a horizontal, water-cooled, RF-induction-heated, quartz-tube reactor with internal diameter of 40 mm. An open 35 mm ID quartz liner contained the susceptor. The susceptor was machined from high-density, isotropic, high-purity graphite. Prior to its first use, it was coated with SiC. Substrates rested within a 0.25 mm deep cavity.

Substrates were (100)-oriented p-type Si, with resistivity of about 150 ohm cm, measuring

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12 mm × 25 mm × 0.38 mm. Prior to placement in the reactor, they were treated with dilute hydrofluoric acid (1 : 10) or with hydrofluoric-nitric-acetic (3 : 5 : 3) acids, and rinsed with deionized water. We found that wet treatment eliminated the susceptor erosion that was observed after etching with gaseous HCl-H₂ mixtures at 1200°C. Erosion of the upstream end of the susceptor gradually produced a taper, and altered the thermal distribution in the substrate. With wet-etched substrates, uniformity of deposition conditions was greatly improved.

Table 1 shows the gas-flow conditions used for the three basic operations of the process. Substrates were heated in pure hydrogen to 1400°C. After allowing time for temperature stabilization, propane was admitted for the buffer-layer-formation (BLF) step, which was carried out for times ranging from 5 to 600 s. Propane flow was terminated at the end of BLF, power was turned off, and the layer was quenched to room temperature in pure hydrogen. Buffer layers and their supporting Si substrates were either removed for examination at this point, or were re-heated to 1400°C in pure H₂. In the latter case when thermal equilibrium was again established, silane and propane were admitted in amounts shown in table 1 for chemical vapor deposition (CVD). For the present study, a uniform CVD time of 15 min was used, after which SiH₄ and C₃H₈ were turned off, and the system cooled in pure H₂.

Buffer layers and CVD SiC crystals were examined by infrared reflectance spectroscopy. We used a Perkin-Elmer Model 180 spectrophotometer, fitted with a standard reflectance attachment. Spectra covered the region from 2.5 to 17 μm (4000–600 cm⁻¹). Interference patterns in the wavelength region shorter than about 8.5 μm (1200 cm⁻¹) were useful for calculation of CVD layer thickness.

Table 1
Gas-flow conditions (flows in ml/min)

Gas	Heating to 1400°C and cooling	Buffer-layer formation (BLF)	Chemical vapor deposition (CVD)
H ₂ purified by diffusion through Pd-Ag alloy	660	660	1400
SiH ₄ (1% in H ₂)	0	0	42
C ₃ H ₈ (1% in H ₂)	0	20	20

3. Results and discussion

Fig. 1 shows the reflection spectrum of a buffer layer which was grown for 30 s and that of a 15 min β-SiC CVD crystal layer deposited on another 30 s buffer layer. Except for details of the 10–13 μm (1000–770 cm⁻¹) region, reflectance spectra of buffer layers grown for periods up to 600 s are virtually identical. The same is true of spectra of CVD layers. Oscillations in reflectance amplitude permit calculation of a thickness of 1.08 ± 0.06 μm for 15 min CVD crystals on buffers deposited for 5, 10, 15, 30, 60, 120, 180, 300 and 600 s. The thickness of the buffer layer of fig. 1 may be only 6.3 nm, based on an initial growth rate of 0.21 nm/sec [6]. Buffer

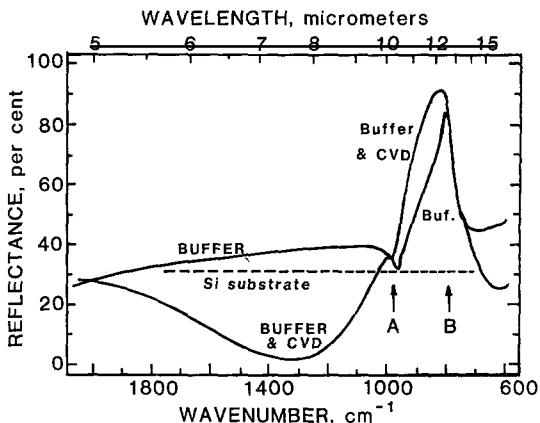


Fig. 1. Infrared reflectance spectrum of a SiC buffer layer formed in 30 s by reaction of propane in hydrogen on (100) Si at 1400°C, and that of a layer of β-SiC grown upon it when CVD was carried out for 15 min using SiH₄ + C₃H₈ + H₂. Interference in the 1000–2000 cm⁻¹ region of that spectrum causes symmetrical oscillations about a 15% reflectance line. A indicates the position of the longitudinal optical phonon and B indicates that of the transverse optical phonon.

layers exhibit reflectance spectra similar to that of the Si substrate, except in the 10–13 μm region.

The buffer-layer reflectance spectrum of fig. 1 passes through a minimum at 965 cm^{-1} and a maximum at 801 cm^{-1} . These frequencies are very close, respectively, to those of the longitudinal (972 cm^{-1}) and transverse (792 cm^{-1}) optical phonons in silicon carbide [9]. As expected, the wave number of maximum reflectivity occurs between those of transverse and longitudinal phonons.

Maximum reflectance for all buffer layers was found between 800 and 802 cm^{-1} , independent of growth time. Maximum reflectance for 15 min CVD layers occurred between 818 and 824 cm^{-1} , with the dependence on BLF time suggested in table 2. Longer CVD times than 15 min produce SiC layers whose spectra have broad reflectance maxima. These occur at higher frequencies (up to 845 – 850 cm^{-1}) and are characteristic of smooth, well-developed CVD SiC crystal layers.

We have observed that any reflectance spectrum of a CVD layer which has sharp spectral features near the frequencies of optical phonons is associated with less-perfect crystalline layers. Fig. 2 shows two extreme cases.

Both SiC crystals of fig. 2 were found by X-ray diffraction to be single crystals. However, that deposited on a buffer (upper curve) had a smooth, shiny appearance. Its frequency of maximum reflectance was 840 cm^{-1} . The crystal deposited on a bare Si substrate had a perceptibly rougher surface. Its maximum reflectance was at 810 cm^{-1} . Table 2 indicates that a BLF time of 30 s favors growth of 15

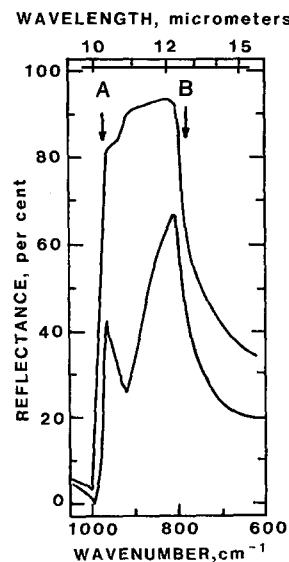


Fig. 2. Reflection spectra of CVD SiC. Upper curve: 120 min deposition on buffer layer formed for 2 min. Shape is typical of good-quality CVD crystals. Lower curve: 60 min CVD without buffer layer. Both depositions on (100) Si at 1380 – 1400°C . Longitudinal (A) transverse (B) optical phonons are indicated.

min CVD β -SiC layers with the highest frequency of maximum reflectance.

Fig. 3 shows the reflectance spectra of four 15 min CVD crystals. Their reflectances are nearly identical from 794 – 801 cm^{-1} and at 975 cm^{-1} . However, in

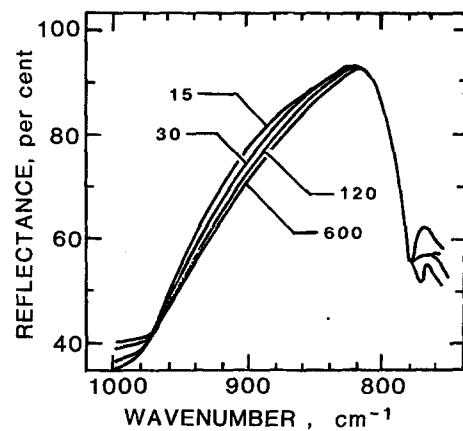


Fig. 3. Reflectance spectra of 15 min CVD crystals, grown at 1400°C on buffer layers formed for different times on (100) Si, also at 1400°C . The growth time in seconds is indicated for each spectrum. Expanded scales were used in recording to reveal differences in the 840 – 940 cm^{-1} region.

Table 2
Peaks in reflectance spectra

Buffer-layer formation (BLF) time (s)	Frequency of maximum reflection (cm^{-1})	
	For buffer layer only	For buffer layer plus 15 min CVD
30	801	824
60	802	820
120	802	818
600	800	818

the region between the maxima and about 940 cm^{-1} , reflectance is clearly a function of BLF time. As mentioned earlier, formation of graphite on the buffer-layer surface [6] may be responsible for disruption of smooth growth. Some evidence for a mechanism of this type is the fact that reflectance spectra of CVD β -SiC crystal layers grown atop 120 s and 600 s buffers differ far less than do those of CVD crystal layers grown on 30 s and 60 s buffers. Once a layer of graphite has formed on the buffer-layer surface additional deposition of graphite is likely to have little effect.

4. Summary and conclusions

The modified CVD process to obtain β -SiC layers on Si substrates has the advantages of ease of control and duplicability. Erosion of the graphite susceptor is entirely avoided by wet etching of the Si substrates. Formation of the buffer layer at 1400°C – after thermal equilibrium is reached – ensures better duplicability of both buffer layers and CVD SiC. Infrared reflectance measurements show that there is no advantage in preparing buffer layers for periods longer than about 30 s.

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