第28卷　第1期
2007年1月

半　导　体　学　报
CHINESE JOURNAL OF SEMICONDUCTORS

Vol.28　No.1
Jan.,2007

Evidence of the Role of Carbon Vacancies in Nickel-Based Ohmic Contacts to n-Type Silicon Carbide*

Guo Hui†, Zhang Yimen, and Zhang Yuming

(*Key Laboratory of the Ministry of Education for Wide Band-Gap Semiconductor Materials and Devices, Microelectronic School, Xidian University, Xi'an 710071, China*)

Abstract: N-wells are created by P^+ ion implantation into Si-faced p-type 4H-SiC epilayer. Ti and Ni are deposited in sequence on the surface of the active regions. Ni_2Si is identified as the dominant phase by X-ray diffraction (XRD) analysis after metallization annealing. An amorphous C film at the Ni_2Si/SiC interface is confirmed by an X-ray energy-dispersive spectrometer (XEDS). The Ni_2Si and amorphous C film are etched away selectively, followed by deposition of new metal films without annealing. Measurement of the current-voltage characteristics shows that the contacts are still ohmic after the Ni_2Si and amorphous C film are replaced by new metal films. The sheet resistance R_{sh} of the implanted layers decreases from 975 to 438Ω/□, because carbon vacancies (V_C) appeared during annealing, which act as donors for electrons in SiC.

Key words: Ni; ohmic contact; silicon carbide; carbon vacancies; P^+ ion implantation
PACC: 7340C; 6170T
CLC number: TN405　**Document code**: A　**Article ID**: 0253-4177(2007)01-0005-05

1 Introduction

Silicon carbide (SiC), with its wide energy bandgap of about 3eV, is an attractive semiconductor material. Its high critical field strength and good thermal conductivity make it an excellent candidate for the development of superior high power, high-temperature, and high-frequency devices. To utilize the excellent properties of SiC in an electronic device, thermodynamically stable ohmic contacts with low specific contact resistance are important, since parasitic resistances generally limit or even jeopardize device operation. Ohmic contacts to SiC are typically formed by the deposition of transition metal layers (possibly in combination with other elements, such as silicon or carbon) onto heavily doped silicon carbide ($>5\times10^{18}cm^{-3}$) followed by high-temperature annealing (>900℃)[1~4]. Nickel is the most widely used metal for the fabrication of ohmic contacts to n-type SiC, although various transition metals have been studied extensively[5]. It is very difficult to achieve a good ohmic contact to n-SiC compared with Si and GaAs devices, and also the real mechanism of formation is not very clear yet.

Carbon vacancies (V_C) in the SiC surface just below the metals during the annealing, were thought to be the reason of the formation of ohmic contacts in the Ni/n-type SiC structure[2,6]. In this work, we attempt to prove the effect of V_C. A Philips X'PERT X-ray diffraction (XRD) system is used to identify the phase formation in the annealed contacts. Analysis of the contact morphology and the chemical composition are performed using a JSM-6360LV scanning electron microscope (SEM) and an X-ray energy-dispersive spectrometer (XEDS).

2 Experiment

The 4H-SiC wafer used in this experiment was purchased from Cree Research Company. The orientation of the substrate was 8° off-axis in the ⟨1000⟩ direction. The patterns were made on a p-type epitaxial layer with a concentration of $N_a = 1.2\times10^{16}cm^{-3}$ and depth of 2μm based on the n-type silicon-faced substrate. N-wells were formed

---

* Project supported by the State Key Development Program for Basic Research of China (No. 2002CB311904), the National Defense Basic Research Program of China (No. 51327010101), and the National Natural Science Foundation of China (No. 60376001)

† Corresponding author. Email: gyc78@sohu.com

Received 25 August 2006, revised manuscript received 17 September 2006

by P^+ ion implantation into the epilayer at 550℃. The energies and doses for ion implantation were 100keV and $8.3\times10^{14}cm^{-2}$, respectively. The targeted phosphorus concentration was $1\times10^{20}cm^{-3}$. 100nm-thick SiO_2 films were deposited on the surface of the SiC wafer. P^+ ion implantation was carried out through the oxide film in order to increase the density of effective carriers in the surface region of the SiC wafer. Post-implantation annealing was done at 1650℃ for 15min in Ar ambient, using a crucible coated by poly-SiC. The samples were cleaned in acetone before metal deposition followed by a standard RCA cleaning process.

Titanium (3nm, especially to improve adhesion) and nickel (200nm) were deposited in sequence on the surface of the whole active region. Finally, High temperature annealing was performed in N_2 for 15min at 1050℃, which is long enough to ensure that there was no further change in the characteristics of interface and electricity.

A Philips X'PERT X-ray diffraction system is used to identify the phase formation in the annealed contacts. XRD results for the prepared samples are shown in Fig. 1. A binary phase of Ni_2Si appears after the metallization annealing.

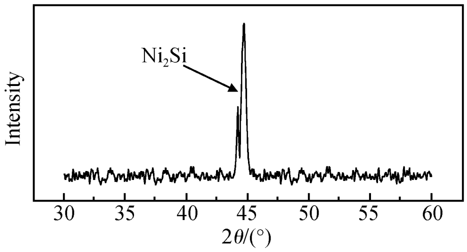

Fig. 1 X-ray diffraction of the contact system after thermal annealing

The experimental details described in the following paragraphs were designed to reveal whether changes occurred in the SiC surface underneath the contact, resulting from the annealing process which contributes to the ohmic behavior. Figure 2 shows the processing steps.

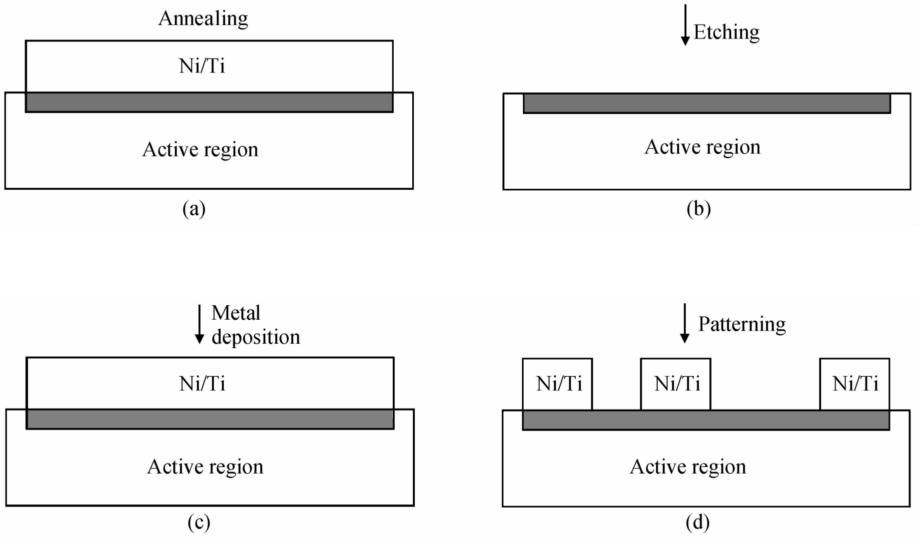

Fig. 2 Schematic illustration of the processing steps The gray areas represent the regions in the surface directly underneath the contacts which changed during the annealing.

The alloy phases formed in annealing were selectively removed from the annealed sample by etching in HF : HNO_3 (1 : 3) solution at room temperature using an ultrasonic bath. Figure 3 shows SEM images of the contact region before and after etching.

The XEDS spectrum was obtained from the active regions after etching (Fig. 4). The C atom percentage was 78.06% at the surface of the active region after the nickel silicide was removed, proving that there were redundant C atoms to form an amorphous C film on the SiC. This film was removed by oxidizing in O_2 for 15min at 500℃.

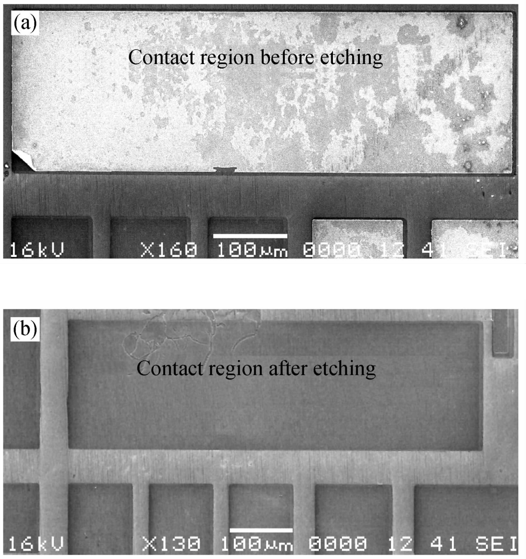

Fig. 3　SEM images of the contact region before (a) and after (b) etching

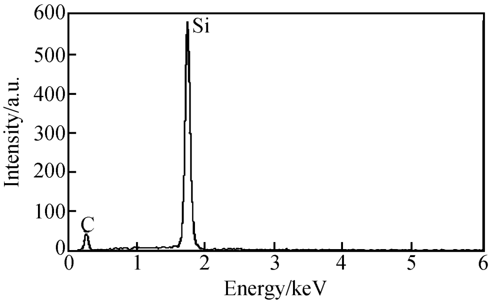

Fig. 4　XEDS spectrum of the active region after etching

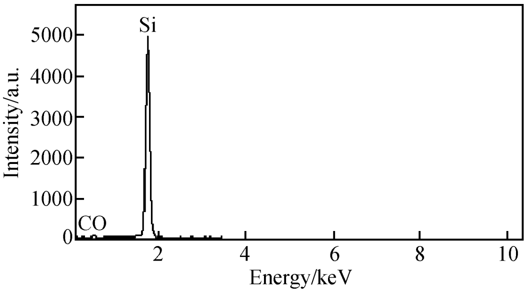

Fig. 5　XEDS spectrum of the active region after oxidizing the amorphous C film

The XEDS spectrum of the active region after oxidizing the amorphous C film is shown in Fig. 5. The atom percentages of C, Si, and O are 28.20%, 59.32%, and 14.48%, respectively. The atom percentage of C is much less than that of Si, which proves that there are carbon vacancies (V_C) in the surface region of the SiC. The presence of O is likely due to the oxidation. Furthermore, the XEDS results (Figs. 4 and 5) show that the nickel silicide was removed completely after etching and oxidizing.

The same metallization, titanium (3nm) and nickel (200nm), was deposited anew on the active regions after the HF treatment of the sample. The structures of the TLM pattern were patterned through conventional photolithography and lift-off techniques (Fig. 6). The *I-V* measurements were made on-wafer at room temperature by an Agilent 4156 semiconductor parameter analyzer. The newly deposited Ni contacts are ohmic as deposited at room temperature. In comparison, the Ni contacts that were directly deposited on n-type 4H-SiC epilayers are usually rectifying. By assuming that the length of each contact is long enough, the total resistance R_T can be expressed as

$$R_T = 2R_C + \frac{R_{sh}L}{W} \tag{1}$$

where W is the width of the contacts, and $2R_C$ is the y-intercept of the linear curve. The specific contact resistances ρ_c can be given as

$$\rho_c = \frac{(R_C W)^2}{R_{sh}} \tag{2}$$

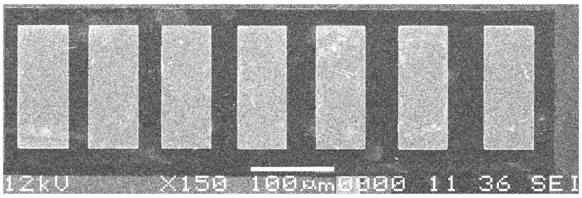

Fig. 6　SEM image of TLM structure

The lowest value of the specific contact resistances is $6.52 \times 10^{-4} \Omega \cdot cm^2$. Furthermore, the sheet resistance R_{sh} is W multiplied by the slope dR_T/dL of the linear curve shown in Fig. 7. The sheet resistance R_{sh} of the implanted layer decreased from 975Ω/□, which is comparable to that of a sample reported elsewhere[7], to 438 Ω/□.

3　Discussion

We determined that nickel silicides were formed during high-temperature annealing as a result of SiC dissociation and chemical reaction between Ni and Si. At temperatures above 950℃

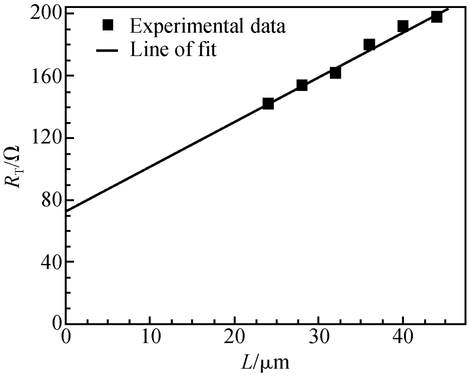

Fig.7 TLM total resistance versus gap spacing

only the Ni_2Si phase is present, which is regarded as the typical temperature to form Ni-based n-SiC ohmic contact[8]. Therefore, in many studies, the formation of Ni_2Si was considered to be responsible for the ohmic behavior of the contact[9]. However, the Schottky barrier height of Ni_2Si/n-SiC is 0.36eV higher than Ni on n-type SiC[10]. In addition, Ni_2Si already exists in the mixture of silicides at temperatures as low as 600℃, while the Schottky-ohmic transition in the contact behavior appears at temperatures around 950℃. It is apparent that Ni_2Si formation is not the major factor in forming ohmic contacts on n-type SiC.

According to thermionic field emission (TFE) and field emission (FE), when the Ni_2Si is formed during high temperature annealing, the density of effective carriers must increase at the same time. There has been some discussion of whether positively charged C vacancies may be associated with an enhanced electron concentration underneath the contacts to promote tunneling in n-type SiC[2,11]. Considering the experimental results, the formation of the ohmic contact in the Ni/n-type SiC system is deeply related to the out-diffusion of C atoms rather than the Ni silicide. In SiC, C vacancies, V_C, act as donors for electrons and Si vacancies, V_{Si}, act as acceptors for electrons. The ionization energy level of V_C is located at 0.5eV, under the bottom of the conduction band, and V_{Si} is at 0.45eV, above the top of the valence band[12,13]. High temperature annealing provides enough V_C as donors, which contribute to the formation of the ohmic contact. This is the real reason of the formation of ohmic contacts in the Ni/n-type SiC structure, that the depletion layer width and effective tunneling barrier height for the transport of electrons are simultaneously decreased, leading to the reduction of specific contact resistance.

In addition to defect-enhanced doping, another plausible explanation may be defect-assisted tunneling or recombination, via point defects near the surface and well within the band gap.

It is believed that metals with better catalytic graphitization activities form better ohmic contacts, such as Ni and Co[1,14]. It should be noted that other metals may also act as graphitization catalysts and a similar mechanism for the creation of carbon vacancies due to the formation of metal carbides may explain ohmic contact formation in the cases of titanium[9,15,16] and tungsten[17].

In this paper, the effect of C vacancies on the SiC surface is shown. The density of effective carriers changes so much that metal contacts are ohmic when deposited without annealing. Obviously, the C vacancies formed during high temperature annealing are the decisive factor for the formation of ohmic contacts. The sheet resistance R_{sh} decreases by almost 55% also because of the high density of effective carriers by C vacancies.

4 Conclusion

In summary, we have made an attempt to show the effect of the C vacancies formed during high temperature annealing. Ni_2Si was identified as the dominant phase by XRD analysis after the metallization annealing. An amorphous C film at the Ni_2Si/SiC interface was confirmed by XEDS. After the Ni_2Si and amorphous C film were etched away selectively, the newly deposited Ni contacts were ohmic as deposited without annealing. The result for sheet resistance R_{sh} of the implanted layers decreased from 975 to 438Ω/□ (almost 55%), because carbon vacancies (V_C) appeared during annealing, which act as donors for electrons in SiC. Furthermore, we have discussed the mechanism of the formation of Ni-based ohmic contacts to n-type SiC in detail.

References

[1] Lu W J, Mitchel W C, Thornton C A, et al. Carbon structural transitions and ohmic contacts on 4H-SiC. J Electron Mater, 2003, 32(5): 426

[2] Nikitina L P, Vassilevski K V, Wright N G, et al. Formation

and role of graphite and nickel silicide in nickel based ohmic contacts to n-type silicon carbide. J Appl Phys, 2005, 97(8): 083709

[3] Yang S J, Kim C K, Jang S W, et al. Study of Co-and Ni-based ohmic contacts to n-type 4H-SiC. Diamond Relat Mater, 2004, 13(4～8): 1149

[4] Getto R, Freytag J, Kopnarski M, et al. Characterization of sputtered titanium silicide ohmic contacts on n-type 6H-silicon carbide. Mater Sci Eng B, 1999, 61～62: 27

[5] Crofton J, Porter L M, Williams J R. The physics of ohmic contacts to SiC. Phys Status Solidi B, 1997, 202: 581

[6] Mohammad F A, Cao Y, Porter L M. Ohmic contacts to silicon carbide determined by changes in the surface. Appl Phys Lett, 2005, 87: 161908

[7] Guo Hui, Zhang Yimen, Zhang Yuming. Investigation of Ti-Al based ohmic contacts to n-type 6H-SiC with P^+ ion implantation. Chin Phys, 2006, 15: 1009

[8] Via F L, Roccaforte F, Raineri V, et al. Schottky-ohmic transition in nickel silicide/SiC-4H system: is it really a solved problem. Microelectron Eng, 2003, 70: 519

[9] Roccaforte F, Via F L, Raineri V, et al. Improvement of high temperature stability of nickel contacts on n-type 6H-SiC. Appl Surf Sci, 2001, 184: 295

[10] Han S Y, Kim K H, Kim J K, et al. Ohmic contact formation mechanism of Ni on n-type 4H-SiC. Appl Phys Lett, 2001, 79: 1816

[11] Via F L, Roccaforte F, Raineri V, et al. Schottky-ohmic transition in nickel silicide/SiC-4H system: the effect of non uniform Schottky barrier. Mater Sci Forum, 2004, 457: 861

[12] Wimbauer T, Meyer B K, Hofstaetter A, et al. Negatively charged Si vacancy in 4H SiC: a comparison between theory and experiment. Physical Review B, 1997: 56: 7384

[13] Aboelfotoh M O, Doyle J P. Defect energy levels in electron-irradiated and deuterium-implanted 6H silicon carbide. Phys Rev B, 1999, 59: 10823

[14] Lu W J, Mitche W C, Landis G R, et al. Catalytic graphitization and ohmic contact formation on 4H-SiC. J Appl Phys, 2003, 93: 5397

[15] Basak D, Mahanty S. Ti/Ni/Ti/Au ohmic contact to n-type 6H-SiC. Mater Sci Eng B, 2003, 98: 177

[16] Goesmann F, Schmid-Fetzer R. Temperature-dependent interface reactions and electrical contact properties of titanium on 6H-SiC. Semicond Sci Technol, 1995, 10: 1652

[17] Deeb C, Heuer A H. A low-temperature route to thermodynamically stable ohmic contacts to n-type 6H-SiC. Appl Phys Lett, 2004, 84: 1117

n型SiC的Ni基欧姆接触中C空位作用的实验证明*

郭　辉[†]　张义门　张玉明

（西安电子科技大学微电子学院，教育部宽禁带半导体材料重点实验室，西安　710071）

摘要： 通过在Si面p型4H-SiC外延层上使用P^+离子注入来形成n阱. Ti和Ni依次淀积在有源区的表面，金属化退火后的XRD分析结果表明Ni_2Si是主要的合金相. XEDS的结果表明在Ni_2Si/SiC界面处存在一层无定型C. 去除Ni_2Si合金相与无定型C之后重新淀积金属，不经退火即可形成欧姆接触. 同时，注入层的方块电阻R_{sh}从975下降到438Ω/□. 结果表明，合金化退火过程中形成了起施主作用的C空位（V_C）. C空位提高了有效载流子浓度并对最终形成欧姆接触起到了重要作用.

关键词： Ni；欧姆接触；SiC；C空位；P^+离子注入

PACC： 7340C；6170T

中图分类号： TN405　**文献标识码：** A　**文章编号：** 0253-4177(2007)01-0005-05

---

* 国家重点基础研究发展计划（批准号：2002CB311904），国家重点基础研究发展计划军用项目（批准号：51327010101）以及国家自然科学基金（批准号：60376001）资助项目

[†] 通信作者. Email: gyc78@sohu.com

2006-08-25收到，2006-09-17定稿