Semiconductors, 2022, Vol. 56, No. 2

Study of heavily doped *n*-3*C*-SiC epitaxial films grown on 6*H*-SiC semi-insulating substraes by sublimation method

© A.A. Lebedev, V.Yu. Davydov, I.A. Eliseev, S.P. Lebedev, I.P. Nikitina,
G.A. Oganesyan, A.N. Smirnov, L.V. Shakhov

Ioffe Institute,
194021 St. Petersburg, Russia

E-mail: shura.lebe@mail.ioffe.ru

Received October 11, 2021
Revised October 18, 2021
Accepted October 18, 2021

Heavily doped 3*C*-SiC films based on semi-insulating 6*H*-SiC substrates were obtained by sublimation epitaxy. The structural perfection of the obtained samples was monitored by X-ray diffractometry. The measurements of the photoluminescence and Hall effect spectra have confirmed the rather high perfection of the obtained epitaxial layers.

Keywords: SiC, heteroepitaxy, cubic silicon carbide, X-ray diffractometry, Hall effect, photoluminescence.

DOI: 10.21883/SC.2022.02.53047.9752

1. Introduction

Among more than two hundred silicon carbide polytypes, one of the most interesting is the cubic polytype (3*C*-SiC). It has the highest mobility among SiC polytypes with mobility $1200\,\mathrm{cm^2/B\cdot c}$ [1], the value of which is independent of the crystallographic direction. Other parameters of 3*C*-SiC (critical field, maximum operating temperatures, electron saturation rate, thermal conductivity) slightly differ from the parameters of hexagonal polytypes. At the same time, both the Laley method [2] and the modified Laley method [3]used to obtain bulk crystals of SiC hexagonal polytypes fail to grow 3*C*-SiC. In 70-th of the last century a technology was developed for obtaining 3*C*-SiC single crystals by the thermal decomposition of trichlorosilane in hydrogen on a heated graphite substrate [4]. However, this method failed to obtain crystals larger than a few millimeters in size. Later, the technology of gas-phase epitaxy of 3*C*-SiC films based on silicon substrates was proposed [5]. With the help of this method, layers of cubic silicon carbide of a large area are obtained, but due to a significant mismatch of crystal lattices ($\sim 20\%$) and low growth temperatures, limited by the melting temperature of silicon, the structural perfection of the obtained films remains low. This does not allow the resulting 3*C*-SiC layers use for the industrial production of semiconductor devices. An alternative technology for growing epitaxial layers of cubic silicon carbide is sublimation epitaxy of 3*C*-SiC based on hexagonal polytype substrates (6*H*-SiC, 4*H*-SiC), whose lattice constants differ in the third decimal place. Previously, we shown the possibility of obtaining thick epitaxial layers of 3*C*-SiC based on substrates of various SiC hexagonal polytypes with an area of $0.5-0.8\,\mathrm{cm^2}$ with a sufficiently high structural perfection [6–9].

The purpose of this paper is to obtain by sublimation heteroepitaxy method and to study heavily doped n^+-3*C*-SiC epitaxial layers. Such layers can be used as emitters in creating various device structures. The resulting layers were studied by Raman spectroscopy (RSS), photoluminescence (PL), and X-ray diffractometry. The concentration of free charge carriers and their mobility were determined based on measurements of the Hall effect.

2. Growth technology

Semi-insulating 6*H*-SiC substrates were used to grow 3*C*-SiC epitaxial layers. Growth was carried out at temperatures of $1800-2000^\circ\mathrm{C}$. The growth time was $1-2\,\mathrm{h}$. To clean the surface of the substrate an oxidation operation was used, followed by chemical removal of the oxide. Oxidation was carried out in a separate reactor in a humid oxygen atmosphere for 3 h at temperature of $1100^\circ\mathrm{C}$. The oxide was etched in hydrofluoric acid followed by a standard washing operation in deionized water and organic solvents.

Commercial SiC with a grain size of $\sim 10-20\,\mu\mathrm{m}$ was used as a growth source. In a series of experiments, silicon (2% of the total mass of the source) with the same grain size was added to the composition of the source. As the source is used, its silicon content runs down, and the density of defects increases in subsequent experiments. To avoid this, we enriched the source with pure silicon. Since the source silicon runs down as the source is used, the defects density at the boundary of the double position increased in subsequent experiments.

Growth was carried out on industrial 6*H*-SiC substrates manufactured by JSC „Svetlana-Electronpribor“. Immediately before he start of growth, sublimation etching of the substrate *in situ* was performed to remove the layer damaged by mechanical polishing and to clean the substrate surface.

3. Results and discussion

Previously, based on optical and X-ray measurements, it was shown that the quality of the grown layer is strongly affected by the crystallographic orientation of the substrate surface. The sizes of twins grown on Si (0001)-faces were almost by order of magnitude smaller than those grown on *C*-faces. Besides, the thickness of the twin boundaries on the Si-face was much larger. This indicates a higher density of defects at the boundary of the twinning regions. In addition to the size of the twins, the difference between the faces was in the number of inclusions of the 6*H* polytype in the cubic epitaxial layer [9]. For this reason, in the present paper, growth was carried out on *C*-face of the 6*H*-SiC substrate. The growing epitaxial layer was doped with nitrogen during growth.

The study of the structural perfection of the obtained samples was carried out on double-crystal spectrometer assembled on the basis of industrial diffractometer DRON-3. We used a wafer of dislocation-free 6*H*-SiC grown by Lely method as a monochromator. This made it possible to avoid the dispersion contribution to the broadening of the rocking curves obtained in the ω-scanning geometry in the first order of reflection (Fig. 1, *a*).

To reliably separate the reflections from 6*H*-SiC and 3*C*-SiC, the rocking curves in the $(\omega, 2\omega)$-scanning geometry were measured on the second reflection order (Fig. 1, *b*).

As can be seen from Fig. 1, *b*, the angular distance between the reflections of 6*H* and 3*C* polytypes (0.079°) almost completely coincides with the calculated values for perfect crystals (0.08°), which indicates the absence of stresses in the direction of the growth axis. On the rocking curve in ω-scanning geometry, there is a broadening of the reflections from both 6*H* substrate and the 3*C* layer (Fig. 1, *a*). This indicates the formation of a dislocation structure at the polytypes interface under the selected technological modes.

RSS and PL studies of 3*C*-SiC samples were carried out using a T64000 spectrometer (Horiba Jobin-Yvon, Lille, France) equipped with a confocal microscope. Micro-RSS spectra were measured at room temperature. The second harmonic of the Nd : YAG laser, $\lambda_{\text{exc}} = 532\,\text{nm}$, was used as the excitation source. Micro-PL spectra were measured in the temperature range $T = 10-300\,\text{K}$. The forth harmonic of the Nd : YAG laser, $\lambda_{\text{exc}} = 266\,\text{nm}$ (4.66 eV) was used as the excitation source. In this case, the laser power on the sample was $\sim 1.5\,\text{MW}$, and the spot size was $\sim 6\,\mu\text{m}$ in diameter, which corresponds to the laser power density on the sample $\sim 5 \cdot 10^3\,\text{W/cm}^2$.

As an example, Fig. 2 shows the Raman spectra for some of the studied 3*C*-SiC samples. The spectra were measured in the $z(xx)\bar{z}$ backscattering geometry, where z axis is directed perpendicular to the (001) sample surface. According to the selection rules for such scattering geometry, only longitudinal optical vibrations (LO) are allowed in the Raman spectra of cubic structurally perfect samples. However, for all samples, the spectra of which are shown in Fig. 2, „forbidden" transverse optical vibrations (TO) are also observed, the occurrence of which, as a rule, is associated with the presence of defects in the crystal structure.

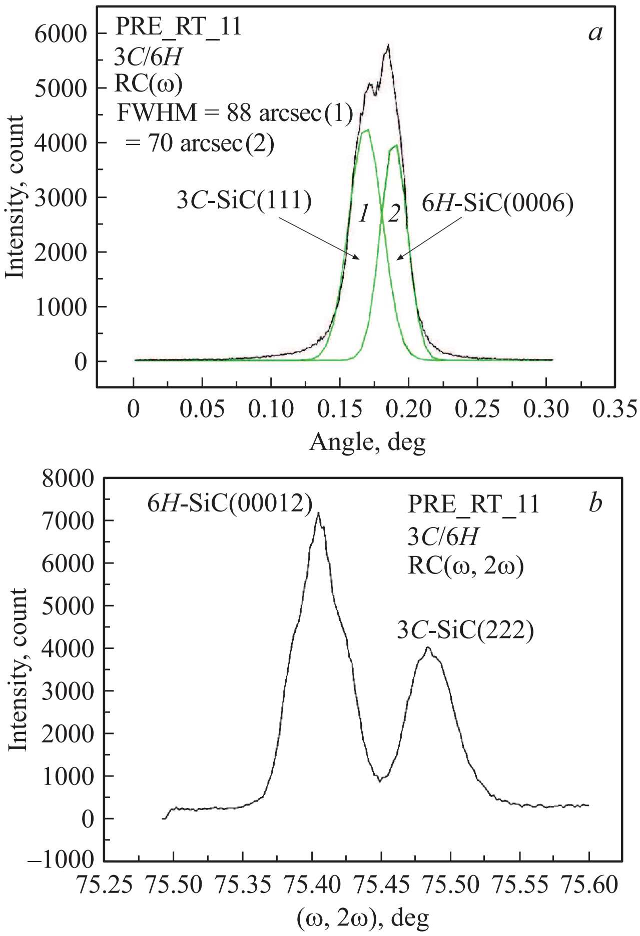

Figure 1. Rocking curves obtained in ω-scanning geometry (*a*) and $(\omega, 2\omega)$-scanning geometry (*b*) of the studied samples 3*C*-SiC/6*H*-SiC.

It is clearly seen that the position of the TO modes in the spectra of all samples is retained, while the position of the LO modes and their shape vary considerably. It is known that in polar materials, which also include SiC, longitudinal optical phonons can interact through a macroscopic electric field with collective excitations of free carriers (plasmons). This leads to the formation of two modes (L^- and L^+ modes), which have a mixed plasmon-phonon nature. With an increase in the concentration of free charge carriers (n), their position in the spectra undergoes a high-frequency shift and a significant broadening of the bands occurs. Studying the energy position of mixed modes using various models makes it possible to estimate the value n in SiC [10–12]. To estimate n in the studied samples, we used graphs relating the position of the L^+ line and the electron concentration, which were calculated up to the values $n < 2-2.5 \cdot 10^{18}\,\text{cm}^{-3}$ for 3*C*-SiC in papers [10,12]. The position of the L^+ band maximum in the spectrum of

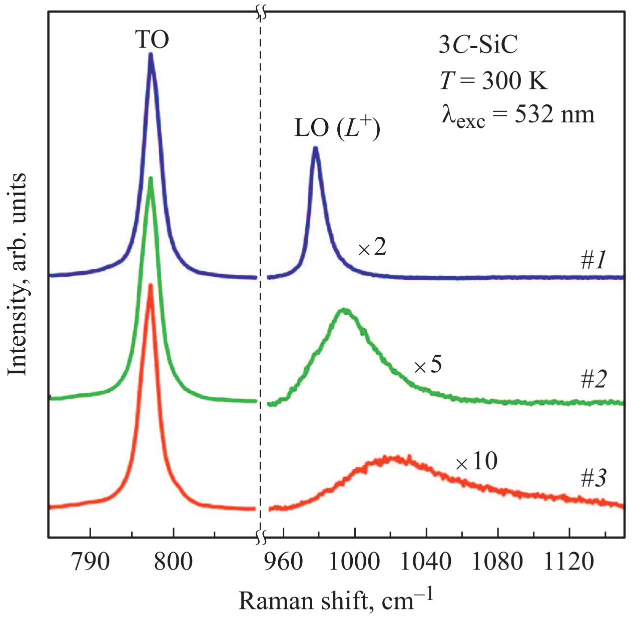

Figure 2. Raman spectra for some of the studied samples $3C$-SiC obtained after subtracting the spectrum of $6H$-SiC substrate.

sample 1 ($\sim 977\,\mathrm{cm}^{-1}$) corresponds to $n \sim 1.3 \cdot 10^{18}\,\mathrm{cm}^{-3}$. The positions of the L^+ band maximum in sample 2 ($\sim 993\,\mathrm{cm}^{-1}$) and in sample 3 ($\sim 10^{20}\,\mathrm{cm}^{-1}$) are well outside the dependences $n < 2{-}2.5 \cdot 10^{18}\,\mathrm{cm}^{-3}$, indicating a much larger value of n. As was shown in paper [13], for $n > 5 \cdot 10^{18}\,\mathrm{cm}^{-3}$ the shape of the band L^+ (and consequently, the position of its maximum, from which the value of n is estimated) strongly depends on the parameter characterizing the decay of the plasmon, and for concentrations exceeding the indicated value, the quantitative estimates of n from the RSS data are in poor agreement with the data obtained by the Hall method.

As an example Fig. 3 shows the PL spectra obtained in a wide temperature range $T = 10{-}300\,\mathrm{K}$ for sample 1 with $n \sim 1.3 \cdot 10^{18}\,\mathrm{cm}^{-3}$. In the spectra measured at room temperature $T = 300\,\mathrm{K}$, a relatively broad peak X (2.28 eV) associated with the forbidden band is observed. Previously, lines similar to the X peak were observed only in $3C$-SiC single crystals at low temperatures. In the low-temperature spectra measured at $T = 80$ and $10\,\mathrm{K}$ a monotonous decrease in the X peak width is observed without any noticeable change in its energy position, which is consistent with the undirect-band nature of the fundamental optical transition in $3C$-SiC. In the low-temperature spectra a broad intense band is also observed, the structure of which is represented by a narrow peak of the zero-phonon line (ZPL), followed by phonon replicas. According to papers [14,10], this PL band is due to the recombination of carriers localized at the donor and acceptor levels bound to N and Al. As can be seen from Fig. 3, the presence of a thin structure in the photoluminescence spectrum of the nitrogen–aluminum pair (donor–acceptor), as well as the presence of exciton photoluminescence confirm the good structural perfection of the grown epitaxial layers.

For measurements by the Hall effect method, epitaxial samples were grown on semi-insulating substrates with high ohmic resistance. As a result of this, it was possible to exclude the influence of the substrate on the conductivity of the epitaxial layers. Ohmic contacts were fabricated to for epitaxial layers by Ni–Ti sputtering followed by their combusting-in at temperatures of 1100°C. The measurements were carried out in the temperature range from liquid nitrogen to room temperature. Figure 4 shows the electrons concentration in the conduction band vs. temperature. From the slope of this dependence the ionization energy

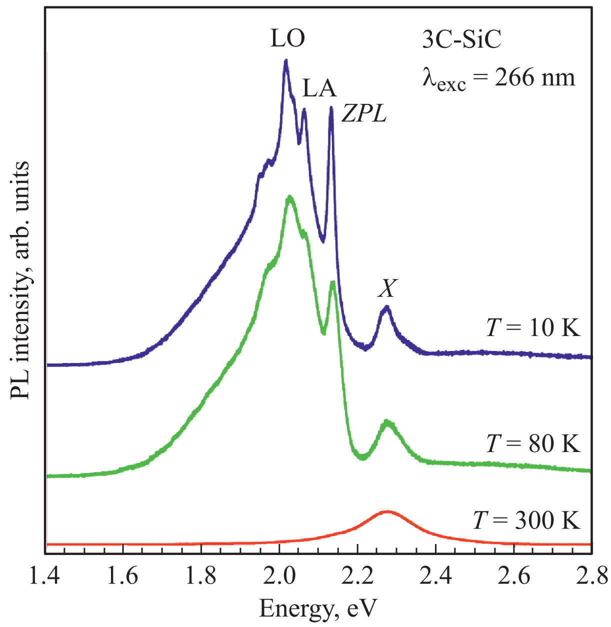

Figure 3. PL spectra of the $3C$-SiC layer recorded at several temperatures. The spectra are normalized to the peak associated with the forbidden band X and are shifted along the vertical axis for clarity.

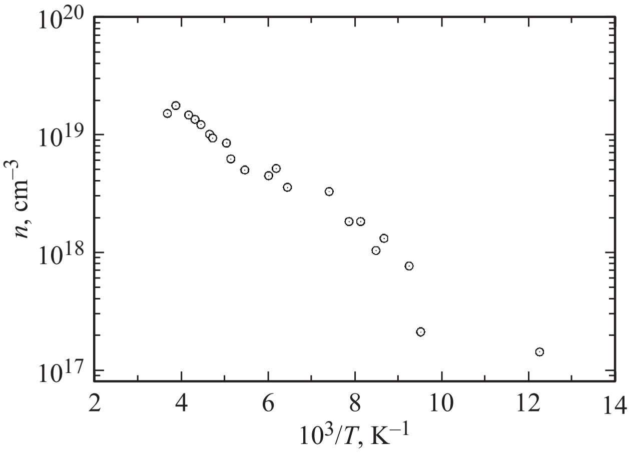

Figure 4. Electrons concentration in the studied samples n-$3C$-SiC vs. temperature.

of the main donor level was calculated, which was equal to 0.056 eV. This value is in good agreement with the literature data on the ionization energy of the nitrogen level in 3C-SiC [1].

The electron mobility was $20-40\,\mathrm{cm^2/V\cdot s}$, which is also close to known literature data for samples with close value of N_d-N_a.

4. Conclusion

A study was made of 3C-SiC epitaxial films grown under technological conditions optimized in the previous work. The technology for growing highly doped 3C-SiC layers was developed. The sufficiently good structural perfection of the grown films was confirmed by X-ray diffractometry. In the PL spectrum, even at room temperature a peak associated with the recombination of a free exciton was observed. The measurements of the Hall effect confirmed the high level of samples doping.

Funding

This work was made with the support of Russian Foundation for Basic Research No. 20-0200117.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] *Properties of Advanced Semiconductor Materials: GaN, AlN, InN, BN, SiC, SiGe*, eds M.E. Levinshtein, S.L. Rumyantsev, M.S. Shur (John Wiley & Sons, N.Y.—Chichester–Weinheim—Brisbane Singapore—Toronto, 2001).

[2] J.A. Lely. Ber. Dt. Keram. Ges, **32**, 229 (1955).

[3] Yu.M. Tairov, V.F. Tsvetkov. J. Cryst. Growth, **43**, 209 (1978).

[4] S.N. Gorin, L.M. Ivanova. Phys. Status Solidi B, **202**, 221 (1997).

[5] S. Nishino, J. Powel, N.A. Will. Appl. Phys. Lett., **42**, 460 (1983).

[6] A.A. Lebedev, E.V. Bogdanova, P.L. Abramov, S.P. Lebedev, D.K. Nel'son, G.A. Oganesyan, A.S. Tregubova, R. Yakimova. Semicond. Sci. Technol., **23**, 075004 (2008).

[7] D.V. Davydov, A.A. Lebedev, A.S. Tregubova, V.V. Kozlovski, A.N. Kuznetsov, E.V. Bogdanova. Mater. Sci. Forum, 338—342, 221 (2000).

[8] A.A. Lebedev, P.L. Abramov, V.V. Zelenin, E.V. Bogdanova, S.P. Lebedev, D.K. Nelson, B.S. Razbirin, M.P. Shcheglov, A.S. Tregubova, M. Suvajarvi, R. Yakimova. FTP, **41** (273), (2007) (in Russian).

[9] L.V. Shakhov, A.A. Lebedev, N.V. Seredova, S.P. Lebedev, V.V. Kozlovski, A.V. Zubov, I.P. Nikitina. Mater. Sci. Forum, **1004**, 278 (2020).

[10] J.A. Freitas, jr., W.J. Moore. Braz. J. Phys., **28** (1), 12 (1998).

[11] S. Nakashima, H. Harima. Phys. Status Solidi A, **162**, 39 (1997).

[12] N. Piluso, A. Severino, M. Camarda, R. Anzalone, A. Canino, G. Condorelli, G. Abbondanza, F. La Via. Mater. Sci. Forum, **645—648**, 255 (2010).

[13] M. Chafai, A. Jaouhari, A. Torres, R. Anton, E. Martin, J. Jimenez, W.C. Mitchel. J. Appl. Phys., **90**, 5211 (2001).

[14] A. Suzuki, H. Matsunami, T. Tanaka. J. Electrochem. Soc., **124**, 241 (1977).