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Oxidation kinetics of SiC deposited from CH_3SiCl_3/H_2 under CVI conditions

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Oxidation tests were performed on SiC deposits prepared from CH_3SiCl_3/H_2 under chemical vapour infiltration conditions, at temperatures ranging from 900–1500 °C under a flow of pure oxygen at 100 kPa (passive oxidation regime). The kinetics of growth of the silica layer were established from thickness measurements performed by spectroreflectometry. They obey classical parabolic laws from which rate constants are calculated. Within 1000–1400 °C, the oxidation process is thermally activated with an apparent activation energy of 128 kJ mol^{-1}. Above 1400 °C and below 1000 °C, an increase in the activation energy is observed which is thought to be related to a change in the mechanism of the oxygen transport across the silica layer for $T > 1400$ °C and tentatively to stress effects for $T < 1000$ °C. The kinetics data are compared to those measured on silicon single crystals (used as a standard) and to other reported data on SiC.

1. Introduction

Silicon carbide is one of the most promising ceramic materials for structural applications at high temperatures owing to its refractory character, low density, excellent mechanical properties and good resistance to oxidation [1]. This latter property is related to the formation of a protective layer of silica and is effective at medium temperatures and high enough oxygen pressures (passive oxidation regime) [2].

Silicon carbide ceramics often contain impurities whose nature and concentration depend on the processing techniques. SiC ceramics prepared according to the powder metallurgy route contain a significant amount of sintering aids (e.g. boron, aluminium, yttrium, etc.). On the other hand, silicon carbide chemically deposited from gaseous precursors (e.g. CH_3SiCl_3/H_2) exhibits a much higher degree of purity as long as the organometallic source has been carefully purified (however, a contamination by the deposition chamber material, usually stainless steel, and/or the substrate remains possible). These impurities are known to modify the oxidation behaviour of SiC ceramics. Finally, the oxidation rate of SiC crystals depends also on the nature of the polytypes and the crystal orientation [2, 3].

An important family of ceramic matrix composites (CMC) consisting of SiC-based fibres embedded in an SiC matrix, referred to as SiC/SiC composites, is being used in rocket engine nozzles and space craft heat shields [4]. In these composites, the SiC matrix is infiltrated in the pore network of SiC-based fibre preforms by chemical vapour infiltration (CVI), a process derived from the well-known chemical vapour deposition (CVD) technique [5]. SiC/SiC composites exhibit, with respect to monolithic SiC, a non-linear mechanical behaviour under tension loading, a higher resistance to crack propagation (by almost two orders of magnitude) and to thermal shocks. This outstanding behaviour for a ceramic material is observed only when the fibres are weakly bonded to the matrix, a requirement which is achieved through the use of a thin layer of a soft material, referred to as the interphase (e.g. pyrocarbon or boron nitride), between the matrix and the fibres [6]. The non-linear stress–strain behaviour of SiC/SiC composites under tension loading is related to the occurrence of various damaging phenomena including a progressive microcracking of the SiC matrix and fibre–matrix debonding [7]. These damaging phenomena, when they take place in a composite maintained at high temperatures in atmospheres containing oxygen, result in new reactive surfaces and oxygen diffusion pathways. Therefore, the knowledge of the oxidation kinetics of the SiC matrix (which has been deposited under specific conditions) is necessary for the modelling of the oxidation behaviour of SiC/SiC composites.

The aim of the present contribution was to establish the oxidation kinetics of SiC deposits, prepared under CVI conditions, and to compare the data with those corresponding to silicon (used as a standard) and other SiC ceramics.

2. Experimental procedure

2.1. Samples

The samples used in the present study were SiC layers

0022-2461

($\approx$ 120 μm thick), deposited from a CH_3SiCl_3/H_2 mixture under CVI conditions (i. e. $T \approx 1000\,°C$ and $P < 50$ kPa), on the external surface of an SiC-based fibre (Nicalon NLM 202 ceramic grade) preform. The isothermal/isobaric (ICVI) process has been described in detail elsewhere [4]. It will be sufficient to recall here that in ICVI the overall deposition process is rate-controlled by the kinetics of the chemical surface reactions and not by mass transfers (of the reactants and products) in the gas phase. As a result, SiC is formed both in the pore network of the preform (infiltration) and on its external surface (coating). At the end of the process, the pores become progressively sealed by the SiC-deposit. Here, the preform has been maintained in the CVI chamber for a long enough time in order to grow an SiC coating about 120 μm thick (Fig. 1a). The SiC coating was polycrystalline (β-modification or 3C-polytype) with (1 1 1) planes preferentially orientated parallel to the substrate. Trace amounts of free silicon were detected by X-ray diffraction (Fig. 1b). However, no significant departure from the stoichiometric Si/C = 1 ratio was observed from the results of electron probe microanalysis (standard: SiC single crystal). Therefore, it was assumed that the silicon in excess was present as isolated precipitates within a stoichiometric SiC phase. The infiltrated/coated SiC/SiC composite was then: (i) cut with a diamond saw into small cubes $3 \times 3 \times 3$ mm^3 and one of their faces, i.e. that with the 150 μm SiC-coating, was polished with a diamond paste (1 μm grain size), (ii) ultrasonically cleaned in acetone and alcohol baths, and finally (iii) dried. It was assumed that the 150 μm coating was representative of the SiC matrix deposited simultaneously in the pore network of the fibre preform.

The oxidation tests, which are described below, were also performed on silicon single crystals (orientation: 1 1 1) cut with a diamond saw in an undoped silicon wafer 300 μm thick, and used as a standard (because their oxidation kinetics have been studied in a detailed manner by many researchers).

2.2. Oxidation tests

All the oxidation tests were performed within the temperature range 900–1500 °C, using an electric furnace equipped with a tube and sample holder made of pure alumina (> 99.9%) and heated with a carbon resistance.

In each test, the alumina tube was first evacuated with a vacuum pump (residual pressure 1 Pa) and then swept with a flow of pure dry oxygen ($H_2O < 2$ p.p.m). The oxidation test was performed with an oxygen flow of $1\,l\,h^{-1}$ under a pressure of 100 kPa. Temperature was raised at a rate of 60 °C min^{-1} and controlled with a Pt/Pt–10%Rh thermocouple set below the sample.

2.3. Characterization of the silica layer

The kinetics of growth of the silica layer were assessed from thickness measurements, performed by spectroreflectrometry (Nanospec/AST model 201) [8]. The accuracy of the measurements was established to be ± 5 nm for $x < 200$ nm and ± 2 nm for $x > 200$ nm.

The nature of the silica layer was characterized by X-ray diffraction (CuK_α radiation) and optical microscopy in reflection.

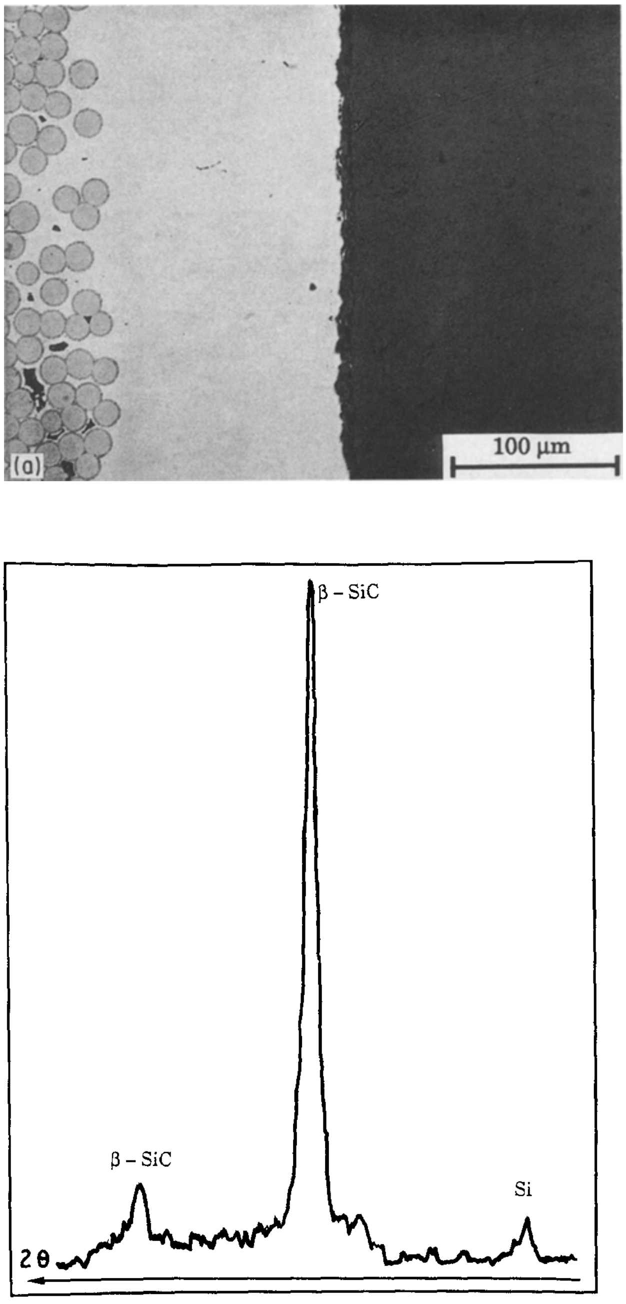

Figure 1 Nature of the SiC deposits prepared from CH_3SiCl_3/H_2 under CVI conditions: (a) optical micrograph of the SiC layer deposited on the external surface of the fibre preform; (b) XRD spectrum of the SiC layer.

3. Results

The variation of the silica layer thickness, x, as a function of the square root of the oxidation test duration, t, at a given temperature, T, are shown in Fig. 2. Linear relationships $x = f(t^{1/2})$ are observed for all the oxidation tests, in agreement with the results of the previous studies reported on the oxidation of both silicon and silicon carbide [2, 9].

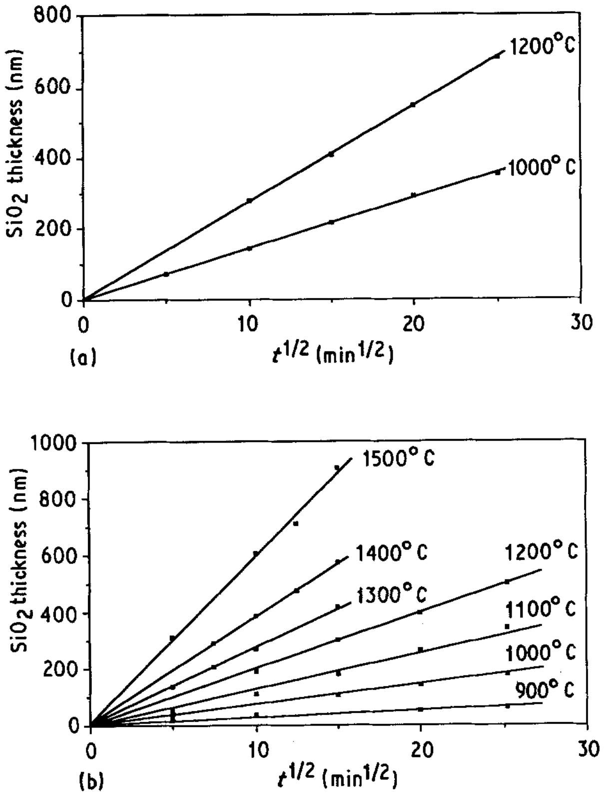

Figure 2 Kinetics of growth of the silica layer in pure oxygen of (a) single-crystal silicon (1 1 1), (b) SiC deposits prepared under CVI conditions.

TABLE I Values of parabolic kinetics constant B, as measured in the present work for single-crystal silicon and SiC deposited from CH_3SiCl_3/H_2. The data of Deal and Grove [9] for single-crystal silicon are given for comparison

Temperature (°C)	B ($nm^2\ min^{-1}$)		
	Single crystal silicon		SiC (CVI), present work
	present work	[9]	
900			5
1000	200	195	49
1100		450	188
1200	735	750	404
1300			777
1400			1406
1500			3365

The values of the parabolic kinetics constant, B, defined according to the parabolic equation $x = B^{1/2}$ $t^{1/2}$ were calculated, by a least squares linear regression procedure, from the slopes of the straight lines shown in Fig. 2. They are listed in Table I as well as those previously reported in the literature for silicon single crystal (1 1 1).

The thermal variations of the parabolic kinetics constant, B, are shown in Fig. 3 as Arrhenius plots $\ln B = f(1/T)$.

The silica layers formed during the oxidation tests are usually amorphous. Cristobalite has been observed only for the oxidation tests performed under the most severe conditions, i.e. $T = 1500\,°C$ and $t > 150$ mn (Fig. 4).

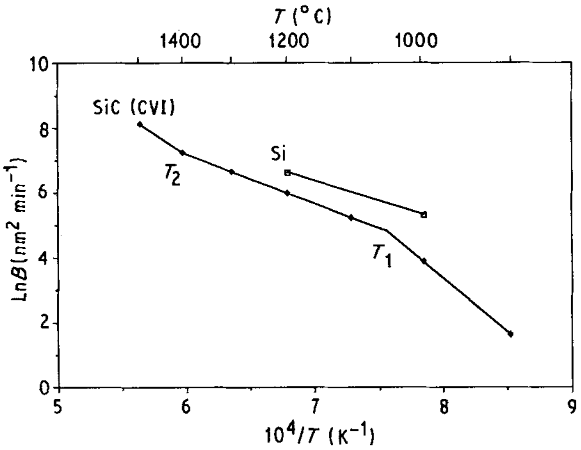

Figure 3 Arrhenius plots of the thermal variations of the parabolic rate constants, B, for the single-crystal silicon (1 1 1) and SiC deposits prepared under CVI conditions.

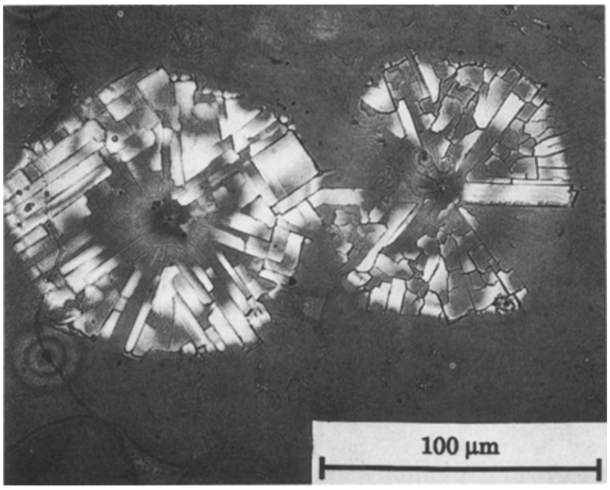

Figure 4 Optical micrograph of the surface of a SiC (CVI) sample maintained for 225 min at 1500 °C under a flow of pure oxygen ($P = 100$ kPa) showing crystals of cristobalite.

4. Discussion

The values of the parabolic rate constant, B, which have been calculated in the present work for silicon single crystals (1 1 1) are very close to those reported by Deal and Grove [9]. This feature suggests that our oxidation test conditions (nature of the tube, sample holder, oxygen purity) were clean enough. On the other hand, Choi *et al.* [10] have reported much higher (× 7) B values for the same material and have assigned this increase in the kinetics of growth of the silica layer to the presence of impurities in their alumina tube.

As shown in Fig. 3, silicon single crystals exhibit a higher oxidation rate in pure oxygen than SiC CVI/CVD deposits, in agreement with the conclusion drawn by Costello and Tressler [11] for pure materials. As an example, at 1200 °C, there is a factor of 2 between the values of the parabolic rate constants, B(Si) and B(SiC), of silicon single crystal and SiC CVI/CVD deposits. At lower temperatures, the $\alpha = B(\mathrm{Si})/B(\mathrm{SiC})$ ratio is higher (e.g. $\alpha = 4$ at 1000 °C).

The explanation which has been given to justify the higher B values for silicon single crystals is based on the hypothesis that an additional oxygen flux is necessary to oxidize the carbon of SiC with respect to that required for the oxidation of silicon [2]. Considering that oxidation occurs according to the following equations

$$Si + O_2 \rightarrow SiO_2 \qquad (1)$$

$$SiC + \tfrac{3}{2} O_2 \rightarrow SiO_2 + CO \qquad (2)$$

$$SiC + 2O_2 \rightarrow SiO_2 + CO_2 \qquad (3)$$

1 mol oxygen per 1 mol silica is necessary to oxidize silicon with respect to 3/2 or 2 for SiC depending on whether Equation 2 or Equation 3 is selected. Therefore, from these considerations an $\alpha = B(\mathrm{Si})/B(\mathrm{SiC})$ ratio equal to 1.5–2 is expected for oxidation tests performed under similar conditions. Costello and Tressler [2] have reported α values in the range 2–2.5 for oxidation tests performed at 1200–1400 °C on silicon and SiC 6H (0001 face) single crystals and concluded that the oxidation of SiC may proceed according to Equation 3. However, Zheng *et al.* [11] have reported higher α-values, i.e. $\alpha = 4$ for oxidation tests run with similar materials (silicon and SiC 4H (0001 face). Furthermore, Schiroky *et al.* [12] have published a comparative study of the oxidation of silicon SiC (CVD) and Si_3N_4 (CVD). From their data, we have calculated that an α ratio of about 5 exists between silicon and SiC (CVD). All these results suggest that the hypothesis based on the additional oxygen flux necessary to oxidize the carbon from SiC (with respect to that necessary to oxidize silicon) is not enough in itself to explain the differences observed experimentally in the B constants between Si and SiC. Other hidden factors might well be involved.

As shown in Fig. 3, the Arrhenius plots observed for SiC (CVD/CVI) is complex and can be analysed on the basis of three domains. Between $T_1 = 1100\,°C$ and $T_2 = 1400\,°C$, the Arrhenius plot is a linear segment corresponding to an apparent activation energy of 128 kJ mol^{-1}, a value which is in agreement with those reported previously [2, 11]. Beyond 1400 °C an increase in the slope of the Arrhenius plot is observed. This transition has been mentioned by other researchers and assigned to a change in the transfer of oxygen across the silica layer [2, 13]: oxygen can diffuse through silica either as molecular species by permeation or as ionic species in the crystal network. Because the latter mechanism has a high activation energy, it is thought to become rate-controlling at high temperatures. In the same manner, another increase in the slope of the Arrhenius plot (and therefore in the apparent activation energy) is noticed below 1100 °C. This transition at a low temperature is not observed for silicon (or if it does occur, it is less noticeable). On the contrary, it has been mentioned already by several authors for SiC [14–16]. According to them (see, for example, [15]), this difference between silicon and SiC could be related to composition defects in the silica layer which could be stoichiometric when formed on SiC and non-stoichiometric on silicon. On the contrary, Blachere and Pettit assumed that silica is stoichiometric when grown on silicon and non-stoichiometric (i.e. SiO_{2-x}) on silicon carbide [17]. According to the latter authors, the contribution of ionic diffusion to the oxygen transport is more and more significant as the departure from stoichiometry increases in SiO_{2-x} grown on SiC. However, because molecular diffusion is favoured at low temperatures (with respect to ionic diffusion), it seems that departures from stoichiometry in silica might not be the appropriate phenomenon to explain the transition occurring at T_1 in the Arrhenius plot.

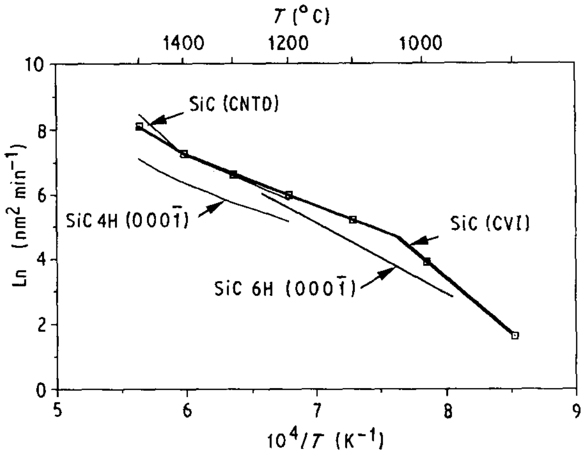

Figure 5 Thermal variations of the parabolic rate constants, B, for SiC (CVI) (present work), SiC (CNTD) [2], 4H-SiC polytype [11] and 6H-SiC polytype [16].

Another possible explanation for the transition at T_1 could be the occurrence of significant stresses in the oxide layer in as much as the effect of this parameter on the oxidation kinetics would be expected to become noticeable at low temperatures. In fact, such an hypothesis has been already discussed for silicon [18–20]. Stresses arise in the oxide layer due to the volume increase inherent to silicon or SiC oxidation. They can influence the oxidant diffusivity in SiO_2 and are particularly noticeable for low oxide thicknesses [20]. Because the oxidation kinetics of SiC is lower than that of silicon, the importance of stress effects may be more pronounced for SiC than for silicon.

Finally, the oxidation kinetics rates of SiC (CVD/CVI) measured in the present work are compared to those mentioned in the literature for different SiC ceramics, in Fig. 5. At high temperatures ($T > 1200\,°C$) our data are very close to those reported by Costello and Tressler for controlled nucleation thermally deposited SiC, prepared according to a modified CVD technique and which also contains some free silicon. On the other hand, the B values measured in the present work are higher, generally speaking, than those mentioned for the hexagonal SiC polytypes (4 H and 6 H) although the thermal variations of the B constants are very similar [11, 16].

5. Conclusions

The oxidation kinetics of silicon carbide, deposited from CH_3SiCl_3/H_2 on an SiC-based fibre preform under CVI conditions, were studied from oxidation tests performed under a flow of pure oxygen ($P = 100$ kPa) for temperatures ranging from 900–1500 °C (passive oxidation regime), with the following main conclusions.

1. The kinetics of growth of the silica layer obey parabolic laws.

2. Between 1100 and 1400 °C, the oxidation process is thermally activated with an apparent activation energy of 128 kJ mol^{-1}.

3. Above 1400 °C, an increase in the apparent activation energy is observed which is thought to be related to a change occurring in the mechanism of the oxygen transport across the silica layer.

4. Below 1100 °C, another increase in the apparent activation energy also occurs which has been tentatively assigned to the effect of stresses in the oxide layer.

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References

1. J. L. CHERMANT, in "Les céramiques thermomécaniques" (Presse du CNRS, Paris, 1989).
2. J. A. COSTELLO and R. E. TRESSLER, *J. Amer. Ceram. Soc.* **69** (1986) 674.
3. W. VON MÜNCH and I. PFAFFENDER, *J. Electrochem. Soc.* **122** (1975) 642.
4. J. C. CAVALIER, A. LACOMBE and J. M. ROUGES, in "Proceedings of the Third European Conference on Composite Materials", edited by A. R. Bunsell, P. Lamicq and A. Massiah, 20–23 March 1989 Bordeaux France (European Association for Composite Materials, Bordeaux) pp. 99–110.
5. R. NASLAIN, J. Y. ROSSIGNOL, J. M. QUENISSET and F. LANGLAIS, in "Introduction aux Matériaux Composites", Vol. 2, edited by R. Naslain (CNRS/IMC Bordeaux 1985) pp. 439–91.
6. A. J. CAPUTO, D. P. STINTON, R. A. LOWDEN and T. M. BESMAN, *Amer. Ceram. Soc. Bull.* **66** (1987) 368.
7. M. BOUQUET, J. M. BIRBIS and J. M. QUENISSET, *Comp. Sci. Technol.* **37** (1990) 223.
8. W. G. SPITZER and M. TANENBAUM, *J. Appl. Phys.* **32** (1961) 744.
9. B. E. DEAL and A. S. GROVE, *ibid.* **36** (1965) 3770.
10. D. J. CHOI, D. B. FISHBACK and W. S. SCOTT, *J. Amer. Ceram. Soc.* **72** (1989) 1118.
11. Z. ZHENG, R. E. TRESSLER and K. E. SPEAR, *J. Electrochem. Soc.* **137** (1990) 854.
12. G. H. SHIROKY, R. J. PRICE and J. E. SHEEHAN, GA Project 3799, December 1986.
13. Z. ZHENG, R. E. TRESSLER and K. E. SPEAR, *J. Electrochem. Soc.* **137** (1990) 2812.
14. E. FITZER and R. EBI, in "Silicon carbide 1973", edited by R. C. Marshall, J. W. Faust and C. E. Ryan (University of South Carolina Press, Columbia, SC, 1973) pp. 320–8.
15. J. SCHLICHTING, *High Temp. High Press.* **14** (1982) 717.
16. R. C. A. HARRIS, *J. Amer. Ceram. Soc.* **58** (1975) 7.
17. J. R. BLACHERE and F. S. PETTIT, in "High Temperature Corrosion of Ceramics" (Noyes, Park Ridge, NJ, 1989) pp. 137–83.
18. R. H. DOREMUS and A. SZEWCZYK, *J. Mater. Sci.* **22** (1987) 2887.
19. S. ALEXANDEOVA, A. SZEKERES and J. KOPRINAROVA, *Semicond. Sci. Technol.* **4** (1989) 876.
20. P. SUTARDJA and W. G. OLDHAM, *IEEE Trans. Electron Devices* **36** (1989) 2415.

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