

SILICON CARBIDE FOR SOLAR ENERGY.

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ABSTRACT

SiC is a wide-bandgap semiconductor that possesses quite a number of interesting properties and is promising for application in power, high-temperature, and radiation hard electronics. Several areas can be distinguished in which SiC is also a promising material for solar power engineering. SiC high temperature power devices and UV detectors can be used at solar energy stations and also SiC can be used as a substrate for growth III-N materials and graphene. New results obtained at the Ioffe Institute, Nitride Crystals Co and National Research University of Information Technologies, Mechanics and Optics in all the above areas of research will be presented in the report

INTRODUCTION

In modern semiconductor physics there are now two very rapidly developing direction of work:

1) changing the properties of a material by modifying the geometric dimensions of the structures, i.e. the physics of nanostructures, and

2) the development and study of the new semiconductor materials.

Important work in the second direction involves the study of wide-gap semiconductors. The potential possibilities of wide-gap materials for creating semiconductor devices were analyzed a long time ago [1-3]. band gap large than in Si and GaAs gives these materials the following advantages:

- ▲ a large operating temperature;
- ▲ ability to construct visible-range, light-emitting devices based on these materials;
- ▲ high critical breakdown fields;
- ▲ high radiation resistance.

In Table 1 presented main parameters of some semiconductor materials.

Table 1 lists the main parameters of some semiconductor materials. It can be seen that wide-bandgap semiconductors surpass in their basic parameters the "classical" materials of semiconductor electronics, with diamond being the most promising. However, there exist several unsolved technological problems (e.g., lack of n⁺ layers), which make presently impossible development of power devices based on this material.

Table 1. Parameters of some semiconductor materials.

| | Si | GaAs | 4H-SiC | GaN | Diamond |
|---|------|------|--------|------|---------|
| Eg, eV | 1,12 | 1,43 | 3,26 | 3,39 | 5,45 |
| Direct band structure | | + | | + | |
| Breakdown field, MV/cm | 0,3 | 0,6 | 2-3 | >3 | 10 |
| Thermo conductivity, Wt/cm*K | 1,5 | 0,46 | 4,9 | 1,3 | 11 |
| Electron mobility, cm ² V*s | 1500 | 8500 | 1100 | 1250 | 2200 |
| Presents of own substrate | + | + | + | | |
| Debye temperature | 650 | 350 | 1200 | 600 | 1850 |
| Saturation velocity, x 10 ⁷ cm/s | 1 | 1 | 2 | 2,5 | 2,7 |

Comparison of SiC and GaN shows that GaN and solid solutions based on this compound surpass all other materials used to manufacture of light-emitting and microwave devices. At the same time, the thermal conductivity lower than that of SiC, problems in

fabricating a heavily doped P⁺ emitter, and lack of a substrate of the same material make GaN less promising for development of power bipolar devices, compared with silicon carbide. However, it is possible that, owing to their substantially lower production cost, GaN Schottky diodes will be competitive with SiC Schottky diodes at voltages of up to 1000 V [4].

The aim of this study was to analyze the possible applications of silicon carbide for modern solar energy.

HIGH TEMPERATURE STABILITY AND RADIATION RESISTANCE OF SiC DEVICES .

Table 1 lists, among other properties of semiconductor materials, the Debye temperature (T_D). It is known that this parameter is defined in terms of the maximum energy of a phonon existing in a given material

$$T_D = E_F/k \quad (1)$$

where k is the Boltzmann constant and E_F -maximum phonon energy in this semiconductor.

As the Debye temperature is exceeded, lattice vibrations become inelastic and this leads to disintegration of the material. For various semiconductors, this disintegration may occur via growth of dislocations, decomposition of binary compounds, etc. Thus, the value of T_D can be regarded as a characteristic of the upper temperature limit for operation of devices based on a given material. It is noteworthy that the T_D of GaN is lower than that of SiC. There also exists a whole class of wide-bandgap materials (II--VI) for which T_D is even lower than that of GaN. This circumstance accounts for the fact that it has been impossible so far to fabricate any high-power high-temperature devices based on II--VI compounds despite their wider energy gap.

Figures 1 and 2 show current--voltage (I--V) characteristics of high-frequency SiC P-i-N diodes fabricated at the Ioffe Institute, which confirm the above conclusion about the temperature stability of devices based on silicon carbide.

It can be seen in Figs. 1 and 2 that the height of the potential barrier in the SiC diode at 1080 K is approximately equal to the same parameter for a Si diode at room temperature. Consequently, the working temperature range of a SiC diode can be raised by 200--300°.

The radiation hardness of SiC and devices based on this material has been extensively studied (see, e.g., [5--7]). Frequently, the radiation hardness of a material has been characterized by the "carrier removal rate" parameter (Vd) calculated by the formula:

$$Vd = (N_0 - N_1) \Delta D \quad (2)$$

Here, N₀ is the N_a -- N_d concentration in the epitaxial layer prior to irradiation; N₁ is that upon irradiation, and D is the irradiation dose.

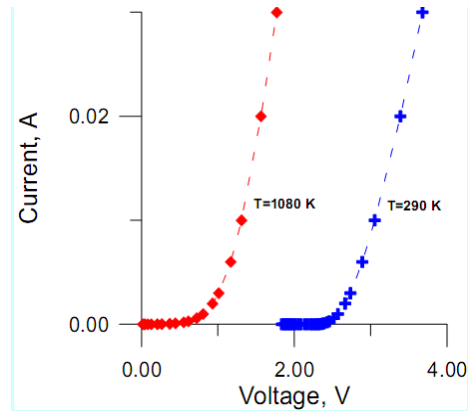


Figure 1 Temperature dependence of forward Current-Voltage characteristics of SiC HF p-i-n diode.

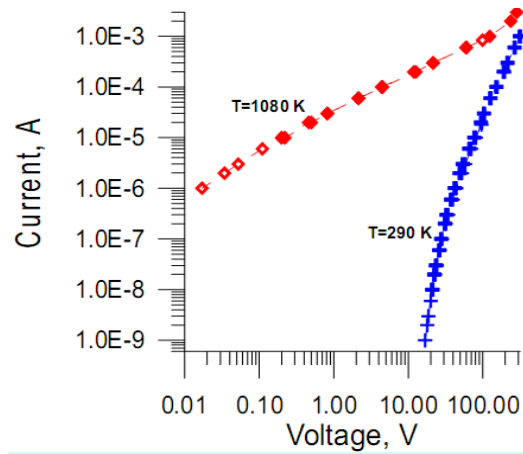


Figure 2 Temperature dependence of reverse Current-Voltage characteristics of SiC HF p-i-n diode.

Let us compare the radiation hardnesses of power devices based on Si and SiC. We consider two diodes with the same breakdown voltage, made of silicon and silicon carbide.

$$U_{brSi} = U_{brSiC} \Rightarrow (E_{cr}^{Si} W^{Si})/2 = (E_{cr}^{SiC} W^{SiC})/2 \Rightarrow W^{Si} = W^{SiC} \times E_{cr}^{SiC} / E_{cr}^{Si} \quad (3)$$

Here, U_{br} is the breakdown voltage, E_{cr} is the critical electric field strength, and W is the width of the space-charge layer at U_{br}. Taking into account that E_{cr}^{SiC}/ E_{cr}^{Si} ≈ 10 and W ~ (Nb)^{1/2}, where Nb is the concentration of the uncompensated impurity in the base region of the diode, we have

$$Nb^{Si} = 100 Nb^{SiC} \quad (4)$$

That is, the base of the SiC diode having the same breakdown voltage will be doped to a two orders of magnitude greater extent than that of the Si diode.

Consequently, even at equal values of V_d , the compensation of the silicon carbide diode will require a 100 times larger irradiation dose than that of the Si diode.

The key parameter in comparison of the radiation hardnesses of detectors is the width of the base region in which the radiation being detected is absorbed. The reverse voltage applied to these detectors is, as a rule, limited to several hundred volts. To make the space-charge layer wider at the same reverse voltage, it is necessary to use an as pure material as possible in devices of this kind. In this case, it is necessary to compare SiC and Si with the same doping level of the base region.

Table 2 lists parameters of Si- and SiC-based nuclear particle detectors upon their irradiation with 1 GeV protons at a fluence of 10^{15} cm^{-2} . It can be seen that the first two parameters nearly coincide for both types of detectors. The recharging time of the deepest radiation defect (RD) in silicon is 12 orders of magnitude shorter than that in SiC. This means that the leakage currents in silicon carbide diodes will grow upon irradiation to a considerably lesser extent as compared with Si.

Table 2. Parameters of Si and SiC detectors upon irradiation by 1 GeV protons with doze $D = 10^{15} \text{ cm}^{-2}$

| | Si | 6H-SiC |
|--|---|--|
| Maximum rate of deep center introduction, cm^{-1} | 0,20 | 0,16 |
| Lifetime, ns | $\tau_N = 0,8$ $\tau_p = 3,7$ | $T_p = 2,4$ |
| Time constant of generation from the deepest radiation defect at 300 K | E-center ($E_c - 0,44 \text{ eV}$) $\tau = 1,2 \times 10^{-6} \text{ s}$ | R-center ($E_c - 1,22 \text{ eV}$) $\tau = 1,2 \times 10^6 \text{ s}$ |
| Maximum device working temperature | $\sim 150 \text{ }^\circ\text{C}$ | $\sim 1000 \text{ }^\circ\text{C}$ |

An additional advantage of SiC detectors is their high working temperature. It is known that interaction of charged particles with the crystal lattice of a semiconductor gives rise to vacancies and interstitials, the so-called primary radiation defects. If a semiconductor is irradiated at low temperatures (0 K), these primary defects hardly recombine, being in the "frozen" state. With increasing temperature, these defects start to move and mostly recombine, with the rest forming complexes with impurity atoms or divacancies to give the more thermally stable secondary radiation defects. Finally, with the temperature increasing further, the secondary defects are also annealed out and the crystal returns to its initial state (that before irradiation).

The annealing stages of radiation defects have been well studied for silicon. It is known that primary defects start to be annealed at a temperature of $\sim 80 \text{ K}$, and secondary defects (A and E centers, divacancies), at temperatures

of $150\text{--}350^\circ\text{C}$. For silicon carbide, two annealing stages can also be distinguished. The first occurs in the range $200\text{--}900^\circ\text{C}$, and the second, at temperatures exceeding $1000\text{--}1200^\circ\text{C}$, when radiation defects are fully eliminated [8].

Thus, the stage in which primary defects are annealed is already complete at room temperature and has not yet commenced in SiC. Because the annealing temperature of primary RDs in silicon carbide is lower than its sublimation temperature, annealing can be used to restore characteristics of a SiC device without its thermal disintegration.

SOLAR BLIND SiC UV PHOTODETECTORS

Although these devices cannot be directly applied in solar power engineering, they can serve to detect the UV radiation level. In contrast to narrower gap semiconductors, SiC does not absorb in the visible spectral range. Therefore, operation of a SiC UV photodetector requires no expensive filters. Silicon carbide is also more promising for fabrication of these devices than other wide-bandgap materials (GaN) for the following reasons: (1) GaN is a direct gap semiconductor, and, therefore, light is absorbed near the surface and the useful signal is strongly reduced by the surface recombination, whereas SiC is a nondirect-gap semiconductor and the effect of the surface recombination is substantially weaker in this case; (2) GaN is a less structurally perfect material than SiC and contains a large number of structural defects, which give rise to leakage currents and make lower the signal-to-noise ratio.

At the Ioffe Institute, selective solar-blind UV detectors were for the first time fabricated on the basis of thin ion-implanted $p\text{--}n$ junctions formed in SiC. These detectors have a photosensitivity spectrum corresponding to the maximum effect of the carcinogenic light (247--254 nm), which is the most hazardous to human health and disintegrates the DNA (Fig. 3).

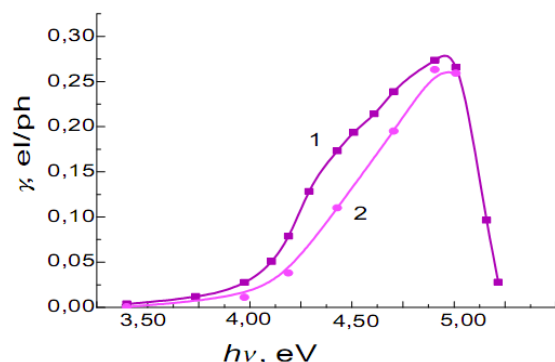


Figure 3. The spectra of the quantum efficiency measured at 300 K, 4H-SiC-based photodetectors: 1-Cr Schottky barriers; 2 - $p + - n$ junctions formed by ion-doped Al

The maximum quantum efficiency of about 0.3 electron/photon at $\lambda = 254$ nm is due to direct optical transitions with an energy of 4.9 eV between the valence and conduction bands near the Γ -point of the Brillouin zone in SiC [9--10].

The temperature coefficient of the quantum efficiency in this spectral range is less than 0.1%/K. These characteristics make it possible to regard the results of these studies as, on the whole, development of SiC-based high-temperature detectors of a new class.

SIC AS A SUBSTRATE FOR III-N GROWTH

InGaN alloys recently emerge as a new solar cell materials system due to their tunable energy band gaps (varying from 0,7 eV for InN to 3,4 eV for GaN, covering almost the whole solar spectrum) and superior photovoltaic characteristics (direct energy band gap in entire alloy range and high carrier mobility, drift velocity, and optical adsorption of 10^5 cm⁻¹ near the band edge). Theoretical calculation shows, that on this material system a solar energy conversion efficiency greater than 50% can be obtained [11].

However, there still is no commercially available GaN substrate of larger size and this material is grown on Al₂O₃ and SiC.

Compared with sapphire, silicon carbide substrates have the following advantages:

- (1) smaller lattice mismatch with GaN (3% against 20% for Al₂O₃);
- (2) higher thermal conductivity;
- (3) existence of a conducting SiC substrate (Al₂O₃ is an insulator), which enables fabrication of III--N devices on SiC in a vertical configuration.

Thus, SiC is a more promising material for fabrication of III--N solar cells than sapphire. In the Russian Federation, "Nitride Crystals" is the leading company in manufacture of SiC substrates and epitaxial GaN layers on these substrates [12--13].

GRAPHEN GROWTH ON SIC

The discovery of new nanosize forms of carbon (nanodiamonds, fullerenes, nanotubes, nanoporous carbon, graphenes, etc.) has initiated studies aimed to create "carbon" electronics as a future alternative to the highly developed silicon electronics. The finite size of these carbon nanostructures distinguishes them from the classical forms of carbon, graphite and diamond, with the stability of the appearing nanoforms determined by quantum effects in their electronic subsystem. There have already been a number of practical achievements on the way to this goal. Among these, mentioned should be made about the field-effect transistor based on a single-layer carbon nanotube, solar cells based on fullerene--polymer composites, supercapacitors based

on nanotubes, and conducting transparent electrodes for graphene-based solar cells. At present, the silicon electronics has reached the parameters determined by fundamental restrictions inherent in silicon as a material. Carbon nanostructures make it possible, in principle, to create electronic devices with characteristics that are substantially better in a number of parameters [14].

It is known that graphene, for whose discovery scientists of Russia's origin, Andre Geim and Konstantin Novoselov, were awarded the 2010 Nobel Prize in Physics, has the form of two-dimensional carbon layers [15]. Graphene possesses certain advantages making it possible to regard it as a material for fabrication of devices that implement principles of ballistic electronics, spintronics, optoelectronics, nanoplasmonics, and other promising alternatives to the conventional semiconductor electronics. Use of graphene as a basis for components of the future nanoelectronics will make it possible to overcome limitations that are characteristic of the conventional silicon electronics and are related to the degree of device miniaturization and energy consumption.

It has been shown at the Ioffe Institute that nanocarbon layers can be formed on the surface of SiC by the method of sublimation in an open system (Fig. 4). This procedure did not require any additional etching of samples in hydrogen or silicon vapor, which considerably simplifies the film growth process. The thickness of the resulting films strongly depended on the annealing temperature [16].

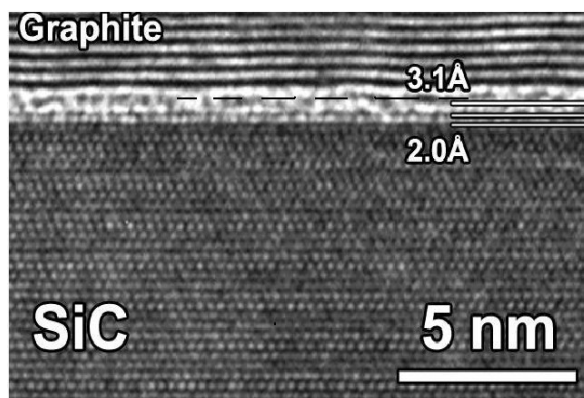


Figure 4 The image of a transversal cut of the structure graphene/SiC, obtained with a help of a high resolution transparent electron microscopy. A dotted line represents the graphene layer. 1.

To perform electrical measurements, test structures were formed on the surface of the samples in the Hall-bar configuration by means of photolithography and argon-beam milling with a photoresist mask. I--V characteristics and the Hall effect were measured in the temperature range 2--300 K. It was found that the layers are constituted by a graphene layer adjacent to the substrate and a multigraphene layer above, covered with a polycrystalline carbene-like phase. In this case, the

magnetoresistance curves and de Haas--Shubnikov oscillations exhibited features characteristic of the single-layer graphene (Fig. 5) [17].

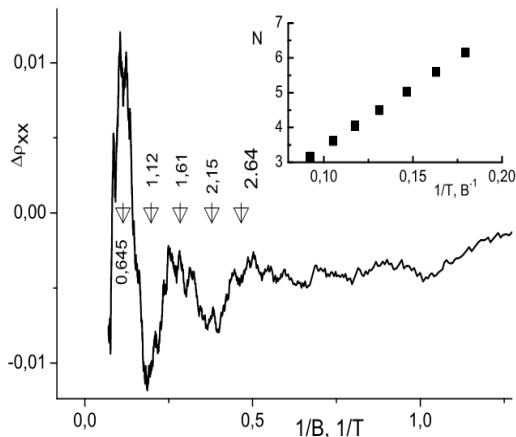


Figure 5 A curve of MR in the scale of inverse magnetic fields. The insert gives the Landau numbers as a function of the positions of SdH maxima for the oscillations of the second type.

Graphene combining transparency with high electrical conductivity can serve as an electrode material for solar cells. An additional advantage of the graphene growth on SiC is the theoretical possibility of repeatedly using the same substrate when developing a technique for detachment of a graphene film from silicon carbide.

CONCLUSION

The analysis of the experimental data obtained in the study and known published sources demonstrated that SiC is promising for application in solar power engineering. High-temperature and radiation-hard devices based on silicon carbide can be used in solar power units of both terrestrial and extraterrestrial types. In addition, SiC is the best substrate for growth of III--N solid solutions and graphene, which are promising materials for development of next-generation solar cell arrays.

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REFERENCES

[1] Jonson E.O. Physical limitations on frequency and power parameters of transistors", *RCA Review*, Vol. 26, 1965 pp 163-177,
 [2] Baliga B.J., Semiconductors for high-voltage, vertical channel field transistors, *J. Appl. Phys*, Vol 53, 1982. pp 1759-1764.

[3] Lebedev A.A. and Chelnokov V.E., Wide-gap semiconductors for high-power electronics, *Semiconductors*, Vol. 33, No. 9, 1999, pp. 999-1001.
 [4] Lei Yong, Shi Hongbiao, Lu Hai, Chen Dunjun, Zhang Rong and Zheng Youdou. Field plate engineering for GaN – based Schottky barrier diodes, *J. of semiconductors*, Vol. 34 N5 2013 p. 054007.
 [5] Luo Z., Chen T., Cressler J.D., Sheridan D.C., Williams J.R., Reed R.A., Marshall P.W., Impact of proton Irradiation on the Static and Dynamic Characteristics of High-Voltage 4H-SiC JBS Switching Diodes, , *IEEE transactions on nuclear science*, Vol. 50, 1No 6 2003, pp. 1821-1826.
 [6] Izzo G., Litrico G., Calcagno L., Foti G., and Almgobel Via F.La. Electrical properties of high energy ion irradiated 4H-SiC Schottky diodes,, *J. Appl. Phys* Vol. 104, 2008, p. 093711.
 [7] Lebedev A.A., Ivanov A.M., Strokana N.B, Radiation resistance of SiC and Nuclear-Radiation detectors Based on SiC Films (A Review), *Semiconductors* Vol 38 No2 2004 pp. 125-147
 [8] Lebedev A.A., and Kozlovskii V.V., Comparison of the radiation hardness of Silicon and Silicon Carbide. *Semiconductors*, Vol 48 No 10, 2014, pp.1293-1295.
 [9] Blank T.V. , Goldberg Y.A. , Kalinina E.V. , Konstantinov O.V., Konstantinov A.O. , Hallen A. .Temperature dependence of the photoelectric conversion quantum efficiency of 4H-SiC Schottky UV photodetectors *Semicond. Sci. Technol.*, Vol. 20, 2005 pp.710-715 .
 [10]Blank T.V. , Goldberg Y.A. , Kalinina E.V. , Konstantinov O.V., Carcinogenic UV photodetector based on 4H-SiC , *Technical Physics*, Vol 53, 2008 pp.81-84.
 [11] Dahal R., Pantha B., Li J., Lin J.Y., and Jiang H.X., InGaN/GaN multiple quantum well solar cells with long operation wavelengths., *Appl.Phys.lett.*, Vol 94 2009, p 063505.
 [12] <http://www.nitride-crystals.com>
 [13] Reschikov A.M., Usikov A., Helava H., Makarov Yu., *Fine structure of the red luminescence band in GaN*, *Appl.Phys. Let* Vol.104, 2014 p. 032103
 [14] Heer Walt A de. The invention of graphene electronics and the physics of epitaxial graphene on silicon carbide. *Phys. Scr* T146 2012, p.014004;
 [15] Novoselov K.S., Geim A.K., Morozov S.V., Jiang D., Dubonos S.V., Grigorieva I.V., Firsov A.A., Electric field effect in atomically thin carbon films, *Science* Vol 306 2004, pp.666-669.
 [16] Lebedev A.A., Agrinskaya N.V., Berezovets V.A., Kozub V.I., Lebedev S.P., Sitnikova A.A., Low temperature transport properties of graphene and multigraphene layers *Materials Science Forum*, V 740-742 (2013) 137-140.
 [17] Lebedev A.A., and Bulat P.V. Overview of the graphene production technologies and instrument application. *Life Science Journal*, Vol 11 (8s) 2014, pp. 404-409.