Semiconductor Physics, Quantum Electronics & Optoelectronics, 2007. V. 10, N 2. P. 21-25.

PACS 85.60.Y

Boron, aluminum, nitrogen, and oxygen impurities in silicon carbide

S.I. Vlaskina[1], V.I. Vlaskin[2], S.A. Podlasov[2], V.E. Rodionov[2], G.S. Svechnikov[2]
[1]Dong Seoul College, 461-714, 423,
Bokjung-Dong, Sungnam-city, Kyonggi-do, Korea
Phone: 82 (031) 7202141, fax 82(031) 7202261; e-mail: svitlana@haksan.dsc.ac.kr
[2]V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine
45, prospect Nauky, 03028 Kyiv, Ukraine
Phone: 380(44) 5253792, fax 380 (44) 5258342; e-mail: businkaa@mail.ru

Abstract. Diffusion of boron, aluminum, and oxygen was conducted at temperatures 1600 – 1700 °C. Very pure original n-SiC crystal (6H-SiC) specially grown by the Lely method annealed in oxygen during 2 h at 1700 °C, in argon during 2 h at 1700 °C, with aluminum and silicon oxide powder during 2 h, and with boron oxide and aluminum during 0.5 h. Electrical characterization of the silicon carbide samples was done by the Hall effect measurements using the square van der Pauw method to determine the sheet resistance, mobility, and free carrier concentration. The model of deep donor level as a complex of nitrogen atom replacing carbon with adjacent silicon vacancy is suggested.

Keywords: silicon carbide, diffusion, *p-n* junction.

Manuscript received 09.02.07; accepted for publication 24.04.07; published online 19.10.07.

1. Introduction

Silicon carbide devices have important applications in motor drives, in power transmission systems, in information systems, in field effect devices (MOSFET, MESFET, JFET, BJT), in the Shottky barrier diodes (SBDs), in switch elements, and in all cases where silicon-based semiconductor electronics cannot operate [1-3].

Such impurities as boron, oxygen, and aluminum are used in fabrication of all devices for the formation of junctions, contacts, and the Shottky barriers [4, 5]. Diffusion of such impurities takes place in the process of fabrication of a junction or in the process of post-implantation annealing. The diffusion experiment had been performed with boron in 4H- and 6H-SiC at temperatures between 1700 and 2000 °C.

Boron depth profiles had been measured with secondary ion mass spectroscopy on implantation and recovery annealing [6] and well described on the basis of the kick-out mechanism giving evidence for the significant role of Si self-interstitials in boron diffusion [7, 8].

Silicon carbide 6H-SiC crystals with a boron impurity on a silicon site [9] and the role of intrinsic point defects are in focus of the theoretical studies and industrial researches [10, 11]. Even the process of self-diffusion of silicon in SiC is not investigated well until now [12, 13] and a lot of fundamental questions are under investigation.

Diffusion of boron, aluminum, and oxygen had been used in the fabrication of various devices of optoelectronics [14]. The best crystals for SiC LEDs were doped by nitrogen ($10^{18}\ldots10^{19}$ cm^{-3}): 6H-SiC, 15R-SIC, 33R-SiC. In these crystals, *p-n* junction had been made by diffusion of aluminum with oxygen (from SiO powder) or boron with aluminum. Diffusion of Al with O was carried out for 2 h at 1700 ºC. Boron and aluminum were diffused for 15 min at 1600 ºC. The sources for oxygen, aluminum, and boron were SiO, 99.99 % Al, and B_2O_3, respectively. The optimal depth (1 μm) of *p-n* junctions had been obtained with the crystals heavily doped by nitrogen. But the mechanism of doping had not been yet understood.

The main goal of this article is the better understanding of the diffusion of boron and aluminum in SiC.

2. Experiment

Diffusion experiments with boron, aluminum, and oxygen were conducted at temperatures from 1600 to 1700 °C. Very pure original n-SiC crystal (6H-SiC) specially grown by the Lely method was cut into several pieces. One piece of this crystal was annealed in oxygen during 2 h at 1700 °C. Another piece was annealed in argon during 2 h at 1700 °C. The next one was annealed

© 2007, V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine

with aluminum and silicon oxide powder for 2 h for aluminum to be diffused. Later on, the same piece was annealed with boron oxide and aluminum for diffusion of boron.

Electrical characteristics of silicon carbide samples was obtained by the Hall effect measurements using the square van der Pauw samples to determine the sheet resistance, mobility, and concentration of free carrier.

According to the equation for space charge neutrality, the electron concentration at equilibrium for two different temperatures is given by:

$$\frac{n_1(n_1+N_a)}{N_d-N_a-n_1}=\beta N_c(T_1)\,e^{\frac{-\Delta E}{kT_1}}, \quad (1)$$

$$\frac{n_2(n_2+N_a)}{N_d-N_a-n_2}=\beta N_c(T_2)\,e^{\frac{-\Delta E}{kT_2}}. \quad (2)$$

Noncompensated impurities (N_d-N_a) can be determined from the extrinsic part of the carrier concentration as a function of temperature. Namely, (N_d-N_a) is virtually constant with variation in temperature, until the concentration of intrinsic carriers becomes comparable with that of extrinsic carriers.

The division of Eqs. (1) and (2) gives

$$N_c(T)\sim A\cdot T^{3/2}. \quad (3)$$

Then, writing the equation for space charge neutrality for the third temperature T_3,

$$\frac{n_3(n_3+N_a)}{N_d-N_a-n_3}=\beta N_c(T_3)\,e^{\frac{-\Delta E}{kT_3}}, \quad (4)$$

we obtain

$$N_a=B_1 f\left(e^{-\frac{\Delta E}{kT_1}}\right), \quad N_a=B_2 f\left(e^{-\frac{\Delta E}{kT_2}}\right), \quad (5)$$

which allows us to determine ΔE.

Very pure single crystal n-SiC specially grown with a concentration of about $10^{17}\ldots10^{16}$ cm^{-3} (at 300 K) and $\mu = 90$ cm^2/Vs was cut into pieces which were annealed in oxygen for 2 h at 1700 °C, in argon under the same condition, in oxygen with aluminum (99.9999) during 2 h, and with boron and aluminum in oxygen for 0.5 h.

The temperature dependence of the free carrier concentration is shown in Fig. 1.

Very pure initial (NCO-7) crystal was more compensated and had steeper (a steeper slope) behavior of the plot log $n = f(1/T)$ than others (Fig. 1a), the concentration $N_d-N_a=1.5\cdot10^{17}$ cm^{-3}, and only one donor level at 0.15 eV was working.

After annealing in argon, the concentration of acceptors was decreased, (N_d-N_a) was increased, but the plot log $n = f(1/T)$ became not so steep (Fig. 1b) and the mobility was increased by two times (Fig. 2b as compared with Fig. 2a). This can occur if the impurity distribution became more uniform. The less fold of the dependence $\mu(T)$ at low temperatures gives us an additional evidence for this fact. It can be only if the concentration of Si vacancies is decreased after annealing in argon. We suggest that Si vacancies have acceptor character.

After annealing in oxygen, (N_d-N_a) for the nitrogen level was $2.5\cdot10^{17}$ at 0.15 eV. But a new deep noncompensated donor level at 0.35 eV appeared (Fig. 1c). This level appears only after annealing in oxygen. The concentration of this level is about $1.06\cdot10^{17}$ (nearby the nitrogen concentration at the zero level of compensation).

It can be only if, at first version, oxygen is responsible for this donor level. In the second version, because the crystal surface is covered by the silicon oxide layer, some amount of Si diffuses to the surface creating new Si vacancies. These vacancies bind nitrogen and create complexes which have donor character.

The concentration of noncompensated donors was increased after annealing with aluminum in oxygen (at a level of 0.15 eV it became $4\cdot10^{17}$, and $1.5\cdot10^{17}$ at 0.35 eV) as shown in Fig. 1d. It seems unusual since the nitrogen concentration should be decreased when we add acceptor (aluminum).

But, if aluminum occupies Si vacancies, the concentration of Si vacancies will be decreased due to aluminum, some part of nitrogen will be electrically active again, and, just in this case, we can explain the increase in the free carrier concentration. The plot in Fig. 1d allows us to calculate a new deep level at 0.35 eV.

After annealing in the presence of boron, a deeper level appears (but we failed to calculate the level's energy from these data), and the compensation was increased, as usual: see Fig. 1e.

Mobility increases, in common, after annealing, but only annealing in argon leads to the increase in the mobility by two times (Fig. 2a, b). In another cases, the mobility was not so increased because we added additional scattering centers.

3. Discussion

A substitution atom of the elements of group III normally acts as an acceptor in SiC since there is a deficit of one valence electron to complete the normal tetrahedral bonding.

A substitution atom of the elements of group V acts as a donor in SiC. It was discovered that B creates a shallow, as well as a deep, acceptor level.

Nitrogen creates a shallow (six levels depending on the hexagonal-like or cubic-like position) donor's levels. The activation energies of impurities in cubic-like sites are larger than those in hexagonal-like sites.

But can nitrogen create a deep, as well as shallow, donor level?

© 2007, V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine

A model of deep acceptor level created by boron was suggested in [15, 16]. The model of Al and Ga in deep acceptor states seems to be the “element of group III – vacancy” pair.

Like the case of oxygen in silicon or nitrogen in diamond and in silicon [17, 18], there exists a mechanism for SiC which drives some impurities off the nominal substitutional sites. Acceptor Al and Ga atoms occupy the Si-substitutional on-center position and B and Be do the off-center position. Nitrogen atoms occupy the C-substitution position.

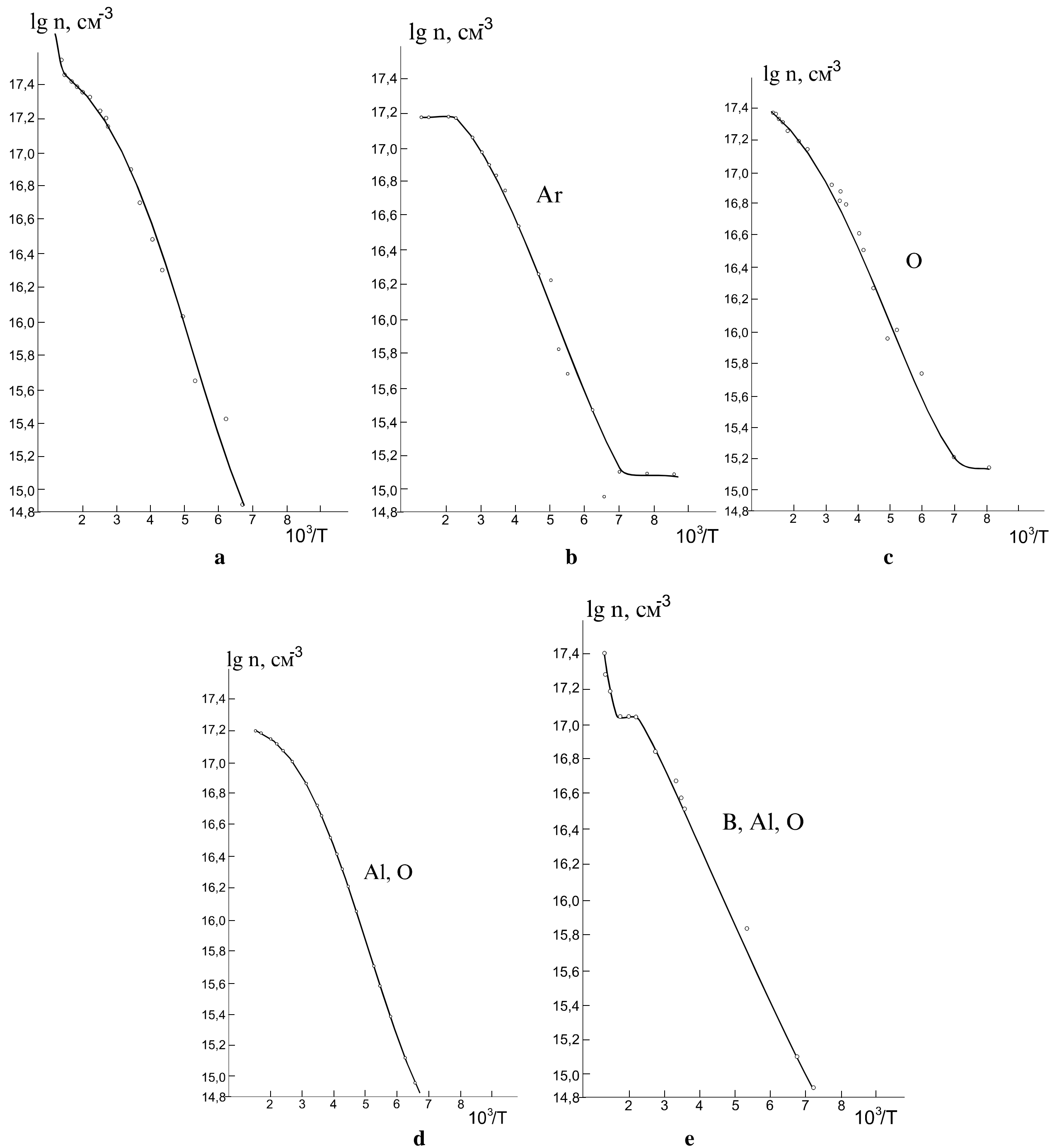
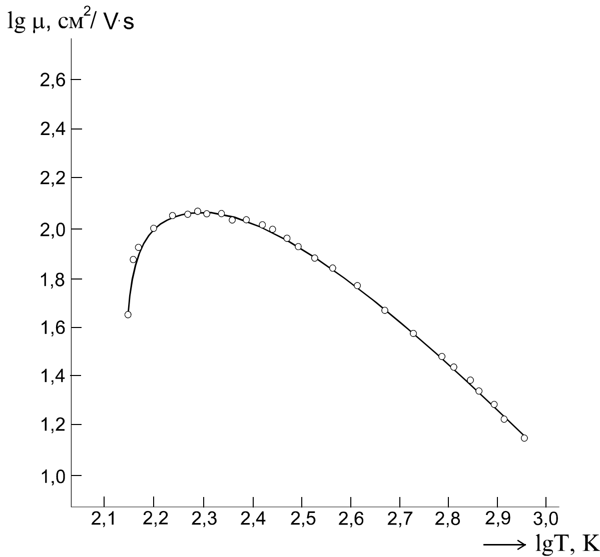
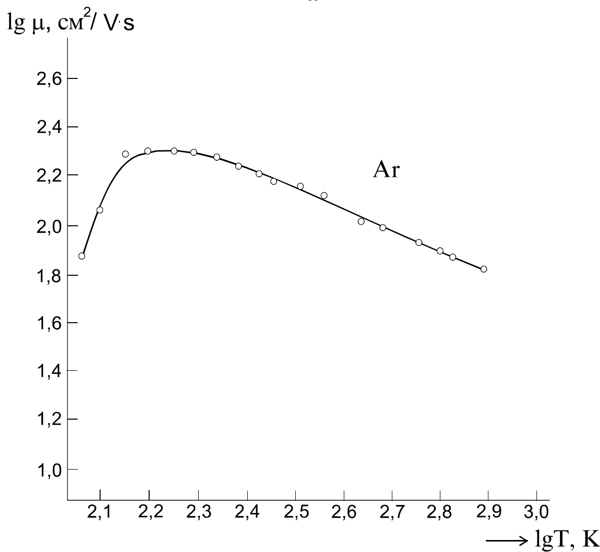


Fig. 1.

© 2007, V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine



a



b

Fig. 2.

We suggest a model of deep donor level created by nitrogen. The model of N in a deep donor state seems to be the "element of group V – vacancy" pair as N_C (like B_{Si}) [16] with the complex which consists of a nitrogen atom replacing a carbon atom (adjacent to a silicon vacancy (V_{Si}) and acts as deep donor (N_C – V_{Si})) similarly to the complex which consists of a boron atom replacing a silicon atom (adjacent to a carbon vacancy (V_C)) and acts as a deep acceptor in the (B_{Si} – V_C) in model [15, 16]

In this case, all our experiments can be explained from this point of view.

In particular, bright-yellow luminescence arises due to a deep probably aluminum-related acceptor [21] rather than due to the recombination involving a deep boron center and N donors or conduction electrons [19, 20]. We suggest that the characteristic high-temperature bright-yellow luminescence in annealed 6H-SiC [22], 4H-SiC [23], and heavy doped 6H-SiC [13] is due to the recombination involving a deep nitrogen center as the complex consisting of a nitrogen atom replacing carbon with adjacent silicon vacancies (V_{Si}) and acting as a deep donor as well. In annealed crystals, deep donors and deep acceptors exist together. The chemical nature and structure of D- and Z-centers, and the acceptor or donor character of deep levels [22, 24] are else open questions.

We mention also another possible model, in which nitrogen replacing Si with adjacent carbon vacancies (V_C) (if B can occupy a C-site, why cannot N occupy a Si-site?) creates a deep donor level. For example, a nitrogen atom responsible for 0.35 eV replaces carbon with adjacent silicon vacancies (V_{Si}) responsible for 0.74 eV or *vice versa*. But this looks not so reasonable. A nitrogen atom replacing carbon with adjacent silicon vacancies (V_{Si}) and acting as a deep donor seems more suitable.

4. Conclusion

So, we can see that all these data of the experiments with very pure SiC crystals ($10^{17}…10^{16}$ cm^{-3}) can be explained only on one base by the participation of vacancies in the diffusion process. A nitrogen atom replacing a carbon atom creates the "element of group V – vacancy" pair (N_C with adjacent silicon vacancies – V_{Si}) and acts as a deep donor (N_C – V_{Si}) similarly to the complex consisting of a boron atom replacing a silicon atom with adjacent carbon vacancies (V_C).

References

1. *http://www.grc.nasa.gov/www/SiC* (internet information).
2. S.C. Kim, W. Bahng, N.K. Kim, E.D. Kim, T. Ayalew, T. Grasser and S. Selberherr // *Materials Science Forum* **483-485**, p. 793-796 (2005).
3. S.I. Vlaskina, Silicon carbide LED // *Semiconductor Physics, Quantum Electronics & Optoelectronics*, **5**(l), p. 71-75 (2002).
4. Simulation, devices, and process technology in silicon carbide, research project of the department of microelectronics and information technology, *http://www.imit.kth.se//forskningsprojekt-detalj.html?projektid=2*
5. Dallas Morisette, Mitch McGlothlin, J.A. Cooper, Jr., M.R. Meloch, SiC Shottky barrier diodes development at Purdue // *http:/www.enc.purdue.edu/WBG/Device-research/Shottky-Diodes/index.html*
6. Diffusion in bulk crystals and heterostructures of compound semiconductors. *http://www.uni-muenster.de/Rectorat/Forschungsberichte2000/follgd03.htm*
7. H. Bracht, N.A. Stolwijk, M. Laube, G. Pensl, Diffusion of boron in silicon carbide: Evidence for the kick-out mechanism // *Appl. Phys. Lett*. **77,** p. 3188-3190 (2000).

© 2007, V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine

8. H. Bracht, N.A. Stolwijk, M. Laube, G. Pensl, Modelling of boron diffusion in silicon carbide // *Mater. Sci. Forum* **353-356,** p. 327-333 (2001).
9. Doping issues in wide band-gap semiconductors, Exeter, United Kingdom, 21-23 March, 2001. *http://widegap2001.ex.ac.uk/sic.html.*
10. M. Bockstedte, A. Mattausch, and O. Pankratov, Boron diffusion in SiC: the role of intrinsic point defects. *http://psi-k.dl.ac.uk/psi-k2000/abstracts/MichelBockstedte.html.*
11. Peter Deak, Materials characterization and modeling of SiC in Europe – From the viewpoint of a theorist // *Mater. Sci. Forum* **483-485,** p. 457-464 (2005).
12. Birnie, P. Dunbar, A model for silicon self diffusion in silicon carbide: anti-cite defect motion // *J. Amer. Ceram. Soc.* **69,** p. 33-35 (1986) (*http://www.mse.arizona.edu/faculty/birnie/abs8601.html*).
13. S.I. Vlaskina, D.H. Shin, Effect of annealing on the impurities of 6H-SiC single crystals // *Jpn J. Appl. Phys. Part 2 -Letters*, **38**, p. L861-L863 (1999).
14. S.L. Vlaskina, K.W. Kim, Y.S. Kim, Y.P. Lee, G.S. Svechnikov, Optoelectronics devices on silicon carbide // *J. Korean Phys. Soc.* **30** (910), p. 117-121 (1997).
15. P.G. Baranov, I.V. Ilyn and E.N. Mokhov // *Solid State Commun*s **100**, p. 371 (1996).
16. A.V. Duijn-Arnold, T. Ikoma, O.G. Poluektov, P.G. Baranov, E.N. Mokhov and J. Schmidt // *Phys. Rev. B* **57**(3), p. 1607 (1998).
17. G. Bachelet, G.A. Baraff and M. Schulter // *Phys. Rev. B* **22**, p. 2842 (1980).
18. S.T. Pantelides, W.A. Harrison and F. Indurain // *Phys. Rev. B* **34**, p. 6038 (1986).
19. H. Kuwabara and S. Yamada // *Phys. status solidi* (*a*) **30**, p. 739 (1975).
20. M. Ikeda, H. Matsunami and T. Tanaka // *Phys. Rev. B* **22**, p. 2842 (1980).
21. E.N. Kalabuhova, S.N. Lukin, E.N. Mokhov, J. Reinke, S. Greulich-Weber and J.M. Spaeth // *Inst. Phys. Conf. Ser.* **142**, p. 333-335 (1996).
22. W. Suttrop, G. Pensl and P. Lanig // *Appl. Phys. A* **51**, p. 231-237 (1990).
23. T. Troffer, Ch. Habler, G. Pensl, K. Holzlein, H. Mitlhner, J. Volki // *Inst. Phys. Conf. Ser.* **142**, p. 281-284 (1996).
24. P.G. Baranov and E.N. Mokhov // *Inst. Phys. Conf. Ser.* **142**, p. 293-296 (1996).

© 2007, V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine