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A. F. Ioffe Physico-Technical Institute, Academy of Sciences of the USSR, Leningrad

Silicon Carbide Doped with Gallium

By

YU. A. VODAKOV, G. A. LOMAKINA, E. N. MOKHOV, E. I. RADOVANOVA,
V. I. SOKOLOV, M. M. USMANOVA, G. F. YULDASHEV, and B. S. MACHMUDOV

Silicon carbide (SiC) films doped with gallium are obtained during the process of epitaxial growth using the sublimation variant "sandwich method" or diffusion. It is determined by neutron activation analysis that the gallium solubility in SiC in the temperature range 1800 to 2400 °C does not exceed $1.2 \times 10^{19} \text{ cm}^{-3}$ at growth on the $\langle 0001 \rangle$ plane of substrate, but is lower at growth on the $\langle 000\bar{1} \rangle$ plane and in the mentioned temperature range the solubility changes from 2×10^{18} to $7 \times 10^{18} \text{ cm}^{-3}$. Data obtained correlate with the hole concentration value in these films determined from the analysis of the temperature dependence of Hall-effect. The thermal activation energy of gallium in SiC defined from the electroconductivity is equal to 0.29 eV. Low-temperature photoluminescence is investigated of SiC samples doped with gallium and nitrogen with n- and p-type conductivity. The absorption spectra are given of grown crystals stimulated by optical transitions between gallium levels and valence band. It is shown that the parameters of the gallium diffusion in SiC excepting the accessible surface concentration are close to the parameters of aluminium diffusion. The surface concentration of gallium does not exceed $7 \times 10^{17} \text{ cm}^{-3}$ at the diffusion.

Слои карбида кремния (SiC), легированные галлием, получены в процессе эпитаксиального наращивания с использованием сублимационного варианта „сэндвич-метода” или путём диффузии. Нейтронно-активационным анализом установлено, что растворимость галлия в SiC в диапазоне температур 1800 до 2400 °C не превышала $1,2 \times 10^{19} \text{ см}^{-3}$ при росте на $\langle 0001 \rangle$ грань подложки, а при росте на $\langle 000\bar{1} \rangle$ грань она ниже и в указанном температурном интервале изменяется от 2×10^{18} до $7 \times 10^{18} \text{ см}^{-3}$. Полученные данные коррелируют со значением концентрации дырок в этих слоях, определёнными из анализа температурной зависимости эффекта Холла. При этом термическая энергия активации галлия оказывается равной 0,29 эв. Исследована низкотемпературная фотолюминесценция образцов SiC, легированных галлием и азотом, электронного и дырочного типов проводимости. Приводятся спектры поглощения выращенных кристаллов, обусловленные оптическими переходами между уровнями галлия и валентной зоной. Показано, что параметры диффузии галлия в SiC, за исключением поверхностной концентрации, близки к таковым у алюминия.

It is known that gallium in silicon carbide is a luminescence-active acceptor impurity [1 to 3]. However, the information given in the quoted papers is confined only to the analysis of luminescence parameters of gallium-doped SiC; especially measurements of the gallium concentration were not performed in these papers. The main reason for the small number of papers on the gallium behaviour in SiC is connected with the difficulties of impurity introduction

during the growth of SiC single crystals by the Lely method [4]. In this work a method is used which allows to control the doping of silicon carbide with gallium. Data on electrophysical, luminescence, and optical properties of the material are given.

Two methods of doping with gallium — diffusion and epitaxial growth — were tried. In both cases the doping component was in the vapour phase. The used system allowed to carry out simultaneously diffusion and epitaxial layer growth under the same conditions (for example, the same gallium vapour pressure). The characteristic diffusion distributions of gallium obtained by the p-n junction method [5] can be described by an erfc function. The surface concentration of gallium amounts to $(5 \text{ to } 7) \times 10^{17} \text{ cm}^{-3}$, in other words (as it will be seen from the following), it is one order lower than the gallium concentration in epitaxial layers. Therefore inversion of conductivity-type was not observed during diffusion annealing on n-type samples with non-compensating donor concentration ($N_D - N_A$) greater than $5 \times 10^{17} \text{ cm}^{-3}$.

The temperature dependence of the gallium diffusion coefficient is represented in Fig. 1 and is expressed by the equation

$$[D(T)]_{\text{Ga}} = 0.17 \times \exp\left(\frac{-5.5 \mp 0.2}{kT}\right) \text{ cm}^2/\text{s}.$$

The parameters of gallium diffusion are very close to the corresponding parameters of aluminium diffusion in SiC [5].

Unfortunately, the penetration depths of gallium are so small that it is difficult to study gallium-diffused layers. Therefore epitaxially grown layers were used for the investigation of gallium-doped SiC. The growth was carried out by the known "sandwich method" improved in such a way that transport of SiC from the source to the substrate was realized not through the gas transport reactions, but through the vapour phase created by sublimation of SiC itself.

The growth took place in vacuum-tight graphite capsules of special purity in an inert gas atmosphere at temperatures from 1800 to 2400 °C. Pure single crystals of n-SiC (6H) with $(N_D - N_A)$ equal to $1 \times 10^{17} \text{ cm}^{-3}$ were used as substrates. Plates of polycrystalline SiC of semiconductor purity or specially pure fine-grained β -SiC obtained by synthesis from methyltrichlorosilane were taken as vapour sources.

Elementary gallium was used as doping component and was placed in the "colder" part of the capsule with a temperature ranging from 1600 to 1800 °C. By changing the composition of the vapour phase, for example by temperature variation of the gallium vapour source or introduction of nitrogen vapour into the system, it was possible to obtain gallium-doped SiC films of p- and n-type conductivity with different degree of compensation.

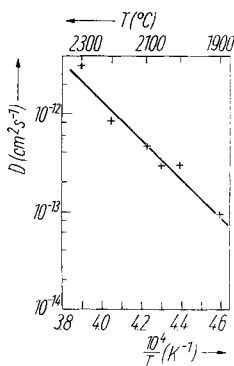


Fig. 1. Dependence of the gallium diffusion coefficient on reciprocal temperature

The velocity of epitaxial layer growth depended essentially on temperature, gallium vapour pressure, and gap size. Usually it was changed from 5 to 100 μm per h.

The quality of epitaxial layers was controlled by optical microscopy and X-ray topography. The dislocation density amounted to 10^2 to 10^3 cm^{-2} , and as a rule it was lower than in the substrates.

In order to determine the solubility of gallium and to investigate the physical parameters of SiC:Ga, films with a thickness of 50 to 250 μm were grown. The total gallium concentration in the doped SiC films was determined with the help of neutron activation analysis using the nuclear reaction $\text{Ga}^{71}(n, \gamma)\text{Ga}^{72}$ (the half-life of the isotope is about 14 h). The samples were irradiated in the channel of the BBP-CM reactor with a flow of 1.8×10^{13} neutrons/ cm^2s during 10 h. From an autoradiographic study of the activated samples it was found that the distribution of gallium in the epitaxial layers was uniform and, as a rule, without apparent inclusions of a second phase. Inclusions of a second phase sometimes appeared in highly doped gallium samples which were grown at high gallium vapour pressure. They were localized on the periphery of the samples. These parts of the crystals were removed before the determination of the solubility. The obtained values of gallium concentration dissolved in SiC at different temperatures are given in Fig. 2. It is seen that the gallium solubility depends on the orientation of the crystal plane, but with rising temperature this difference becomes smaller. In the 1800 to 2200 $^\circ\text{C}$ range the gallium solubility in the epitaxial films grown in $\langle 0001 \rangle$ direction does not change (within the experimental accuracy of the neutron activation analysis, $\approx 15\%$), but in films grown in $\langle 000\bar{1} \rangle$ direction the solubility increases considerably with rising temperature.

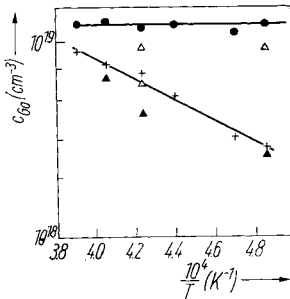


Fig. 2

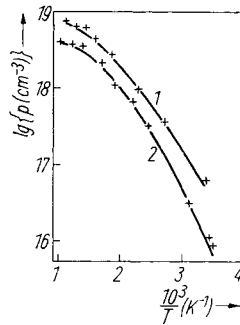


Fig. 3

Fig. 2. Gallium concentration in epitaxial layers grown in $\langle 0001 \rangle$ (●) and $\langle 000\bar{1} \rangle$ (+) direction. Δ , \blacktriangle acceptor concentrations, taking into account compensation: Δ determined by the method of [6]; \blacktriangle determined by measurement of the Schottky barrier capacitance

Fig. 3. Temperature dependence of the free hole concentration in epitaxial layers doped with gallium. (1) direction of growth is $\langle 0001 \rangle$; (2) direction of growth is $\langle 000\bar{1} \rangle$. $T_{\text{growth}} = 2100^\circ\text{C}$. (1) $(N_A - N_D) = 8 \times 10^{18} \text{ cm}^{-3}$, $N_D = 4 \times 10^{17} \text{ cm}^{-3}$, $\mu_p = 63 \text{ cm}^2/\text{Vs}$;

(2) $(N_A - N_D) = 4 \times 10^{18} \text{ cm}^{-3}$, $N_D = 1 \times 10^{18} \text{ cm}^{-3}$, $\mu_p = 46 \text{ cm}^2/\text{Vs}$

Fig. 3 shows the typical temperature dependences $\lg p = f(1/T)$ measured on epitaxial films grown in the same run on the (000 $\bar{1}$) "carbon" planes and (000 $\bar{1}$) "silicon" planes of n-type crystals. From a comparison with the results of neutron activation analysis it is concluded that practically the total gallium concentration is in the electrically active state. The ionization energy of gallium is, within experimental errors, equal to 0.29 eV for concentrations $N_A = (2 \text{ to } 8) \times 10^{18} \text{ cm}^{-3}$. The best agreement of theoretical Hall curves with experimental ones was obtained at $N_D = 1 \times 10^{18} \text{ cm}^{-3}$ and $N_D = 4 \times 10^{17} \text{ cm}^{-3}$ for films grown on "C" and "Si" planes, respectively, with $N_V/gT^{3/2} = 5 \times 10^{16} \text{ cm}^{-3}$. It is interesting to note that the same value of $N_V/gT^{3/2}$ was found for p-type samples obtained by long-time boron diffusion into initial n-SiC (6 H) samples with concentration $(N_D - N_A) = 5 \times 10^{17} \text{ cm}^{-3}$. Such a great value of the effective density of states (about one order greater than for a simple valence band with $m_p = m_0$) is stipulated by the complex structure of the valence band, which consists of three bands in α -SiC, two of which, E_1 and E_3 , have anisotropic effective mass; the third one, E_2 , is the band of heavy holes [7].

Gallium-doped SiC films below room temperature show one intensive photoluminescence (PL) band in the green-blue part of the spectrum. The most effective photoluminescence was observed in compensated samples with $N_{Ga} = N_N = 10^{18} \text{ cm}^{-3}$. Such samples had a long after-glow in the green-blue part of the spectrum. It is necessary to note that a rather intensive photoluminescence remained in samples with an extremely high level of gallium doping ($\approx 1.2 \times 10^{19} \text{ cm}^{-3}$). Photoluminescence spectra were recorded with the spectrophotometer DFS-12 at 77 and 4.2 K. Spectrophotometer and photomultiplier were calibrated with the help of a standard tungsten lamp. Fig. 4 (curve 1) shows a 77 K PL spectrum of p-type samples grown at 2350 °C. An analogous

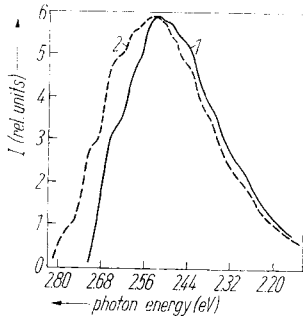


Fig. 4

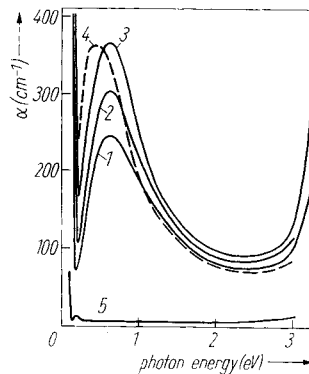


Fig. 5

Fig. 4. Luminescence spectra (77 K) of epitaxial layers doped with gallium and grown at different temperatures. (1) 2350 °C, gallium concentration $6.6 \times 10^{18} \text{ cm}^{-3}$; (2) 1800 °C, gallium concentration $2.7 \times 10^{18} \text{ cm}^{-3}$. Direction of growth is $\langle 0001 \rangle$

Fig. 5. Absorption spectra of SiC epitaxial layers doped with gallium. $E \perp c$, $T = 20^\circ \text{C}$, direction of growth $\langle 0001 \rangle$. Gallium concentration: (1) $5.6 \times 10^{18} \text{ cm}^{-3}$, (2) $9.6 \times 10^{18} \text{ cm}^{-3}$, (3) $1.23 \times 10^{19} \text{ cm}^{-3}$; (4) absorption of samples doped with aluminium [10]; (5) absorption of a pure sample

spectrum was observed on other samples grown at temperatures higher than 2100 °C.

The luminescence spectrum does not depend on the type of conductivity. However, the positions of characteristic points in the emission spectrum differed from sample to sample. It is due to the different relative intensity of luminescence bands of which the integral spectrum consists.

In the same figure (curve 2) a PL spectrum of a sample grown at lower temperature (≈ 1800 °C) is included. In this case the character of PL is more complex. It consists of a spectrum represented by curve 1, and a so-called "blue" luminescence which is characteristic of "pure" SiC crystals, the latter being due to donor-acceptor nitrogen-aluminium pair emission [8, 9]. The relative contribution of the "blue" luminescence increases with decreasing growth temperature and with decreasing gallium-to-nitrogen ratio. n-type samples with gallium concentration smaller than $5 \times 10^{17} \text{ cm}^{-3}$ and nitrogen concentration greater than $2 \times 10^{18} \text{ cm}^{-3}$ showed bright "blue" photoluminescence. Lowering the crystal temperature to 4.2 K led to a small relative intensification of the "blue" band, but the green "gallium" band practically did not change.

In Fig. 5 the absorption spectra of p-type samples with different gallium doping are given. The absorption coefficient was determined from transmission measurements of epitaxially grown samples. Thin platelets (75 to 100 μm) were prepared by mechanically removing the substrate. The reflection coefficient was taken equal to 0.185. It is seen from Fig. 5 that a broad asymmetric absorption band with maximum near 0.6 eV appears in the spectrum of gallium-doped samples. The absorption coefficient rises with increasing gallium concentration. The short-wave wing of this band extends up to the interband absorption. The lineshape of the absorption band observed in the spectrum of gallium-doped samples is similar to that observed on aluminium-doped samples [10], but the former is shifted to larger energies by about 0.15 to 0.20 eV. For comparison the absorption spectrum of aluminium-doped samples from [10] is shown in Fig. 5 by a dashed line.

Apparently the observed absorption is connected with the photoionization of acceptor centres as in the case of aluminium doping [10]. The activation energy of gallium evaluated from this spectrum is about (0.35 ± 0.06) eV.

It is interesting to note that the ratio of activation energies of gallium and aluminium, which substitute silicon atoms in SiC, is close to the activation energy ratio of these impurities in silicon.

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