Ceramics International 23 (1997) 409-411
© 1997 Elsevier Science Limited and Techna S.r.l.
Printed in Great Britain. All rights reserved
0272-8842/97 $17.00 + 0.00
PII: S0272-8842(96)00047-8

Influence of Impurities and Intrinsic Defects on Physicomechanical Properties of Silicon Carbide Single Crystals

Anatoly Garshin, Elena Lavrenova, Yury Vodakov & Evgeny Mokhov

St. Petersburg State Technical University, Russia A.F. Ioffe Physicotechnical Institute, Russian Academy of Sciences, 195251, St. Petersburg, Russia

(Received 15 June 1995; accepted 17 January 1996)

Abstract: Microindentation with a Vickers diamond pyramid was used in a study of mechanical properties of 6H-SiC with different concentrations of impurities (nitrogen and aluminium) and of intrinsic defects generated by irradiation or during growth under nonstoichiometric conditions. It was found that SiC crystals containing nonstoichiometric and radiation defects, as well as samples with high nitrogen concentration ($C_N \simeq 10^{20}$ cm^{-3}), have a greater tendency for cracking, which results in deterioration of the microstrength characteristics. An analysis of the results obtained leads to the conclusion that the observed changes are primarily caused by intrinsic defect clusters rather than dislocations. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

It is known that intrinsic defects, which may be generated in SiC single crystals by irradiation with high-energy particles, increase the lattice parameter and promote the formation of both vacancy and interstitial clusters.[1-3] The density and dimensions of these are governed by the radiation dose and annealing temperature. Changes in the lattice parameters are also observed in SiC single crystals and epitaxial films grown under nonstoichiometric conditions in the presence of excess silicon[4] and of impurities[5] which should affect the binding energy of atoms in the lattice and, consequently, the physicomechanical properties of a material.[6] The purpose of the present investigation was to determine the physicomechanical properties of SiC single crystals containing nonequilibrium intrinsic defects and impurities, and to carry out a comparative analysis not only of the elastoplastic properties of the samples, but also of their strength parameters.

2 EXPERIMENTAL PROCEDURE

We investigated 6H-SiC single crystals prepared under various conditions and divided into four batches: (1) crystals grown under industrial conditions by the Lely method and doped with nitrogen (nitrogen concentration approximately 10^{18} cm^{-3}); (2) crystals and epitaxial films heavily doped with nitrogen or aluminium impurities (concentration of 10^{20} cm^{-3}); (3) crystals grown under nonstoichiometric conditions by the sublimation "sandwich method"[7] in the presence or a relative excess or deficiency of silicon; (4) crystals were irradiated with high-energy (neutron or α-particles). The reactor neutron dose was 10^{16}–10^{21} cm^{-2} (the fraction of fast neutrons was 20%). The density of dislocations in samples belonging to the first and second batches was 10^2–10^3, whereas in the third and fourth batches it was 10^3–10^4 cm^{-2}.

The physicomechanical properties of the investigated samples were determined by microindentation with a Vickers diamond pyramid under loads of 0.5–8.0 N in specially developed microhardness meters of the PMT-3 type characterized by an improved accuracy.[8] Single crystals of SiC were indented in all cases on the (0001) C face and the size of the SiC single crystals, 6H-SiC polytype was 5–7 mm.

It is known[8] that microindentation can cause plastic deformation accompanied by local brittle fracture giving rise to cracks localized near the indentation. The process of elastoplastic deformation can be described by the expression $P = f(d) = a_d d^{n_d}$, where a_d is a dimensional constant, n_d is a dimensionless constant and d is a diagonal of the indentation. According to Ref. 8 the brittle fracture process is characterized by two stages: during the first stage cracks form and grow slowly to a certain critical size D_{cr}. The extent to which a crack grows is proportional to the size of the indentation made by the diamond pyramid, i.e. the process is mainly of elastoplastic deformation. During the second stage when the load exceeds the crytical value ($P > P_{cr}$), stable growth of cracks occurs and it is described by the expression $P = f(D) = a_D D^{n_D}$, where D is the size of the brittle fracture zone, a_D is a dimensional constant representing the brittle properties of the investigated sample and n_D is a dimensionless constant reflecting the intensity of the brittle fracture processes.

The second stage is characterized by stable brittle fracture. For this reason the strength parameters and the brittleness of the samples are best determined during this stage.

The parameters of the elastoplastic deformation and brittle fracture processes were found quantitatively by measuring d and D. They were then used to calculate the microhardness H_d, the microstrength σ, the microbrittleness γ, and the critical coefficient representing the stress intensity K_{1C}. We also determined the load P_{cr} above which the process of brittle fracture was initiated by microindentation.

The values of H_d, σ, γ and K_{IC} were found from the equations $H_d = \frac{1854P}{d^2}$ GPa, $\sigma = \frac{1000P}{D^2}$ GPa, $\gamma = \frac{D^2-d^2}{d^2}$, $K_{1C} = 0.015(\frac{E}{H})^{1/2} P D^{-3/2}$MN/m^3, where E is elastic modulus, $E_{SIC} = 394.0$ GPa. It should be noted that the microhardness H_d represents the hardness and plastic characteristics of the material, the microbrittleness γ reflects a relation between the brittle and plastic properties, whereas σ and K_{1C} describe the resistance to cracking.

3 RESULTS AND DISCUSSION

Table 1 gives the physicomechanical characteristics of the investigated SiC samples. An analysis of the results (Table 1) shows that in practice for the same value of the microhardness, the parameters σ, γ and K_{1C} could differ quite considerably. In particular, the highest microstrength σ was exhibited by SiC single crystals grown by the Lely method under standard conditions. Heavy doping of SiC single crystals with aluminium to $\sim 5 \times 10^{20}$ cm^{-3} had practically no effect on these parameters (Table 1), whereas the microstrength was considerably lower in the case of crystals heavily doped with nitrogen and in the case of SiC films grown under nonstoichiometric conditions.

A lower microstrength and a tendency for crack formations were exhibited by SiC single crystals irradiated with neutrons or α-particles, i.e. by single crystal containing radiation defects.

The results presented in Table 1 are well correlated with the data obtained in a study of the dependences of the parameters d and D on the load P applied to the diamond pyramid (Fig. 1). The greatest differences between the dependences $D(P)$ were observed for different samples at relatively low loads.

An analysis of the experimental data allowed us to assume that a reduction in the microstrength of samples belonging to the third and fourth batches was a consequence of higher density of dislocations which lowered, in accordance with Ref. 8, the critical stress needed to set cracks in motion; such a high dislocation density could promote plastic deformation. This could probably account for the higher microbrittleness of SiC samples heavily doped with nitrogen. However, in the case of neutron-irradiated SiC single crystals such an explanation could not be valid, because the density of dislocations in these single crystals was the same as in the standard SiC samples grown by the Lely method. We compared the mechanical properties of 6H-SiC single crystals (1 and 4 bathes) which have the same density of dislocations (10^3 cm^{-2}) and showed that the microbrittleness was considerably greater than that of the standard samples. Therefore, the change in the physicomechanical

Table 1. Microstrength characteristics of the SiC 6H polytype

No.	Information on sample	H_d (GPa)	σ (GPa)	$\gamma_{r.u.}$	P_{cr} (N)	K_C
1	Grown under standard cond., n-type, $N_D = 3 \times 10^{18}$ cm^{-3}	32.64	1.65	9.6	18.0	1.8
2	Aluminium-doped, p-type, $C_{Al} = 5 \times 10^{20}$ cm^{-3}	32.64	1.65	9.6	—	1.8
3	Nitrogen-doped, n-type, $C_N = 1 \times 10^{20}$ cm^{-3}	32.64	1.01	16.5	12.0	1.26
4	Grown with excess of Si in SiC–Si_{lig} system, $N_D = 3 \times 10^{18}$ cm^{-3}	32.64	0.97	21.0	—	1.07
5	Grown with deficit of Si, $N_D = 3 \times 10^{18}$ cm^{-3}	28.46	0.91	16.0	15.0	1.17
6	Irr. with α-particles, $\Phi = 10^{16}$ cm^{-2}, $E = 20$ MeV	32.64	1.25	13.1	17.0	1.47
7	Irr. with neutrons, $\Phi = 10^{20}$ cm^{-2}	32.64	1.29	12.9	27.0	1.53
8	Irr. with neutrons, $\Phi = 10^{21}$ cm^{-2}	27.50	0.80	17.0	—	1.23

Note: Samples 1, 6, 7 and 8 were grown by the Lely method ($T_g = 2600$ °C); samples 2, 3, 4 and 5 were grown by the sublimation "sandwich method".[7]

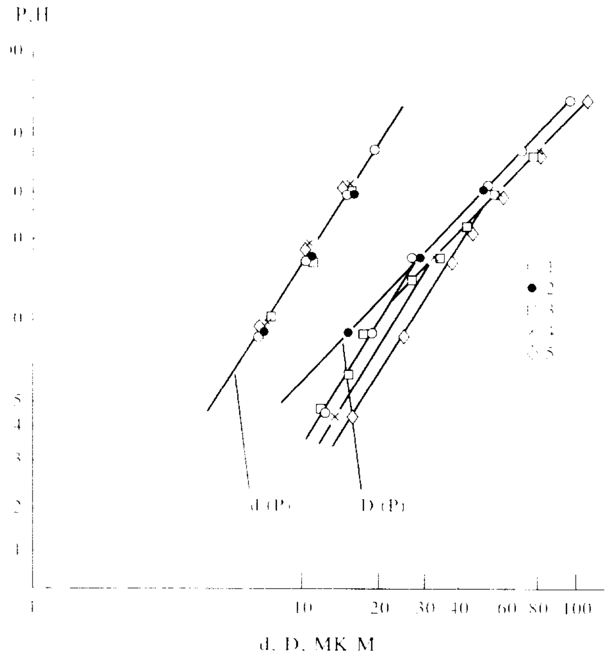

Fig. 1. Changes in the parameters d and D with the load P applied to a diamond pyramid during microindentation. The curves are plotted using logarithmic coordinates by analogy with the Meyer graph and the Onitsch hardness curve.[9,10] The numbers in the figure represent the serial numbers of the samples of SiC single crystals in Table 1.

properties of SiC single crystals should be attributed to the presence of clusters which could act as stress concentrators in SiC and reduce the threshold energy of crack formation. The same clusters were also observed in single crystals and in epitaxial layers grown under nonstoichiometric conditions.[2,3]

These clusters could represent graphite or silicon inclusions, and could be detected by transmission electron microscopy (TEM) and X-ray difractometry (XRD).[11,12] It has been established by the ESR method[13] that such nonstoichiometric samples contain stressed regions which obviously formed because of a distribution of nonequilibrium intrinsic defects, inhomogeneous on the microscopic scale, in SiC single crystals, which also tended to increase the brittleness of these samples. The interstitial type clusters are observed by TEM in the SiC single crystals doped with nitrogen impurity.[14] Probably the dependence of the dislocation density on the nitrogen doping level can be explained by the presence of such defects and the second phase inclusions.[15] Despite the forming of nitrogen doped SiC crystals the clusters evidently do not form SiC(Al) crystals (see Table 1). A comparatively low dislocation density even in highly doped SiC(Al) crystals ($C_{Al} = 10^{21}$ cm^{-3}) is the evidence of this fact.[16] The results of this article also show that some impurities do not reduce the microstrength characteristics of the SiC crystals. The same effect is observed in other compounds with partly ionic type of bonding.[17]

4 CONCLUSIONS

Changes in the mechanical properties observed in SiC crystals containing nonequilibrium intrinsic defects or impurities are primarily the result of crack-formation processes which may be activated by clusters or inclusions of a second phase present in these crystals which could act as stress concentrators in SiC and reduce the threshold energy of crack formation.

REFERENCES

1. KYUTT, R. N., LEPNEVA, A. A., LOMAKINA, G. A., MOKHOV, E. N., TREGUBOVA, A. S., SHEGLOV, M. M. & YULDASHEV, G. F., *Fiz. Tverd. Tela*, **30** (1988) 2606.
2. MOKHOV, E. N., RADOVANOVA, E. I. & SITNIKOVA, A. A. Abstracts of *3rd Int. Conf. on SiC (ICACSC '90)*, Washington DC, 1990, p. 6.
3. MOKHOV, E. N., RADOVANOVA, E. I. & SITNIKOVA, A. A. Abstracts of *4th Int. Conf. on SiC (ICACSC '91)*, Santa Clara, 1991, p. V. 7.
4. LEVIN, L., TAIROV, YU. M. & TSVETKOV, V. F., *Fiz. Techn. Poluprodn.*, **18** (1981) 747.
5. KYUTT, P. N., MOKHOV, E. N. & TREGUBOVA, A. S., *Fiz. Tverd. Tela*, **23** (1981) 3496.
6. KULISH, U. M., *Izv. Acad. Nauk SSSR Neorgan. Mater.*, **24** (1988) 563.
7. VODAKOV, YU.A., MOKHOV, E. N., RAMM, M. G. & ROENKOV, A. D., *Krist. Techn.*, **14** (1981) 729.
8. CHERNOV, A. A., *Modern Crystallography* (in Russian), Vol. 4, Nauka, Moskow, 1981, pp. 7–232.
9. *Microhardness: Its Theory and Practice with the Reichert Microhardness Tester*, Vienna, 1950.
10. MOTT, B.W., *Micro-Indentation Hardness Testing*, Butterworths, London, 1956.
11. GIRKA, A. L., MOKRUSHIN, A. D., MOKHOV, E. N., OSADCHIEV, B. M., SVIRIDA, S. V. & SHISHKIN, A. V., *J. Exper. Theor. Phys. (in Russian)*, **97** (1990) 578.
12. SITNIKOVA, A. A., MOKHOV, E. N. & RADOVANOVA, E. I., *Phys. Stat. Sol.*, **135A** (1993) K45–K49.
13. KALABUKHOVA, E. N., LUKIN, S. N., SHANINS, B. D., ARTAMONOV, L. V. & MOKHOV, E. N., *Fiz. Tverd. Tela (Leningrad)*, **32** (1990) 818 [*Sov. Phys. Solid State*, **32** (1990) 482].
14. MOKHOV, E. N., RADOVANOVA, E. I. & SITNIKOVA, A. A., *Springer Proceedings in Physics Vol. 56, Amorphous and Crystalline SiC III*, Springer-Verlag, Berlin, 1992, p. 231.
15. LEVIN, V. L., TAIROV, YU.M. & TSVETKOV, V. F., *Izv. Acad. Nauk SSSR Neorgan. Mater.*, **13** (1977) 254.
16. ALEXANDER, H., *Rad. Eff. Def. Sol.*, **111-112** (1989) 1.
17. MILVIDSKY, M. G. & OSVENSKY, V. B., In *Structural Defects in Semiconductor Crystals* (in Russian), Metallurgy, Moscow, 1984, 256pp.