The Influence of High-Power Ion Beams and High-Intensity Short-Pulse Implantation of Ions on the Properties of Ceramic Silicon Carbide

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Abstract. The paper is focused on the study of the structural, electrical and optical characteristics of the ceramic silicon carbide before and after irradiation in the regimes of the high-power ion beams (HPIB) and high-intensity short-pulse implantation (HISPI) of carbon ions. The dominant mechanism of transport of charge carriers, their type and the energy spectrum of localized states (LS) of defects determining the properties of SiC were established. Electrical and optical characteristics of ceramic before and after irradiation are determined by the biographical and radiation defects whose band gap (BG) energy levels have a continuous energetic distribution. A dominant p-type activation component of conduction with participation of shallow acceptor levels 0.05–0.16 eV is complemented by hopping mechanism of conduction involving the defects LS with a density of $1.2{\cdot}10^{17}$–$2.4{\cdot}10^{18}$ $eV^{-1}{\cdot}cm^{-3}$ distributed near the Fermi level.The effect of radiation defects with deep levels in the BG on properties change dominates after HISPI. A new material with the changed electronic structure and properties is formed in the near surface layer of SiC after the impact of the HPIB.

1. Introduction

Silicon carbide SiC is a wide-band semiconductor material promising for high-power, high-temperature and radiation-resistant electronic devices. That stimulates study of the influence of the various kinds of radiation on the characteristics of SiC and of devices based on it [1–3]. SiC has a high chemical and mechanical resistance [3–5]. The band gap (BG) of SiC depending on the polytype varies in range 2.83–3.23 eV, and the threshold energy of defect formation it is 25–35 eV, that defines the high radiation resistance of the material. The characteristics of localized states in the BG of radiation defects (RD) induced by high-energy particles and their effect on properties of material depend on the type of particle and on the mode of irradiation [1–3]. The study of the effect on the properties of RD in the ceramic SiC is difficult and leads to ambiguous results owing to its complex structural hierarchy and high content of impurities and biographical defects (BD). Improvement of electrical characteristics of the epitaxial layers of SiC in devices is achieved by the ion implantation and subsequent thermal annealing owing to an annihilation and redistribution of RD and modify of the structure of the material surface [4–7]. High-intensity short-pulse implantation (HISPI) of ions followed by heating of the surface layer provides simultaneous annealing of RD [8, 9].

The aim of the work is to study the structural, electrical and optical characteristics of ceramic SiC before and after irradiation in the regimes of high-power ion beams (HPIB) and HISPI of carbon ions C^+ and to establish the reasons of the properties change.

2. Experimental

The investigations of morphology of the ceramic surface before and after irradiation by methods described in [8] were performed by scanning electron microscopy. The elemental composition was studied by energy dispersive microanalysis. Raman spectra were studied by using spectrometer Nanofinder (λ=532 nm). The dark surface conduction σ and photoconduction $\Delta\sigma_{ph}=\sigma_{ph}-\sigma$ (σ_{ph} is conduction under lighting), photosensitive $K(U, T, h\nu)=\Delta\sigma_{ph}/\sigma$ were measure data constant voltage on the electrodes U=0.01–300 V, at temperature T=300–700 K, and photon energy hν=1.5–4.0 eV. The temperature dependences of σ, $\Delta\sigma_{ph}(T)$ were approximated by the equation for activation mechanism

$$\sigma_a(T) = \sigma_0 \times e^{(-\varepsilon_\sigma / k \cdot T)}, \qquad (1)$$

where σ_0 is a pre–exponential factor, ε_σ is an activation energy, k is the Boltzmann constant and by the equation for the hopping mechanism of transfer between the localized states (LS) near the Fermi level E_F in BG in the Mott model

$$\sigma_p(T) = \sigma_0' \times e^{(-(T_0 / T)^{0.25})}, \qquad (2)$$

where σ'_0 is a pre–exponential factor, T_0 is an activation energy [10]. The LS density $N(E_F)$ near the Fermi level was calculated from T_0 according to [10]. The sign of the dominant charge carriers was determined by the photo- and thermostimulated current amplitude $I_{PhTSC}(I_{TSC})(T, h\nu, U=0)$ [10]. The spectral dependence of the absorption coefficient α(hν) in the intervalhν=1.4–3.6 eV was calculated from the spectra of the diffuse reflection [11].

3. Result and discussion

Ceramics after irradiation by HPIB (samples SiC1,2) at the energy density J=2.4 J/cm^{2}andatthe number of pulses n=3, 50is characterized by the presence of cracks and pores on the surface due to the high-speed cooling of the melt and peculiarities of structure of SiC. Melting occurs more rapidly and in a higher volume of the near surface layer of SiC with growing of n. Melting not fixed after HISPI at J=0.2–0.3 J/cm^{2}and n=300 (samples SiC 3–5). The inclusions of metals are identified: Fe (0.03–0.31 at.%), Cr and Ni (≤0.03 at.%). The obvious differences between the unirradiated SiC and SiC, irradiated by HPIB and HISPI, is not found according to X-ray analysis. Both modifications of the silicon carbide such as cubic SiC-3C and hexagonal presented by the polytypes 2H, 4H and 6H were revealed. Raman spectra indicate the presence of impurity of amorphous a–C, existing prior to irradiation, or introduced after implantation. The line of silicon at ν=520 cm^{-1}after the HPIB increases with n growth and after HISPI this line is suppressed. The lines at ν=500–1000 cm^{-1}fixed after the HPIB correspond to a carbide phases. The lines atν=795 and 972 cm^{-1}correspond to optical transverse and longitudinal oscillations of the 3C–SiC and line at ν=778 cm^{-1}to optical transverse oscillations of the 4H (6H)–SiC. Both polytypes of 4H(6H)–SiC and 3C–SiC were detected after HISPI. Here with the ratio of the hexagonal phase to a cubic was higher than after HPIB.

Current voltage characteristic (CVC) I(U) of the SiC before the irradiation are nonlinear and obeys the power $I \propto U^s$ (s=1.5–2) or the polynomial law $I=a\cdot U^2+b\cdot U+c$ ($a=(4–20)\cdot 10^{-7} A\cdot V^{-2}$, $b=(2–9)\cdot 10^{-7}$ S, $c=(2–40)\cdot 10^{-8}$ A, a/b=2.5–3.3) (figure 1). It is typical for epitaxial SiC [1, 2]. CVC allows us to conclude that the concentration of electrical active defects N', their population by charge carriers n' and their degree of population n'/N' increase with depth of level ε in BG. The exponential distribution of the LS on energy N'(ε) is realized in analogy with [1, 10, 11]. The coincidence of the CVC at U>0 and U<0 indicates a weak influence of the space charge on the dependence σ(U). Annealing until T=700–800 K increases the value of σ in 2–3 times due to the redistribution of charge carriers between shallow (ε_σ<0.1 eV) or more deep traps ($\varepsilon_\sigma \geq 0.1$ eV). Ceramics has a weak photosensitivity K≤0.01 due to the influence of the BD with a high concentration of N>10^{18} cm^{-3}distributed on the grain boundaries. Then–type of σ_{ph} and σdominates, as photo and thermostimulated currents I_{PhTSC}(I_{TSC})(T) show. Influence of the donor BD having the impurity or vacancy nature on the transport of charge carriers prevails. Temperature dependences ofσ, σ_{ph}(T) within the intervalT=300–700 K are determined by the thermally stimulated electron exchange between shallow donor levels with the activationenergies$\varepsilon_{\sigma1}$=0.06–0.061 eV, $\varepsilon_{\sigma2}$=0.2–0.21 eV,$\varepsilon_{\sigma3}$=0.4–0.43 eV and conduction band (CB) (figure 2). Population of traps by charge carriers is redistributed between the single levels of energy $\varepsilon_{\sigma1-3}$aftersequential heating owing to low values of their degree of population n'/N'=10^{-10}–10^{-6}. The factor σ_0 indicates that $(n'/N')_3 >> (n'/N')_2 >> (n'/N')_1$. The values ε_σ below their values for intrinsic defects of SiC [1–3] due to the interaction between BD and a continuous distribution of LS in the BG, by analogy with [10, 11]. The shallow donor levels with ε_σ<(0.1–0.3) eV may be due to impurity atoms N and Ti or vacancy V_{Si}^{2-} [1, 2]. Oxygen atoms (content<5.5 at. %) in complexes with BD as well as Vatoms have a deep levels (ε=0.65–1.59 eV [2]), which impact on reduce of values of σ.

The electrical parameters ε_σ, σ_0, K, n'/N' indicate the effect on transport of the hopping conduction that is verified by approximation σ(T) by the Eq. (2) within the interval T=300–700K. LS density with the participation of which carried out σ_p(T) is N(E_F)=(2–9)·$10^{17}$$eV^{-1}$·$cm^{-3}$. The value of the most probable jump distance calculated according to [10] with the values N(E_F) is R=7–11 nm. The electronic structure of materials such as ceramics can be described in frame of the model with the function N(ε), which varies little with depth of LS in BG [10, 11]. The sharp edges of the valence band (VB) and CB as in crystals do not exist. Fermi level in SiC is pinned near the middle of the BG at ε=1.5 eV due to the high concentration of defects and impurity atoms O, V, Ti. This is confirmed by low values of $\sigma \leq 2\cdot10^{-6}$S (figures 1 and 2) and K≤0.01 and by localization of a strong bands at energies ε=1.4 and 1.7 eV in the absorption spectra $\alpha(h\nu)$. Despite the dominance of n–type of σ and σ_{ph} we cannot exclude the influence of acceptor defects on the properties.

Irradiation of SiC significantly alters the morphology and structure of the surface and thin near surface layer (until 200 nm), which is reflected in CVC, σ(T), in change of the type of σ (n→p) and in parameters $\varepsilon_{\sigma,}$ σ_0, T'_0, σ'_0, N(E_F), R and in spectra $\alpha(h\nu)$ (figures 1–3). Influence of HPIB and HISPI on properties change is different (figures 1–4). Changes of the elemental composition of SiC after HPIB and HISPI showed that increase of the content of silicon from 20 to 40 at. % has the greatest effect on the growth of conduction (figure3). At the same time the content of carbon atoms in layers of SiC decreases from 80 to 40 at. % and oxygen decreases from 6 to 1 at. % (figure 4). A similar correlation between the content of C, Si and concentration of the donors was fixed in 6H–SiC (n–type ofσ) [2]. HPIB significantly increases σ and changes its characteristics (figures 1 and 2). CVC becomes almost linear (s=0.99–1.05, a/b=0.01–0.02) (figure 1). The depth of the shallow centers decreases from $\varepsilon_{\sigma1}$=0.06 to 0.034 eV and from $\varepsilon_{\sigma2}$=0.21 to 0.123 and 0.155 eV and values of $(n'/N')_{1,2}$ increases in 10^2–10^3 times as shown a factor σ_0. The deep centers with $\varepsilon_{\sigma3}$ do not appear. Currents I_{TSC}(T) and their ε_σ indicate the predominance of exchange between holes and VB and LS with $\varepsilon=\varepsilon_v+\varepsilon_{\sigma1,2}$ (ε_v is the top of VB).The manifestation of stable defects V_C–C_{Si} is more probable in SiC with p–type of conduction while the defects $V_{Si}^{-(2-)}$ dominate in case of n–type of σ[1, 2]. Shallow acceptor levels are associated with impurity of Al (≤0.09 at.%) whose energetic levels at $\varepsilon=\varepsilon_v$+(0.1–0.3) eV activated by interaction with RD[2]. I_{PhTSC}(T)<0 show that deep donor levels withε>1.5 eV have the effect on parameters also.LS density for hopping conduction increases from N(E_F)=(2–9)·$10^{17}$to (1.2–2.4)·$10^{18}$$eV^{-1}$·$cm^{-3}$,and jump distance decreases from R=7–11 to 5–7 nm, which means increasing the role ofσ_p. The surface morphology change occurs due to its melting and the impact of nanoparticles of Si, C and metals. Partial annealing of RD and their association in a complex with BD occur owing to heating of surface.

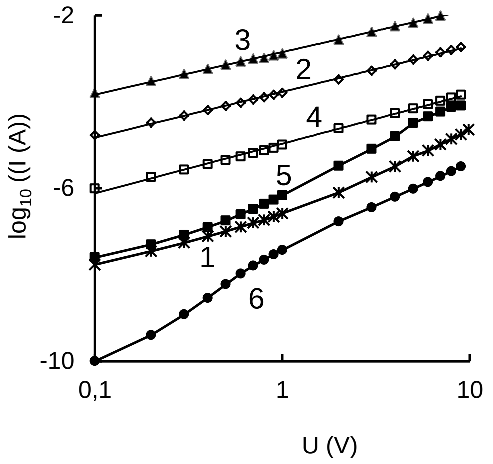

Figure 1. CVC of SiC before (curve 1) and after HPIB (curves 2 and 3) and HISPI (curves 4–6): J=2.4 J/cm^2, n=3 (curve 2), 50 (curve 3); J=0.2–0.3 J/cm^2, n=300 (curves 4–6).

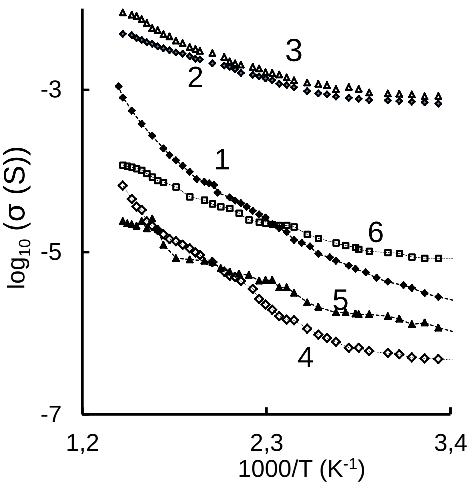

Figure 2. Temperature dependencies σ(T) of SiC before (curve 1) and after HPIB (curves 2 and 3) and HISPI (curves 4–6): J=2.4 J/cm^2, n=3 (curve 2), 50 (curve 3); J=0.2–0.3 J/cm^2, n=300 (curves 4–6).

After HISPI σ decreases or not changes and nonlinearity of CVC increases (s=1.2–2.3, a/b=2–5) (figure1).This is caused by the accumulation of RD with deep LS that are centers of trapping of charge carriers. Parameters of RD with$\varepsilon_{\sigma1}$are close to their values prior to irradiation and of centers with $\varepsilon_{\sigma2}$– to parameters levels induced by HPIB. Deep centers with $\varepsilon_{\sigma3}$ appear also. Effect of donors increases, as shown I_{TSC}(T).LS density for realization of σ_p is $N(E_F)=(1.2–11)\cdot10^{17}eV^{-1}\cdot cm^{-3}$ at R=6–12 nm. LS density decreases with σ increasing. Comparison of parameters of σ_p and σ_a shows that the influence of BD after HISPI is more greatly than after HPIB. Interrelation between electrical parameters allows to clarify mechanism of transport charge (figure 4).

Value of α decreases in 2–5 times after HPIB while α not changes or increases in 1.2–1.5 times after HISPI. Shape of α(hν) after HPIB changes similarly as in SiC after a powerful laser irradiation[6]. Absorption band at 1.4–2.8 eV induced by BD (concentration $N=(2–20)\cdot10^{18}cm^{-3}$) separates from the band of interband absorption at 2.8–3.3 eV characteristic for amorphous and highly

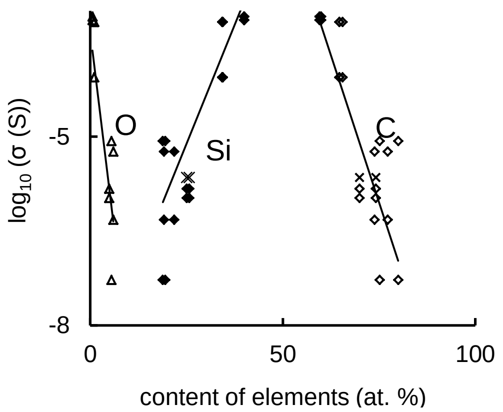

Figure 3. Effect of the elemental composition of SiC on its conduction σ before and after irradiation in the regimes of HPIB and HISPI.

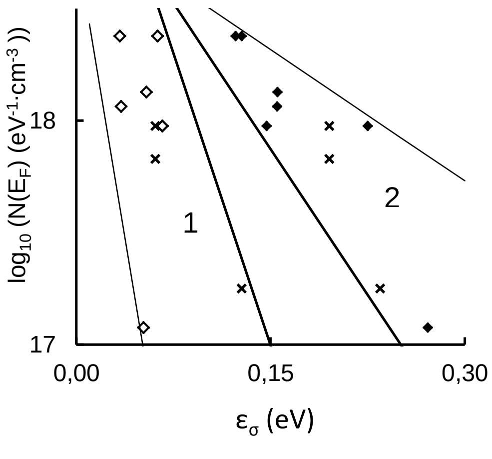

Figure 4. N(E_F) vs. $\varepsilon_\sigma$in SiC before (x) and after irradiation (♦, ◊).

defective materials. Average value of BGE$_{g0}$=3 eV is in limits of the values E_g=2.83–3.23 eV peculiar to different polytypes of SiC [6].Conservation of this band after HISPI indicates a negligible change of the absorption edge.Accumulation of the RD levels after HISPI strengthens the pinning of E_F near the middle of BG. There are three groups of bands with centers at ε_1=1.4 eV; ε_2=1.72 eV, ε_3=2.4 eV. The concentration of these centers before irradiation is: $N_1=(2–2.3)\cdot10^{18}cm^{-3}$, $N_2=(5–7)\cdot10^{19}cm^{-3}$, $N_3=(6–7.3)\cdot10^{18}$ cm^{-3}. After HPIB $N_1=(1–1.2)\cdot10^{18}cm^{-3}$,$N_2=(2–2.2)\cdot10^{19}cm^{-3}$, $N_3=(2.5–2.7)\cdot10^{18}cm^{-3}$. Taking into account [1, 2] bands with ε_{1-3}were identified with vacancy RD $V_{C,Si}$. Single RD clearly manifest after HISPI. Transitions between the LS with a continuous distribution dominate after HPIB. Formation after HPIB of a new material with changing electronic structure and properties has an effect on dependencies $\alpha(\sigma,\varepsilon_\sigma)$ also. Dependency $N(E_F)(\varepsilon_\sigma)$ in SiC before and after irradiation is typical for materials containing a high concentration of defects (figure4) [10]. Parameters $N(E_F)$ and ε_σ are distributed on two arrays for shallow and more deep centers (figure4). Decrease of LS density from $N(E_F)=2.4\cdot10^{18}$to $1.2\cdot10^{17}eV^{-1}\cdot cm^{-3}$correlates with the increasing of absorption coefficient from $\alpha=3\cdot10^3$to $10^4cm^{-1}$and decreasing of $\sigma$by analogy with [10]. The impact of σ_p on transport charge for values $N(E_F)$ and ε_σ in band 1 is higher than in band 2 (figure4).

4. Conclusion

Electrical and optical properties of SiC ceramic before and after irradiation are conditioned by BD and RD whose levels are continuously distributed on energy in BG. Defects and impurities with high concentration $(2–20)\cdot10^{18}cm^{-3}$are heterogeneously distributed along the boundaries between the structural fragments of ceramic. The activation component of the p–type conduction after irradiation is realized in the exchange of holes between the VB and shallow acceptor levels with the activation energy of ε_σ<0.3 eV and is complemented by the hopping mechanism of transport on LS near the Fermi level which localized in the middle of BG. Density of LS for realization of hopping conduction is changed after irradiation from $(2–9)\cdot10^{17}$ to $(1.2–24)\cdot10^{17}eV^{-1}\cdot cm^{-3}$ and impact of hopping component on electrical parameters is amplified. Influence of RD with deep levels on the optical and electrical properties of SiC dominates after HISPI. A new material with the changed electronic structure and properties is formed in the near surface layer of SiC after the impact of the HPIB.

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