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SCIENCE DIRECT

Journal of Solid State Chemistry 177 (2004) 580–585

JOURNAL OF SOLID STATE CHEMISTRY

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Comparative optical investigations of sintered and monocrystalline black and green silicon carbide (SiC)

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Received 14 June 2002; received in revised form 22 April 2003; accepted 29 April 2003

Abstract

Crystalline SiC appears in many different polytypes of cubic, hexagonal, and rhombohedral structures. These polytypes are colorless transparent or exhibit various colors evoked by doping with different elements. Dense sintered S-SiC (solid-state sintered) and LPS-SiC (liquid-phase sintered) were known in black color only, but recently a new liquid-phase sintering process was developed to achieve green LPS-SiC as well. Whereas in S-SiC the polycrystalline grains are homogeneously doped with 0.2 wt% boron, in the LPS-types the SiC grains contain up to 1.2 wt% Al, 0.3 wt% N and 0.1% O having a structure comprising a SiC(Al,N,O) mixed crystal shell and a pure SiC core. The difference in color of polycrystalline SiC bodies seems to result from small amounts of carbon in the sintered specimens (0.2–0.5 wt% C). Green sintered LPS-SiC is obtained, after free carbon has largely been removed by a suitable oxidation process prior to sintering. To get information on the various types of sintered SiC, the optical extinction and absorption spectra of black and green sintered SiC and green Acheson-SiC single crystals were quantitatively measured in the spectral range between about 1.4 and 4.1 eV. While the absorption coefficients of the single crystals vary between about 50 and 200 $\mathrm{cm^{-1}}$, the extinction coefficients of the sintered materials are between 2000 and 7000 $\mathrm{cm^{-1}}$. Nevertheless the absorption bands in the more or less transparent region of the green and black materials can easily be attributed to one another. Hence, the reason for these absorption processes must be assumed to be the same. In the same way, position and slope of the absorption edges are correlated amongst green or black SiC, irrespective of, whether the material is single crystal or sintered.

Keywords: SiC; Silicon carbide; Black SiC; Green SiC; Sintered SiC; Single crystal SiC; Doped SiC; Optical absorption; Optical reflectivity

1. Introduction

Silicon carbide is often considered the most important carbide. Its great hardness, high heat resistance, strong oxidization resistance and the small thermal extension coefficient favor it for many technical applications. Initially, SiC was largely used as abrasive and raw material for refractories. Actually, because of the progress in sintering covalent ceramics, it has become the most frequently used nonoxide engineering ceramic. High-density SiC components are commercially available in various forms prepared by solid-state sintering (SSiC) or liquid-phase sintering (LPSSiC).

Recently, the electronic properties of SiC have attracted much attention. Based on the well-known blue luminescence of silicon carbide, blue-emitting diodes were realized. Actually its properties as a wide-gap semiconductor and its thermoelectric properties are object of investigation.

Crystalline SiC appears in many different polytypes: a lone cubic (3C), a large number of hexagonal structures (2H, 4H, 6H,...) and a large number of rhombohedral structures (15R, 21R,...) [1]. These polytypes are colorless-transparent or exhibit various colors that are evoked by doping with different elements [1–3]. Technical ceramics are sintered from fine-grained SiC powder. Pure SiC powders cannot be densified, not even under pressure; successful sintering of SiC requires the use of suitable additives. For solid-state sintering

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doi:10.1016/j.jssc.2003.04.006

mixtures of boron and carbon, for liquid-phase sintering mixed additions of yttria (Y_2O_3) or yttrium–aluminum–garnet ($Y_3Al_5O_{12}$) and aluminum nitride (AlN) are commercially used [3]. From both processes, only black workpieces have been obtained. However, recently a new liquid-phase sintering process was developed to achieve green LPS-SiC as well [4].

To get some insight into the properties of this new green sintered SiC, we made a comparative optical investigation of green and black sintered SiC and green and black Acheson single crystals obtained from industrial production.

2. Investigated materials

2.1. Acheson-SiC single crystals

Green and black crystals have been produced by the ESK-process from pure quartz sand and petroleum coke, in electrically heated resistance furnaces [3]. The green crystals exhibit high purity (Al- and N-dissolved in the SiC lattice <50 ppm each) and extremely high 6H phase contents of $>90\%$. Black SiC forms from reaction mixtures composed of new material together with partially reacted material. In black crystals, an Al content of >500 ppm is accompanied by a prevailing Al-stabilized 4H polytype [3] and an increasing number of particular inclusions (unreacted elemental carbon and metal silicides, etc.). For determination of SiC polytype compositions and chemical analysis of Acheson-SiC crystals see Refs. [5,8], respectively.

2.2. Sintered polycrystalline SiC

Two liquid-phase sintered SiC samples and one solid-state sintered SiC sample were investigated:

2.2.1. EKasic T green/black (LPSSIC)

The EKasic T samples were prepared from a raw materials mix consisting of green α-SiC powder (mean particle size: 0.7 μm, adhering SiO_2: 0.9 wt%), yttrium–aluminum–garnet (YAG) and aluminum nitride. 3–6 wt% addition of YAG + AlN lead to full density in a two-stage gas pressure sintering cycle (5 and 95 bar argon pressure, 1 h hold at 1960°C final temperature). The color of EKasic T green results after the pressed body is subjected to a decarburizing treatment in air at temperatures up to 500°C prior to the liquid-phase sintering [4]; the free carbon in the pressed body is removed to less than 0.1 wt%.

Without being subjected to the decarburizing treatment, when subjected only to the usual heat treatment for binder removal under argon atmosphere, the body contains ~ 0.5 wt% free carbon, approximately half of which originates from the SiC powder or from the organic pressing aids. Although fully densified during liquid-phase sintering, the color of the body is black. This is attributed to the presence of an accompanying phase of elemental carbon in quantities >0.1 wt%. Due to solution and reprecipitation of SiC during sintering [6], the SiC grains have a core/shell structure: The core contains SiC only; the shell comprises a mixed crystal SiC(Al,N,O). The binder phase contains a continuous segregation film in virtually all SiC–SiC boundaries and crystalline YAG ($Y_3Al_5O_{12}$) at the triple junctions of the SiC grains (for details see Ref. [7]). For chemical analysis of the residual SiC grains, see Refs. [4,8].

2.2.2. EKasic BM black

The solid-state sintered SiC was prepared by the usual press and sinter process [9] using green α-SiC submicron powder with minimized boron and carbon additions, and a final HIP-densification step to eliminate residual pores. The microstructure of the resulting EKasic BM was fine grained (mean grain size: 2.7 μm) with inter- and intragranular graphite particles up to 1 μm in size. The free carbon originates from defined quantities of carbon added as a sintering aid to remove SiO_2 and to activate the shrinkage process [10].

In contrast to LPSSiC, the grain boundaries in (B,C)-doped SiC are characterized by their high purity: The SiC–SiC interfaces are pure, and without any layers of doping or impurity elements [11]. The low boron doping (0.2 wt% B), which corresponds to the solubility limit [12], and the absence of boron at the SiC grain boundaries suggest that most or even all boron is dissolved in the SiC structure. We assume that the black color of EKasic BM results from excess elemental carbon and not from the 0.2 wt% boron doping of the SiC grains.

3. Sample preparation

The samples for the optical absorption and reflectivity measurements were cut from Acheson single crystals and sintered rods, respectively. The surfaces were mechanically ground and polished using diamond powders of gradually reduced grain size (finest grade 1 μm). For the reflectivity measurements sufficiently thick samples were used to avoid mistakes from reflection from the back surface. Because of the high optical absorption/extinction of sintered SiC, in this case, for transmission measurements, it was necessary to prepare samples of less than 20 μm thick. To obtain reliable quantitative absorption spectra, in the case of single crystal SiC with its low absorption the sample thicknesses were chosen in the way that the measured transmission was essentially determined by the absorption process and not by surface reflexion or the small amounts of light scattering.

4. Optical spectra

In Fig. 1 the reflectivity spectra of the different samples are displayed, measured with an Al mirror used for reference. The reflectivity of Al is higher than 90% down to about 230 nm, besides a range between about 650 and 950 nm. To show the difference between sintered and crystalline SiC more clearly, in Fig. 2 the spectra are shown as obtained with a green Acheson single crystal used for reference. As can be seen in Fig. 1, the structure in the spectra close to 2.5 eV is largely due to the crystal. Only in the spectrum of EKA SiC black there is a weak structure in this spectral range as well, however, slightly shifted in energy.

The absorption spectra of single crystal SiC and sintered SiC, respectively, are displayed in Figs. 3 and 4. The absorption coefficient is calculated from the measured transmission and the measured reflectivity (Fig. 1) according to (see Ref. [13])

$$\alpha = (1/d)\ln(A + \sqrt{A^2 + R^2}) \qquad (1)$$

with $A = (1 - R^2)/2i_d$ (d, sample thickness; R, reflectivity; i_d, transmission).

The sintered samples are very dense. Here even in very thin samples no holes occur or scattering at surface lumps must be taken into account. Therefore, the weakening of radiation is due to volume effects only; nevertheless, it cannot be excluded that the high absorption in sintered SiC is partly due to volume scattering. Accordingly the ordinate in Fig. 4 is denoted as extinction coefficient α^*. Eq. (1) holds for the extinction coefficient as well.

While the absorption coefficients of the single crystals vary between about 50 and 200 cm^{-1}, the extinction coefficients of the sintered materials are between 2000 and 7000 cm^{-1}. Nevertheless, the absorption bands in the more or less transparent region of the green and black materials, respectively, can easily be attributed to one another. Hence, the physical reason for these absorption processes is assumed to be the same. In the same way position and slope of the absorption edges are correlated amongst green or black SiC, each, irrespective of, whether the material is single crystal or sintered. This is quantitatively confirmed in Tables 1 and 2, where the electronic transition energies are listed as determined by the decomposition of the absorption edges in Figs. 3 and 4 according to the theories of interband transitions [14] and deep-level to band transitions [15]. The high-energy transitions agree, even irrespective of, whether SiC is black or green. Accordingly, these transitions belong to the intrinsic properties of SiC. To determine these optical transition energies, a local software program was used that allows to make linear fits to the absorption data, when plotted according to the energy dependences of the different transitions. The results satisfactorily agree with energy gaps of SiC reported in Ref. [1].

The visual appearance of green SiC can be easily derived from the optical absorption spectra in Figs. 3

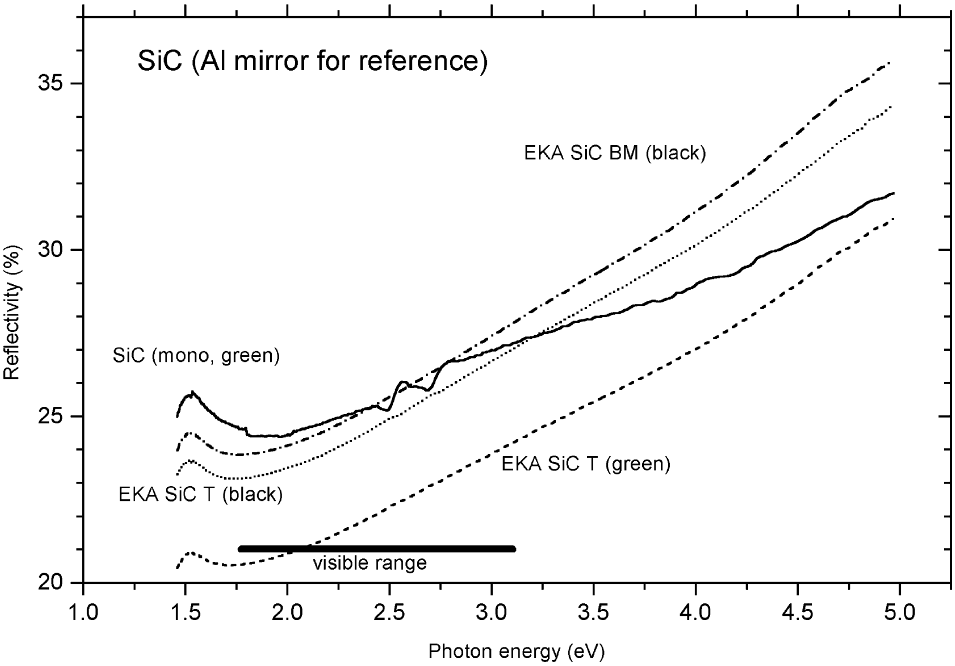

Fig. 1. Reflectivity of single crystal green SiC and sintered SiC prepared by different processes (EKA SiC T green and EKA SiC T black (LPS type); EKA SiC BM black (S type) with an Al-mirror used for reference measured at nearly normal incidence. Accordingly, the small deviation of Al reflectivity from 100% and its weak spectral variation are uncorrected errors in these spectra.

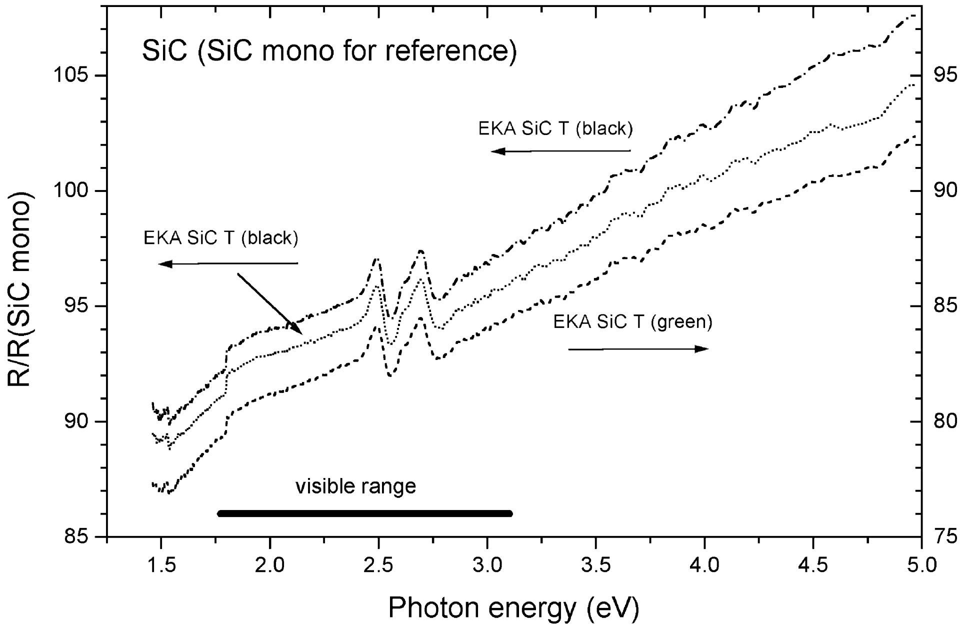

Fig. 2. Reflectivity of sintered SiC prepared by different processes (EKA SiC T green and EKA SiC T black (LPS type); EKA SiC BM black (S type) with single crystal green SiC used for reference. As can be seen form Fig. 1, the similar structures in all spectra between about 2.3 and 2.7 eV are evoked by the single crystal properties.

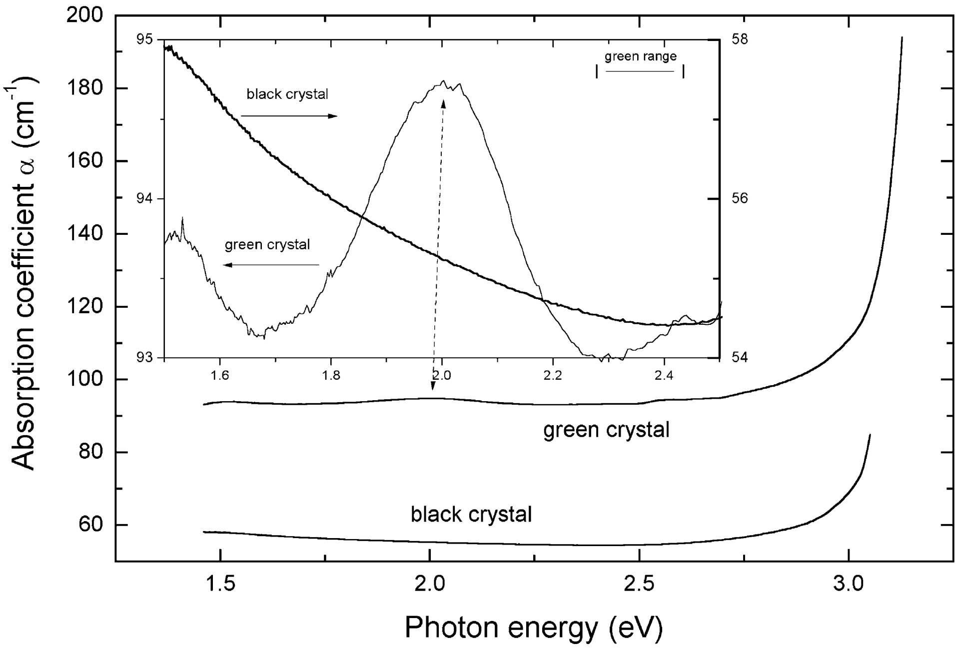

Fig. 3. Absorption coefficient of black and green Acheson SiC single crystals plotted vs. photon energy.

and 4, where in the insets the green section of the visible spectral range is marked. While at higher energies the optical transmission of SiC is strongly reduced by the absorption edge caused by electronic interband transitions, in green SiC the absorption band with maximum at about 2 eV reduces the light intensity in the yellow and red part of the spectrum. Accordingly, the light in the green range is less weakened and determines the visual appearance. Because of the high sensitivity of the human eye, even the relatively small difference of the spectral absorption in the visible range is sufficient to lead to the impression of color.

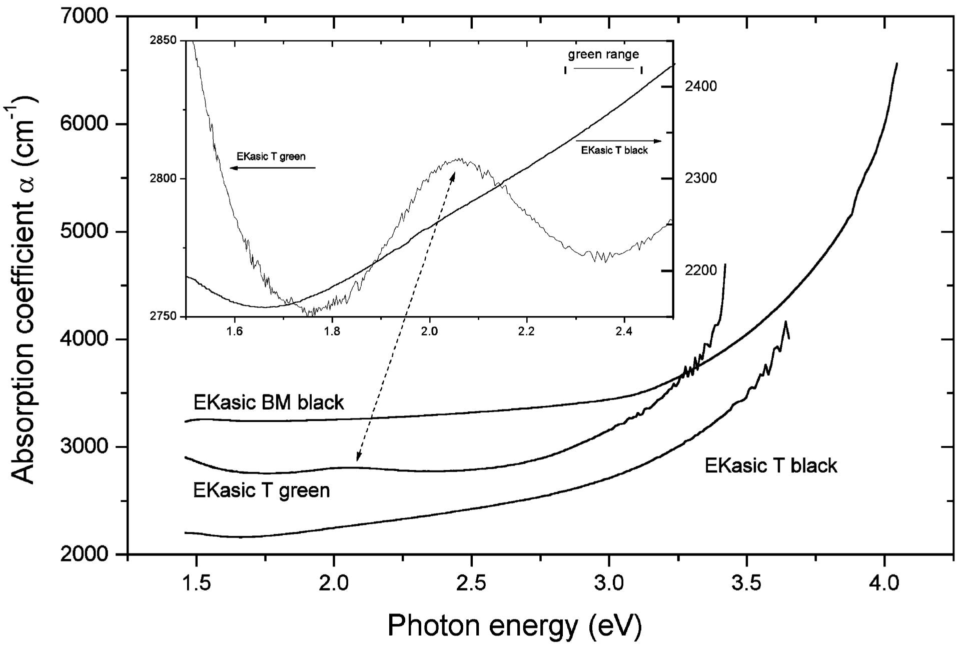

Fig. 4. Extinction coefficient of sintered SiC; EKA SiC T green and EKA SiC T black (LPS type); EKA SiC BM black (S type).

Table 1
Electronic transition energies of green SiC

No.	Transition energies (eV)		Transition type
	Crystalline	Sintered (T green)	
1	1.66(3)	1.63(3)	Deep level to band
2	2.19(2)	2.18(2)	Indirect, allowed
3	2.49(3)	2.48(3)	Indirect, allowed
4	2.69(2)	2.69(2)	Direct, forbidden
5	2.88(2)	2.88(2)	Indirect, allowed
6	3.01(2)	3.02(2)	Indirect forbidden

Table 2
Electronic transition energies of black SiC

No.	Transition energies (eV)			Transition type
	Crystalline	Sintered (T black)	Sintered (BM black)	
1	1.65(3)	1.62(3)	1.66(2)	Deep level to band
	1.94(3)			Direct, forbidden
2	2.19(10)		2.25(10)	Indirect, allowed
	2.47(5)			Indirect, allowed
	2.65(3)			Indirect, forbidden
3	2.88(2)	2.80(5)		Indirect, allowed
4	2.99(3)	3.00(3)	2.99(2)	Indirect, allowed
5		3.55(5)	3.60(2)	Indirect, allowed
6			3.83(2)	Indirect, allowed

5. Conclusion

Green sintered LPS-SiC is obtained, after free carbon has largely been removed by a suitable oxidation process prior to sintering; otherwise, SiC is black. The absorption bands of the green and black materials can easily be attributed to one another, even if they are quantitatively different. Hence, the reason for the absorption processes is assumed to be the same. In the same way, the position and slope of the absorption edges are correlated amongst green or black SiC, irrespective of, whether the materials are single crystal or sintered.

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