

Ni and Ni Silicides Ohmic Contacts on N-type 6H-SiC with Medium and Low Doping Level

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Abstract. Ni silicides contacts, which are expected to be advantageous contact materials on SiC, were tested in this work. Prepared contact structures were ohmic with low contact resistivity approximately $8 \times 10^{-4} \Omega \text{ cm}^2$ after annealing at 960°C as far as the SiC substrate with a medium doping level was concerned, no matter whether Ni or Ni silicides were used. At lower annealing temperatures, only Schottky behavior was observed by means of I-V characteristics measurements. In the case of SiC substrate with a low doping level, the behavior differed. It was necessary to anneal the structures at 1070°C to see ohmic behavior appearing with resistivities reaching $8 \times 10^{-3} \Omega \text{ cm}^2$ and this was valid only for Ni and Ni_2Si . Raman spectroscopy measurements confirmed formation of single Ni silicides as expected. It was found that Ni silicides can keep as good resistivity as Ni contacts while they interact with SiC in limited way and their undesirable drop-like morphology is expected to be overcome for example with a covering layer.

Keywords

Silicon carbide, ohmic contact, silicide, Raman.

1. Introduction

As one of semiconductors with a wide band gap, hexagonal SiC offers many interesting properties like high thermal conductivity, good chemical stability, high breakdown field and others [1]. Hence, it finds its potential in high speed or power electronics [1], [2]. Ohmic contacts are essential parts of electronic components. Nickel belongs to the most used materials for making ohmic contacts on SiC and these contact structures were broadly investigated across many studies [1], [3], [4]. So a lot is known about Ni/SiC contact structure features and nature. In order for the Ni/SiC contact structure to become ohmic it is annealed in vacuum at temperatures higher than 900°C usually for 10 mins and a solid state reaction takes place between Ni and SiC. Ni silicides and carbon phases are formed during the reaction. Contact resistivities of these contact structures are fairly low, but the reaction including SiC decomposition is undesirable. The reaction brings contact morphology worsening, which may undermine

contact's reliability. There have been some works studying contact materials which are not expected to decompose underlying SiC yet yielding low resistivity [5], [6]. Ni silicides are one example. They have been prepared by various ways of deposition, either directly, or Si and Ni thin layers in appropriate stoichiometry have been deposited and later annealed to form the silicide [6-8]. These pure Ni silicides/SiC contact structures after annealing at temperatures higher than 900°C had indeed good resistivity and good reliability in comparison with Ni/SiC contact structures [7], [8].

In our study, several Ni silicides on n-type 6H-SiC with a medium and low doping level were tested. It could be interesting to compare Ni silicides structures with Ni structures on a substrate with low doping level, too, as there are studies dealing with Ni structures on SiC with low doping level [9]. Raman spectroscopy was used to analyze formed species during contact preparation. Raman spectroscopy is a very useful technique for contacts' chemistry examination and many studies have achieved valuable observations thanks to this technique.

The aim of this study can be summarized in such a way that several Ni silicide contact structures were prepared to be compared with Ni structures in terms of chemical composition, electrical behavior and to find whether an optimized contact structure could be suggested.

2. Experimental

Samples of n-type nitrogen doped 6H-SiC(0001) from SiCrystal AG were used for our experiments. The first substrate's doping level was 5.5×10^{17} and the second substrate's one was $5.5 \times 10^{15} \text{ [cm}^{-3}\text{]}$. Before deposition, samples were cleaned by RCA-like treatment. Samples were blown dry with N_2 . Silicides Ni_2Si , NiSi and NiSi_2 were prepared by Si and Ni multilayer deposition to fulfill the respective stoichiometry. Layers' sequence and thickness was as follows: SiC/12 nm Si/13 nm Ni/12 nm Si/13 nm Ni for Ni_2Si , SiC/18 nm Si/9.75 nm Ni/18 nm Si/9.75 nm Ni for NiSi and SiC/20 nm Si/5.4 nm Ni/20 nm Si/5.4 nm Ni for NiSi_2 . It is important to remark that silicides were supposed to form not until after appropriate annealing. Deposition was carried out by e-gun in vacuum chamber at 2×10^{-6} Pa. Samples were placed in a sample holder and

kept at 135°C during deposition. Contact structures were defined through a metal mask with 150×200 μm dimensions and 1 mm spacing between each other. For annealing the samples were placed into resistively heated Mo trays in vacuum chamber at 3×10⁻⁶ Pa. Annealing temperatures were 620°C for 90 mins, 850°C for 30 mins and 960°C for 10 mins. Samples were annealed successively at these temperatures and there were some more samples which passed through only 960 and 1070°C for 10 mins. Contact resistivity measurements were carried out by modified four-point probe method and also I-V characteristics in antiparallel configuration were measured both at room temperature after every annealing step. Samples were analyzed by means of Raman spectroscopy after annealing at 960°C. A LabRam system (Dilor) with a 532.2 nm laser line and 1 μm spot size was used for this analysis.

3. Results and Discussion

3.1 Electrical Measurements

Contact resistivity and I-V characteristics measurements are summarized in Tab. 1 for substrates with the medium doping level.

annealing temperature	620°C	850°C	960°C
average contact resistivity [Ωcm^2]	$> 10^2$	$10^2 - 10^3$	8×10^4
contact resistivity scatter in percents of average value	$> 15\%$	$> 15\%$	15%
I-V characteristics	Schottky	quasilinear	linear

Tab. 1. Electrical measurements on SiC with the medium doping level.

It is apparent that contact resistivity decreased when higher annealing temperatures were used. When I-V characteristics are concerned, ohmic behavior of contacts was observed first after annealing at 960°C. It is interesting to note that resistivity values and I-V characteristics represented by Tab. 1 with minor deviations hold for each silicide. Also much lower scatter in resistivities was observed after annealing at 960°C. Electrical properties of tested Ni silicides are very similar to pure Ni contacts. Ni/SiC contacts had resistivities $8 \times 10^4 \Omega\text{cm}^2$ after annealing at 960°C, scatter was low and I-V characteristics were linear, too.

Electrical properties for contacts prepared on SiC substrate with the low doping level are summarized in Tab. 2. The first thing which is clearly different in Tab. 2 is that single silicides had to be distinguished in their electrical behavior contrary to the contacts on the substrate with the higher doping level presented in Tab. 1. Further, as it can be expected for low doping level, contact resistivity is high and also higher annealing temperatures were necessary for a decrease in resistivity. The only silicide which provided ohmic contacts was Ni₂Si. Contacts prepared from silicides rich in silicon did not show perspective re-

sults. If we compare Ni silicides with pure Ni contacts, Ni and Ni₂Si contact structures have very close properties.

annealing temperature	960°C	1070°C
average contact resistivity [Ωcm^2] for Ni ₂ Si	$10^1 - 10^2$	$> 8 \times 10^3$
average contact resistivity [Ωcm^2] for NiSi	$10^0 - 10^2$	$> 10^2$
average contact resistivity [Ωcm^2] for NiSi ₂	$> 10^1$	$> 10^1$
I-V characteristics for Ni ₂ Si	some samples linear, some Schottky	linear
I-V characteristics for NiSi and NiSi ₂	Schottky	Schottky

Tab. 2. Electrical measurements on SiC with low doping level.

3.2 Raman Spectroscopy Results

Raman spectroscopy served for examination of silicides, which were expected to form during annealing in contact structures. All spectra shown are further unprocessed.

In Fig. 1 there is a Raman spectrum collected after annealing at 960°C for the Ni₂Si sample. There are evident two quite large peaks around 99 and 140 cm⁻¹. These peaks correspond to Ni₂Si [10]. When going to higher wavenumbers two smaller peaks at 185 and 206 cm⁻¹ are apparent. They may show evidence of NiSi but they are quite shifted to lower wavenumbers [11-13]. In all spectra there are also peaks corresponding to the SiC substrate and peaks at 1354 and 1589 cm⁻¹ which correspond to free carbon [14]. So it can be concluded that the expected Ni₂Si silicide was formed.

Fig. 2 and 3 show other Raman spectra. Fig. 2 is for NiSi sample and Fig. 3 is for NiSi₂ sample, all annealed at 960°C. Two distinct peaks and two broader peaks at 192, 214, 288 and 360 cm⁻¹ in Fig. 2 support the evidence for NiSi [11-13], [15]. In the case of NiSi₂ sample, four broad peaks corresponding to NiSi₂ were identified at 231, 288, 321 and 396 cm⁻¹, which is in good agreement with observations in other studies [15], [16].

In all spectra there is a peak around 150 cm⁻¹, which is clearly visible in NiSi and NiSi₂ samples. This peak is one of SiC peaks according to bare 6H-SiC spectrum (not presented here). In the Ni₂Si sample it is also apparent, but it overlaps with one of Ni₂Si peaks. Another interesting feature is that there are not peaks evidencing for free carbon at NiSi and NiSi₂ samples in whole spectra shown in the upper right corner of respective figures. Carbon present in samples may come from interaction of silicide with SiC, however, it is much more probable that there was deposited a slight excess of Ni over stoichiometry and this Ni decomposed underlying SiC forming carbon as a reaction product. Silicides richer in silicon very probably consumed all Ni during their formation so SiC decomposition did not take place and there are really negligible traces of free carbon in spectra of NiSi or NiSi₂ samples.

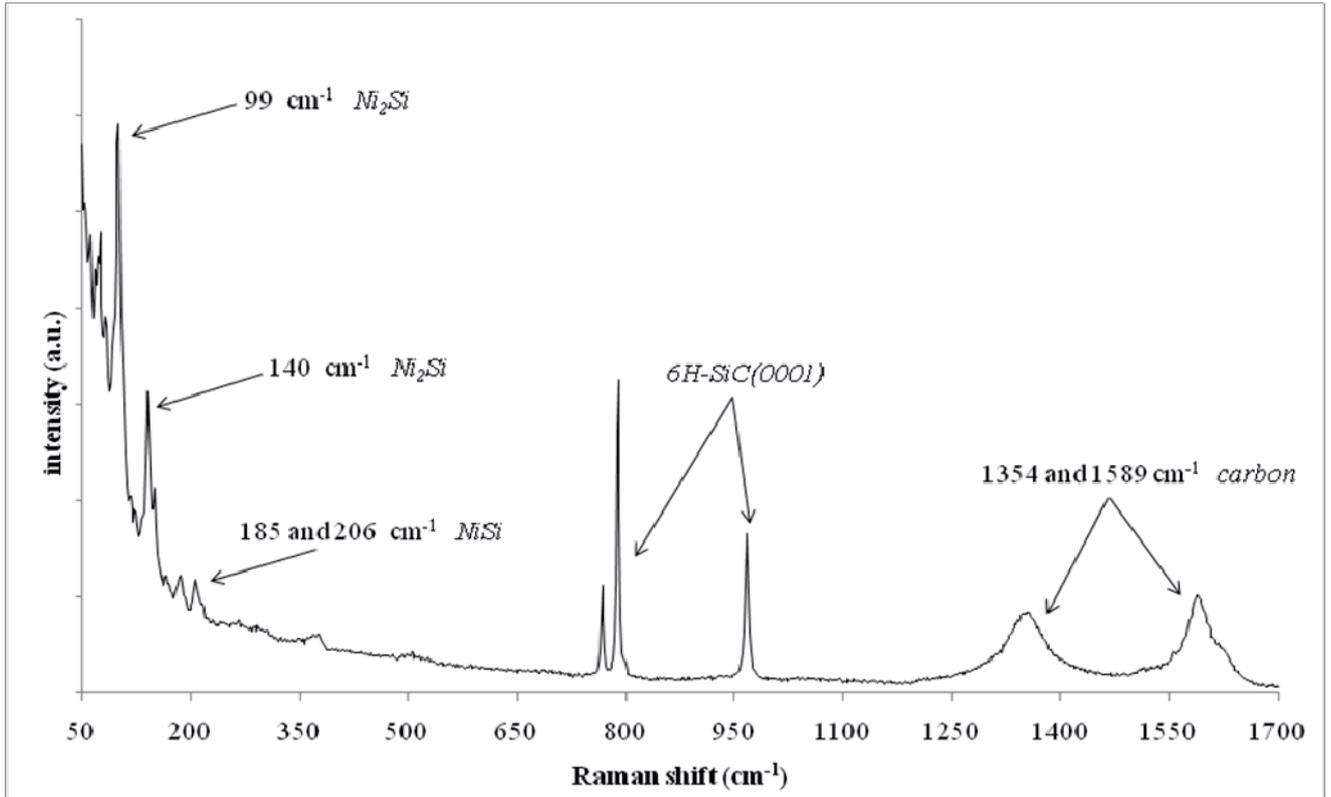


Fig. 1. Raman spectra for $\text{Ni}_2\text{Si}/\text{SiC}$ sample annealed at 960°C .

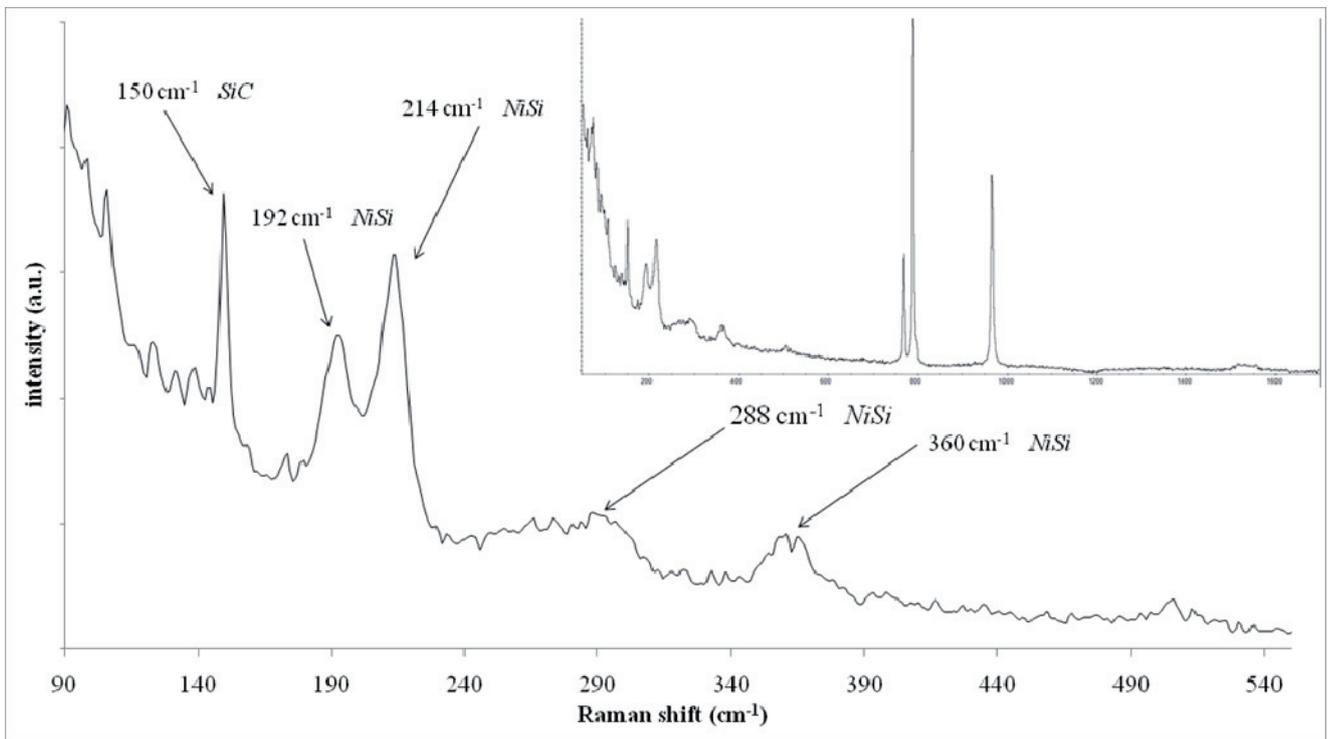


Fig. 2. Raman spectra for NiSi/SiC sample annealed at 960°C .

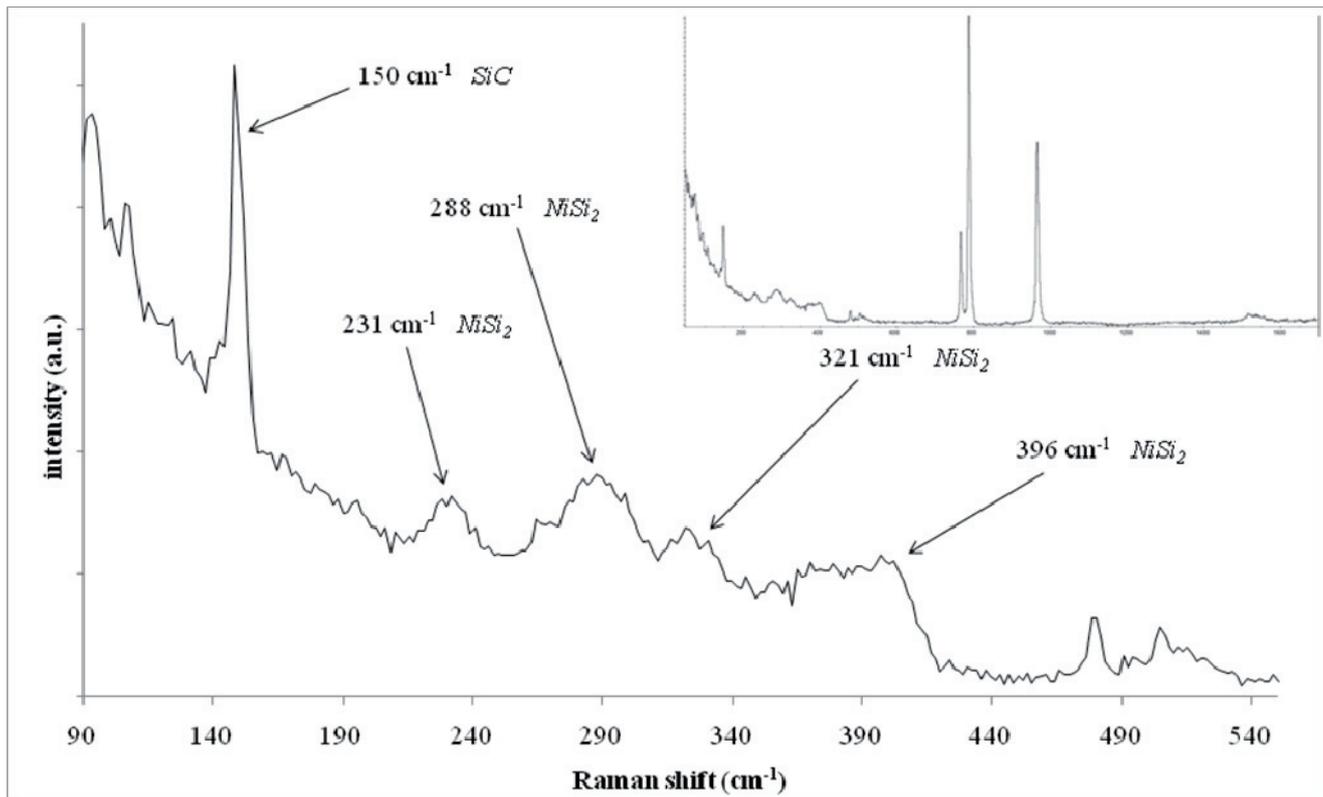


Fig. 3. Raman spectra for NiSi₂/SiC sample annealed at 960°C.

3.3 Optical Microscopy Results

Formed contact structures were observed by optical microscopy. Ni₂Si structures had good morphology. But once annealed NiSi or NiSi₂ were considered, their continuous morphology transformed into regularly aligned isolated islands. The area of the original contact had been 150×200 μm and formed islands had diameter around 1-10 μm and were separated from each other for approximately the same distance. It is important to mention that when these samples were probed by Raman spectroscopy, the analyzing laser beam was thoroughly focused right into an island. When an area among islands was probed, SiC spectrum was obtained without visible marks of silicides peaks. Also the surface among the islands looked like original SiC substrate surface under the optical microscope. The islands formation could be described as coalescence. There are some studies that encountered these issues as well [8], [17].

Nevertheless, contact resistivity was not affected by islands formation at NiSi and NiSi₂ contact structures when compared with Ni or Ni₂Si contact structures as far as SiC substrate with the medium doping level was concerned. Because NiSi and NiSi₂ do keep low resistivity despite the fact that their morphology is not ideal, for example another layer of a suitable material could be deposited on these structures as a covering layer for ensuring better contacts reliability. This did not hold true for the low doping level. However, it is not clear if the coalescence is the real reason why NiSi and NiSi₂ contact structures show worse electrical properties on the substrate with the low doping level.

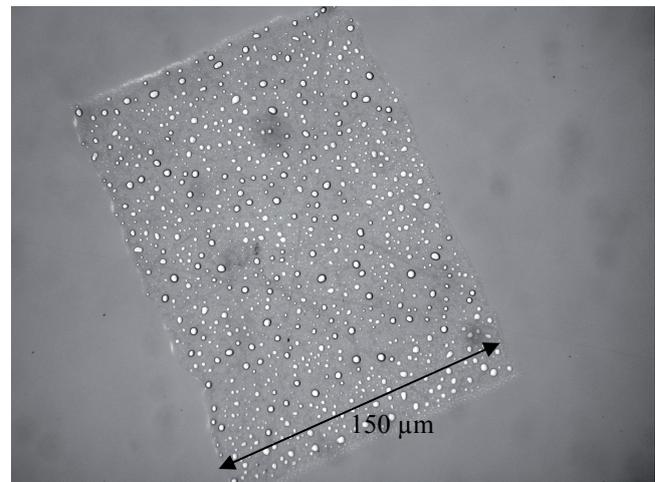


Fig. 4. Photography of a silicide contact rich in silicon after annealing at 960°C.

4. Conclusions

Ohmic behavior was achieved for SiC substrate with the medium doping level for Ni and as well as all Ni silicides with contact resistivity approximately $8 \times 10^{-4} \Omega\text{cm}^2$ after annealing at 960°C. At lower annealing temperatures only Schottky behavior was observed. Situation changed on substrate with the low doping level, where annealing at 1070°C was necessary for obtaining ohmic structures with resistivities reaching minimal value $8 \times 10^{-3} \Omega\text{cm}^2$. Moreover, this holds only for Ni and Ni₂Si contact structures.

NiSi and NiSi₂ had very high resistivity and Schottky behavior.

Raman spectroscopy measurements confirmed formation of intended Ni silicides. Ni₂Si samples were identified with an amount of free carbon possibly coming from reaction of excess Ni with SiC.

Ni₂Si silicide seems to be the most perspective. It holds good morphology after annealing, good resistivity on both substrates with different doping level and can be expected to interact with SiC minimally. NiSi and NiSi₂ can be perspective for SiC substrate with medium doping level after a morphology optimization for example with a covering layer.

Acknowledgements

This study was financially supported from specific university research (MSMT no. 21/2010) and from Project No. 126881004, IGA ICT, Prague, Czech Republic.

References

- [1] PORTER, L. M., DAVIS, R. F. A critical-review of ohmic and rectifying contacts for silicon-carbide. *Materials Science and Engineering B*, 1995, vol. 34, no. 2-3, p. 83 – 105.
- [2] TREU, M., RUPP, R., BLASCHITZ, P., HILSENBECK, J. Commercial SiC device processing: Status and requirements with respect to SiC based power devices. *Superlattices and Microstructures*, 2006, vol. 40, no. 4-6, p. 380 – 387.
- [3] MARINOVA, T., KAKANAKOVA-GEORGIEVA, A., KRAS-TEV, V., KAKANAKOV, R., NESHEV, M., KASSAMAKOVA, L., NOBLANC, O., ARNODO, C., CASSETTE, S., BRYLINSKI, C., PECZ, B., RADNOCZI, G., VINCZE, G. Nickel based ohmic contacts on SiC. *Materials Science and Engineering B*, 1997, vol. 46, no. 1-3, p. 223 -226.
- [4] HAN, S. Y., KIM, K. H., KIM, J. K., JANG, H. W., LEE, K. H., KIM, N.-K., KIM, E. D., LEE, J.-L. Ohmic contact formation mechanism of Ni on n-type 4H-SiC. *Applied Physics Letters*, 2001, vol. 79, no. 12, p. 1816 – 1818.
- [5] GUZIEWICZ, M., PIOTROWSKA, A., KAMINSKA, E., GRASZA, K., DIDUSZKO, R., STONERT, A., TUROS, A., SOCHACKI, M., SZMIDT, J. Ta-Si contacts to n-SiC for high temperatures device. *Materials Science and Engineering B*, 2006, vol. 135, no. 3, p. 289 – 293.
- [6] DEEB, C., HEUER, A. H. A low-temperature route to thermodynamically stable ohmic contacts to n-type 6H-SiC. *Applied Physics Letters*, 2004, vol. 84, no. 7, p. 1117 – 1119.
- [7] NAKAMURA, T., SATOH, M. Schottky barrier height of a new ohmic contact NiSi₂ to n-type 6H-SiC. *Solid-State Electronics*, 2002, vol. 46, no. 12, p. 2063 – 2067.
- [8] KUCHUK, A., KLADKO, V., PIOTROWSKA, A., MINIKAYEV, R., STONERT, A., RATAJCZAK, R. Fabrication and characterization of nickel silicide ohmic contacts to n-type 4H silicon carbide. *Journal of Physics: Conference Series*, 2008, vol. 100, part 4.
- [9] EDMOND, J.A., RYU, J., GLASS, J. T., DAVIS, R. F. Electrical contacts to beta-silicon carbide thin-films. *Journal of the Electrochemical Society*, 1988, vol. 135, no. 2, p. 359 -362.
- [10] HARIMA, H. Raman scattering characterization on SiC. *Microelectronic Engineering*, 2006, vol. 83, no. 1, p. 126-129.
- [11] BHASKARAN, M., SRIRAM, S., PEROVA, T. S., ERMAKOV, V., THOROGOOD, G. J., SHORT, K. T., HOLLAND, A. S. In situ micro-Raman analysis and X-ray diffraction of nickel silicide thin films on silicon. *Micron*, 2009, vol. 40, no. 1, p. 89-93.
- [12] WAN, L., REN, Y., TANG, B., CHENG, X., ZHANG, X., XU, D., LUO, H., HUANG, Y. Polarized Raman spectroscopy study of NiSi film grown on Si(001) substrate. *Applied Physics A*, 2009, vol. 97, no. 3, p. 693-697.
- [13] CONTI, G., LAZIK, C., URITSKY, Y. Micro-Raman characterization of phase formation and thermal stability of nickel silicide thin films. *Microscopy and Microanalysis*, 2005, vol. 11, p. 2094 – 2095.
- [14] CAO, Y., NYBORG, L., YI, D.-Q., JELVESTAM, U. Study of reaction process on Ni/4H-SiC contact. *Materials Science and Technology*, 2006, vol. 22, no. 10, p. 1227 – 1234.
- [15] HUANG, W., ZHANG, L., GAO, Y., JIN, H. Effect of a thin W, Pt, Mo, and Zr interlayer on the thermal stability and electrical characteristics of NiSi. *Microelectronic Engineering*, 2007, vol. 84, no. 4, p. 678 – 683.
- [16] ZHAO, F. F., ZHENG, J. Z., SHEN, Z. X., OSIPOWICZ, T., GAO, W. Z., CHAN, L. H. Thermal stability study of NiSi and NiSi₂ thin films. *Microelectronic Engineering*, 2004, vol. 71, no. 1, p. 104 – 111.
- [17] BARDA, B., MACHÁČ, P. Reactions of nickel-based ohmic contacts with n-type 4H silicon carbide. *Electroscope* (ISSN 1802-4564). Electronic Devices and Systems IMAPS CS International Conference 2009, Brno (Czech Republic).

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