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Highly (111)-oriented SiC Films on Glassy Carbon Prepared by Laser Chemical Vapor Deposition

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ABSTRACT

SiC films were prepared on glassy carbon substrates by laser chemical vapor deposition under a high pressure of 10^4 Pa using a diode laser (wavelength = 808 nm) and a polysilaethylene precursor. (111)-oriented SiC films were formed at a deposition temperature (T_{dep}) range of 1150 - 1422 K. At T_{dep} = 1262 K, the SiC film with a high Lotgering factor of above 0.96 showed an exhibited pyramid-like surface morphology and flower-like grains. The highest deposition rate (R_{dep}) was 220 μm h^{-1} at T_{dep} = 1262 K.

Key words : SiC film, Laser chemical vapor deposition, (111) orientation, Glassy substrate, High-speed growth

1. Introduction

Silicon carbide (SiC) has been widely used as semiconductor in electronic devices, protective coatings, and high-temperature structural materials due to its high melting point, wide band gap, high thermal conductivity, high electron saturated drift velocity, large radiation resistance, and excellent chemical inertness.[1-4] Among more than 200 polytypes of SiC, β-SiC has the highest electron mobility (~ 800 cm^2/V s) and saturated drift velocity (~ 2.5 × 10^7 cm/s), twice as that of Si.[5] Moreover, (111)-oriented cubic β-SiC films have a great potential as a buffer layer for the growth of AlN, GaN, InN, and SiC/Ge[6–9] epitaxial layers because of a smaller mismatch of the lattice and thermal expansion compared with sapphire and Si substrates. As the (111) plane of β-SiC is a polar surface, the chemical and electrical properties depend on the polarity.[10] Therefore, highly (111)-oriented β-SiC films could be prepared for various applications.

SiC films have been prepared by sputtering,[11] plasma-enhanced chemical vapor deposition (PECVD),[12] and hot wire chemical vapor deposition (HWCVD).[13,14] Laser chemical vapor deposition (LCVD) is a promising technique for depositing coatings at a high deposition rate with a wide variety of microstructures.[15-17] Zhang *et al*. reported synthesis of epitaxial β-SiC films on Si substrates at high deposition rates (40 - 3600 μm h^{-1}) and low deposition pressures (200 - 800 Pa).[18-20] Two types of regimes for the growth of (111)-oriented β-SiC films with different morphologies, namely, pyramid-like and needle-like, were observed.[20] To date, however, there are few publications on the preparation of β-SiC films under relatively high pressure (above 10^3 Pa) at high temperatures by LCVD.[21]

In this study, SiC films were prepared on glassy carbon substrates by LCVD at deposition temperatures (T_{dep}) of 1150 - 1470 K and a total pressure (P_{tot}) of 10^4 Pa using a diode laser (wavelength = 808 nm) and a polysilaethylene (PSE) precursor. The effect of T_{dep} at a high deposition pressure of 10^4 Pa on the orientation, microstructure, and deposition rate was investigated.

2. Experimental Procedure

A cold wall-type LCVD apparatus was developed to prepare β-SiC films. A schematic of the LCVD apparatus can be found in the literature.[19] The PSE precursor ([SiH_2–CH_2]; Starfire® CVD-4000, Starfire Systems, Schenectady, USA)[14] was evaporated at 433 K and the vapor was brought into the deposition chamber with Ar as the carrier gas. Here, the evaporation rate of the precursor was 5 × 10^{-4} g s^{-1} and the flow rate of Ar was 8.3 × 10^{-6} $m^3 s^{-1}$. The temperatures of the gas lines and the nozzle were maintained at 403 K by a thermocouple. The Ar flow rate was fixed at 500 sccm. The total pressure in the chamber was maintained at 10^4 Pa. Glassy carbon plates (8 mm × 8 mm × 0.5 mm, Tokai Fine Carbon Ltd., Japan) were used as substrates. The substrate was placed on a hot stage heated at 773 K for 1.8 ks in the chamber. The entire substrate surface was irradiated by a diode laser beam (InGaAlAs, wavelength = 808 nm) through a quartz glass window with a laser beam of approximately 20 mm in diameter. The laser was operated in the continuous mode with a power (P_L) of 90 - 190 W. T_{dep} was measured by a thermocouple and a pyrometer (CHINO IR-AH) and was maintained within ±5 K over the entire substrate at 1100- 1500 K. The deposition time was 0.6 ks.

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Table 1. Deposition Condition of SiC Films

Precursor	Polysilaethylene (PSE)
Substrate:	Glassy carbon
Precursors pre-heating temperature (T_{Pre}):	433 K
Deposition temperature (T_{dep}):	1150 - 1500 K
Substrate pre-heating temperature (T_{sub}):	773 K
Total pressure (P_{tot}):	10^4 Pa
Laser power (P_L):	90 - 190 W
Ar carrier gas flow rate:	500 sccm
Distance between the nozzle and the substrate:	25 mm
Deposition time (t):	0.6 ks

Table 1 summarizes the deposition parameters for the preparation of the β-SiC films.

The crystal phases were identified by X-ray diffraction (XRD; θ-2θ; Ultima IV, Rigaku, Tokyo, Japan) using CuKα radiation at 2θ = 5° – 70° and a scan rate of 10° min^{-1}. The Lotgering factor (F)[22] was employed to quantify the degree of orientation. F is defined as a fraction of XRD peak intensity of a specific crystallographic plane, as per eq. (1):

$$F(hkl)=\frac{P(hkl)-P_0(hkl)}{1-P_0(hkl)} \quad (1)$$

where P (hkl) is the ratio of the XRD intensity of the (hkl) reflection to the sum of the reflections in the scanned range, and P_0 (hkl) is an equivalent value for a randomly oriented SiC (JCPDS, file No. 29−1129). The F value varies from 0 for non-orientation to 1 for the complete orientation. Microstructures and chemical compositions of the films were analyzed by using a scanning electron microscope equipped with an energy dispersive x-ray spectrometer (SEM-EDX) (S-3100H; Hitachi, Tokyo, Japan). The deposition rate was calculated using the film thickness and deposition time (0.6 ks).

3. Results and Discussion

Figure 1 shows the XRD patterns of the β-SiC films prepared at a T_{dep} of 1185−1470 K. At T_{dep} = 1185 K (Fig. 1(a)), the XRD pattern showed reflection peaks at 35.6° and 60.0°, which are indexed to 111 and 220, respectively, of 3C-SiC (JCPDS, No. 29-1129). The significantly high intensity of the 111 reflection indicates that the 3C-SiC film was strongly oriented to (111). By increasing T_{dep} to 1262 K (Fig. 1(b)), the 220 reflection was almost negligible, whereas the intensity of 111 reflection was significantly high. At a T_{dep} of 1383 K (Fig. 1(c)), the relative intensity of 111 decreased and the reflections of 200 and 220 were higher compared with those in case of the XRD patterns of the SiC films prepared at 1185 - 1262 K (Figs. 1(a) and (b)). The sharp reflection peak at around 25° indicates graphitization of the glassy carbon substrate at 1383 K. With further increase in T_{dep} to 1470 K

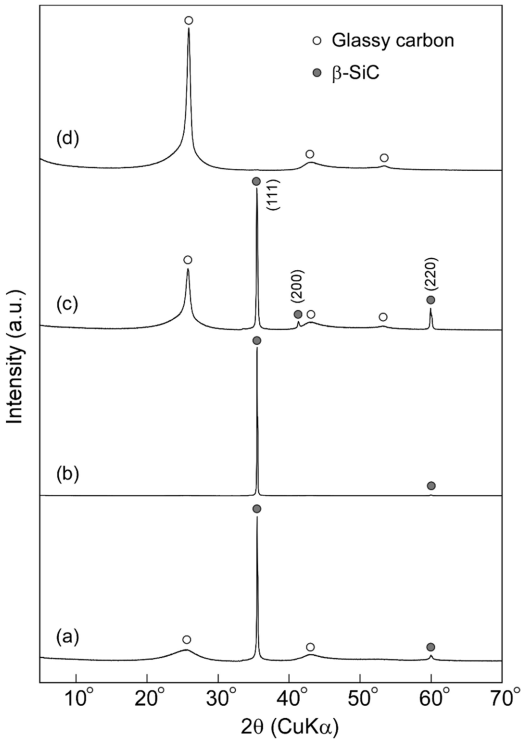

Fig. 1. XRD patterns of the β-SiC films prepared at a P_{tot} of 10^4 Pa; (a) P_L = 90 W, T_{dep} = 1185 K; (b) P_L = 110 W, T_{dep} = 1262 K; (c) P_L = 140 W, T_{dep} = 1383 K; and (d) P_L = 191 W, T_{dep} = 1470 K.

(Fig. 1(d)), no reflections from the deposited film were identified, although the peaks of carbon substrate were observed.

Figure 2 depicts the effect of T_{dep} on the Lotgering factor of the (111) orientation of SiC films. The Lotgering factor of (111) was 0.65 for the SiC film prepared at T_{dep} = 1185 K. The Lotgering factor of (111) for β-SiC increased when T_{dep} increasing and reached the maximum value of 0.96 at 1262 K. At T_{dep} above 1262 K, the Lotgering factor of β-SiC (111) became as low as 0.3.

Figure 3 displays the surface and cross-sectional SEM images of β-SiC films prepared at a T_{dep} of 1185−1470 K. At T_{dep} = 1185 K, the surface of the (111)-oriented SiC film showed dome-shape morphology with approximately 10 μm size, as shown in Fig. 3(a). Each dome-shaped grain consisted of small cauliflower-like grains with sizes below 1 μm. The (111)-oriented SiC film had a cross-section with a dense configuration, as shown in Fig. 3(b). The composition measured by EDX was almost stoichiometric SiC (Si : C = 50.2 : 49.8 (at.%)). At T_{dep} = 1202 K, the (111)-oriented SiC film comprised faceted grains of several microns in size (Fig. 3(c)), also with a dense cross-section (Fig. 3(d)). The highly (111)-oriented SiC film at T_{dep} = 1262 K exhibited pyramid-like surface morphology with flower-like grains (Fig. 3(e)) and had a columnar cross-section (Fig. 3(f)). At T_{dep} = 1375 K, the (111)-oriented SiC film showed a

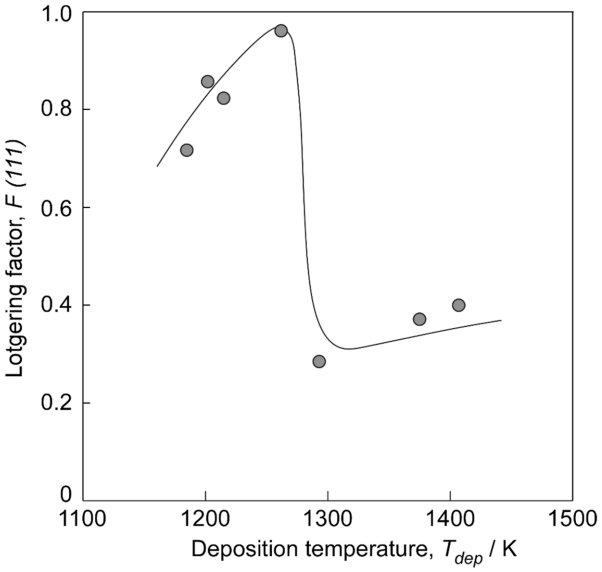

Fig. 2. Effect of T_{dep} on the Lotgering factor of SiC (111) films prepared at a P_{tot} of 10^4 Pa.

pyramid-like surface (Fig. 3(g)) and a columnar cross-section (Fig. 3(h)). At T_{dep} = 1470 K, the film had a cone-like morphology (Fig. 3(i)) with a dense and laminar cross-section (Fig. 3(j)), in which the composition was carbon with small amounts of silicon and oxygen. Precursor vapors of PSE was pyrolytically decomposed at such high temperature, forming a pyrolysis carbon film.

The effect of T_{dep} on the deposition rate of SiC films is shown (in the Arrhenius format) in Fig. 4, in which deposition rates of β-SiC films prepared by various methods are also included. The deposition rate increased with increasing T_{dep} and reached 220 μm h^{-1} at T_{dep} = 1262 K. With further T_{dep} increase, the deposition rate slightly decreased to approximately 100 μm h^{-1} at a T_{dep} above 1300 K. In the CVD process, the film growth is generally controlled by chemical reactions at low temperatures and the deposition rate increases with the deposition temperature. On the other hand, the mass transfer becomes a rate-limiting process at high temperatures, with the deposition rate depending on the supply rate and the concentration of the precursor instead of the deposition temperature. At higher temperature, the homogeneous nucleation in a gas phase would occur, resulting in a depletion of the deposition rates. Zhang *et al.* reported that the deposition rate of β-SiC epitaxial films was 40 μm h^{-1} at T_{dep} = 1203 K.[18] Boo *et al.* reported the synthesis of (111)-oriented β-SiC films by PECVD at a deposition temperature of 1123 K and a deposition rate less than 2 μm h^{-1}.[23] Epitaxial β-SiC films were reported to be deposited by magnetron sputtering[24] and by the solid-source molecular beam epitaxy,[25] where the deposition rates were 1.7 and 0.1 μm h^{-1}, respectively. The PECVD technique increased the deposition temperature of monolithic β-SiC films at 1400 - 1600 K, but the deposition rate was less than 8 μm h^{-1}. In contrast, the deposition rate was less than 1 μm h^{-1} when conventional CVD was used at the same deposition temperature.[12] (100)-oriented epitaxial β-SiC films were fabricated at 1600 K with a deposition rate of 1 - 3 μm h^{-1} using RTCVD.[26] Li *et al.* recently reported the deposition rate of SiC films prepared by LCVD at 7000 Pa and 1156 K were 180 - 240 μm h^{-1}.[21] In the present study, the deposition rate of β-SiC films was 60 - 220 μm h^{-1} by using LCVD at a high pressure (10^4 Pa), which is 10 - 10^2 times greater than those reported in the literature by using other CVD techniques.

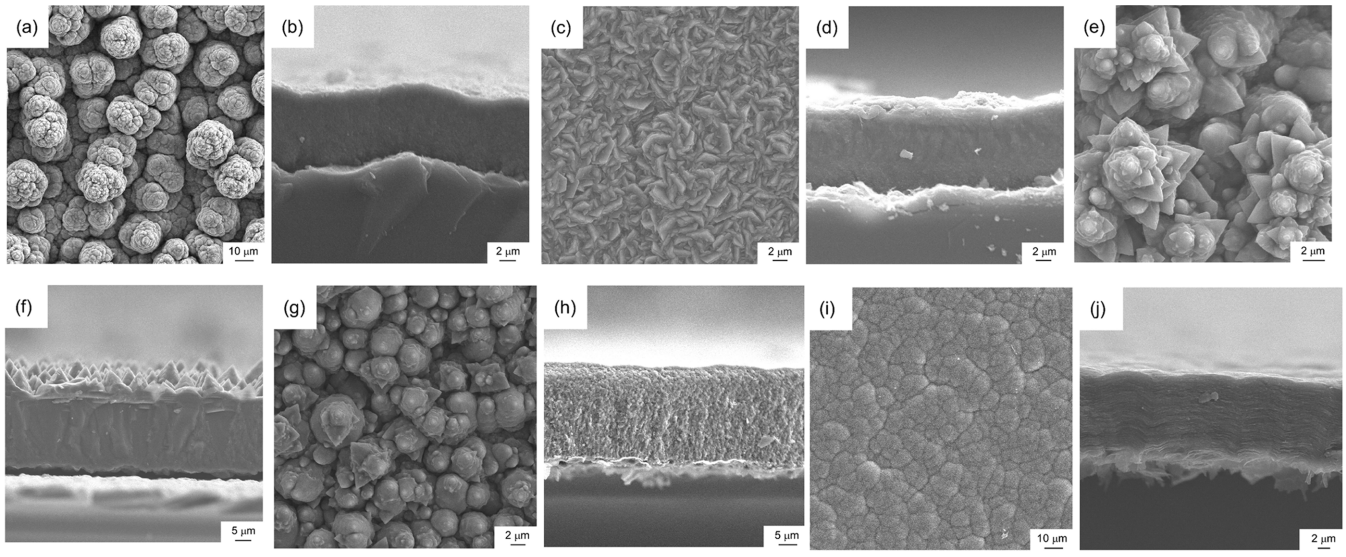

Fig. 3. Surface and cross-section morphology of β-SiC films prepared at a P_{tot} of 10^4 Pa: (a) (b) P_L = 90 W, T_{dep} = 1185 K; (c) (d) P_L = 120 W, T_{dep} = 1202 K; (e) (f) P_L = 110 W, T_{dep} = 1262 K; (g) (h) P_L = 148 W, T_{dep} = 1375 K; and (i) (j) P_L = 191 W, T_{dep} = 1470 K. (a) (c) (e) (g) (i): surface; (b) (d) (f) (h) (j): cross-section.

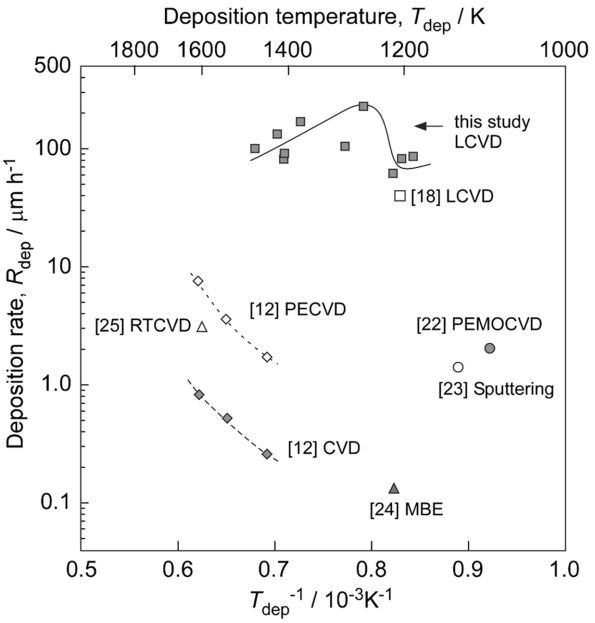

Fig. 4. Comparison of laser CVD and other methods regarding deposition rate and deposition temperature of SiC films.

4. Summary

Highly (111)-oriented β-SiC films were deposited on glassy carbon substrates by laser CVD. At a deposition temperature of 1262 K, the SiC film with a high Lotgering factor of above 0.96 showed a pyramid-like surface morphology with flower-like grains and a columnar cross-section with sharp tips. The deposition rates of these SiC films were 10–10^2 times greater than those of other CVD methods and the highest deposition rate was 220 μm h^{-1} at T_{dep} = 1262 K and P_{tot} = 10^4 Pa.

Acknowledgments

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REFERENCES

1. S. Madapura, A. J. Steckl, and M. Loboda, "Heteroepitaxial Growth of SiC on Si(100) and (111) by Chemical Vapor Deposition Using Trimethylsilane," *J. Electrochem. Soc.,* **146** 1197-202 (1999).
2. N. G. Wright and A. B. Horsfall, "SiC Sensors: A Review," *J. Phys. D. Appl. Phys.*, **40** 6345-54 (2007).
3. J. B. Casady and R. W. Johnson, "Status of Silicon Carbide (SiC) as a Wide-Band Gap Semiconductor for High-Temperature Applications: A Review," *Solid State Electron.*, **39** 1409-22 (1996).
4. R. Maboudian, C. Carraro, D. G. Senesky, and C. S. Roper, "Advances in Silicon Carbide Science and Technology at the Micro- and Nanoscales," *J. Vac. Sci. Technol. A,* **31** [5] 050805 (2013).
5. W. C. Lien, N. Ferralis, and C. Carraro, "Growth of Epitaxial 3C-SiC Films on Si(100) via Low Temperature SiC Buffer Layer," *Cryst. Growth Des.*, **10** [1] 36-9 (2009).
6. M. Kim, J. Ohta, A. Kobayashi, H. Fujika, and M. Oshima, "Low-Temperature Growth of High Quality AlN Films on Carbon Face 6H-SiC," *Phys. Status. Solidi. Lett.*, **2** [1] 13-5 (2008).
7. R. F. Davis, T. Gehrke, K. J. Linthicum, T. S. Zheleva, E. A. Preble, P. Rajagopal, C. A. Zorman, and M. Mehregany, "Pendeo-Expitaxial Growth of Thin Films of Gallium Nitride and Related Materials and their Characterization," *J. Cryst. Growth,* **225** [2-4] 134-40 (2001).
8. M. S. Cho, N. Sawazaki, K. Sugita, A. Hashimoto, A. Yamamoto, and Y. Ito, "Characterization of MOVPE InN Films Grown on 3C-SiC/Si(111) Templates," *Phys. Status Solidi C*, **4** [7] 2441-44 (2007).
9. L. Li, Z. Chen, T. Lin, H. Pu, J. Li, and Q. Li, "Structure Analysis of SiCGe Films Grown on SiC," *Surf. Interface Anal.,* **40** [5] 935-38 (2008).
10. M. Sabisch, P. Kruger, and J. Pollmann, "Ab Initio Calculations of Si(110) and GaAs(110) Surfaces: A Comparative Study and the Rile of Ionicity," *Phys. Rev. B*, **51** [9] 13367-79 (1995).
11. L. Gou, C. Qi, J. Ran, and C. Zheng, "SiC Film Deposition by DC Magnetron Sputtering," *Thin Solid Films*, **345** 42-4 (1999).
12. J. Y. Seo, S. Y. Yoon, K. Niihara, and K. H. Kim, "Growth and Micro Hardness of SiC Films by Plasma-Enhanced Chemical Vapor Deposition," *Thin Solid Films*, **406** [1] 138-44 (2002).
13. K. Abe, Y. Nagasaka, T. Kida, T. Yamakami, R. Hayashibe, and K. Kamimura, "Characterization of Polycrystalline SiC Films Grown by HW-CVD Using Silicon Tetrafluoride," *Thin Solid Films*, **516** [5] 637-40 (2008).
14. G. Boisselier, F. Maury, and F. Schuster, "SiC Coatings Grown by Liquid Injection Chemical Vapor Deposition Using Single Source Metal-Organic Precursors," *Surf. Coat. Tech.*, **215** 152-60 (2013).
15. P. Zhao, A. Ito, and T. Goto, "Effect of Deposition Temperature on the Orientation and Electrical Properties of $YBa_2Cu_3O_{7-\delta}$ Films Prepared by Laser CVD Using Liquid-Source Evaporation," *Ceram. Int.*, **40** [1] 2057-61 (2014).
16. C. Chi, H. Katsui, and T. Goto, "Preparation of Na-Beta-Alumina Films by Laser Chemical Vapor Deposition," *Surf. Coat. Technol.*, **276** 534-38 (2015).
17. Y. Gong, R. Tu, and T. Goto, "Microstructure and Preferred Orientation of Titanium Nitride Films Prepared by Laser CVD," *Mater. Trans.,* **50** [8] 2028-34 (2009).
18. S. Zhang, R. Tu, and T. Goto, "High-Speed Epitaxial Growth of β-SiC Film on Si(111) Single Crystal by Laser Chemical Vapor Deposition," *J. Am. Ceram. Soc.*, **95** [9]

2782-84 (2012).
19. S. Zhang, Q. Xu, R. Tu, T. Goto, and L. Zhang, "High-Speed Preparation of <111 >- and <110 >-Oriented β-SiC Films by Laser Chemical Vapor Deposition," *J. Am. Ceram. Soc.*, **97** [3] 952-58 (2014).
20. S. Zhang, Q. Xu, R. Tu, T. Goto, and L. Zhang, "Growth Mechanism and Defects of <111>-Oriented β-SiC Films Deposited by Laser Chemical Vapor Deposition," *J. Am. Ceram. Soc.*, **98** [1] 236-41 (2015).
21. B. Li, Q. Li, H. Katsui, T. Goto, and R. Tu, "Effect of the Vacuum Degree on the Orientation and the Microstructure of β-SiC Films Prepared by Laser Chemical Vapour Deposition," *Mater. Lett.*, **182** [1] 81-4 (2016).
22. F. K. Lotgering, "Topotactical Reactions with Ferrimagnetic Oxides Having Hexagonal Crystal Structures," *J. Inorg. Nucl. Chem.*, **9** [2] 113-23 (1959).
23. J. H. Boo, M. C. Kim, S. B. Lee, S. J. Park, and J. G. Han, "Growth of SiC Thin Flms on Graphite for Oxidation-Protective Coating," *J. Vac. Sci. Technol. A*, **18** [4] 1713-17 (2000).
24. Q. Wahab, M. R. Sardela Jr., L. Hultman, A. Henry, M. Willander, E. Janzen, and J. E. Sundgren, "Growth of High-Quality 3C-SiC Epitaxial Films on Off-Axis Si (001) Substrates at 850°C by Reactive Magnetron Sputtering," *Appl. Phys. Lett.*, **65** [6] 725-27 (1994).
25. A. Fissel, B. Schroter, and W. Richter, "Low-Temperature Growth of SiC Thin Flms on Si and 6H–SiC by Solid-Source Molecular Beam Epitaxy," *Appl. Phys. Lett.*, **66** [23] 3182-84 (1995).
26. A. J. Steckl and J. P. Li, "Epitaxial Growth of β-SiC on Si by RTCVD with C_3H_8 and SiH_4," *IEEE Trans. Electron Dev.*, **39** [1] 64-74 (1992).