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Raman study of Ni and Ni silicide contacts on 4H– and 6H–SiC

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ABSTRACT

Ni_2Si, NiSi and $NiSi_2$ contacts were prepared on n-type 4H– and 6H–SiC(0001) by deposition of Ni and Si multilayers in the respective stoichiometry after high-temperature annealing, as well as pure Ni contacts. After annealing, the individual contacts were analyzed by Raman spectroscopy and electrical property measurements. Contact structures were then etched-off and subsequently observed by means of AFM (Atomic Force Microscopy). Ni reacted with SiC, forming Ni_2Si and carbon. At Ni_xSi_y/SiC contact structures the respective silicides were already formed at low annealing temperatures, when only Schottky behavior of the structures was observed. The intended silicides, once formed, did not change any further with increasing annealing temperature. All contact structures provided good ohmic behavior after being annealed at 960 °C. By means of combined AFM and Raman analysis of the etched-off contacts we found that the silicide contact structures very probably did not react with SiC which is in accordance with the thermodynamic assumptions. After annealing the silicide contact structures at such temperature, when Schottky behavior changed to ohmic, a certain form of interaction between the SiC substrate and the silicide contact structures must have occurred.

1. Introduction

Semiconducting materials with a wide bandgap, for example SiC, are nowadays asserting themselves in the field of power electronics [1]. In particular, the 4H– and 6H–SiC polytypes are highly interesting. Much attention is paid to research and development of this material for applications in electronics; for example, the Schottky diodes are now widely spread [1,2]. There are however still areas of SiC processing where further progress is necessary in order to extend the potential of this material; for example ohmic contacts.

An element often used for its good properties is nickel [1,3]. After being annealed, reaction between Ni and SiC takes place and the structure reaches ohmic character. Should the contact not be annealed at sufficiently high temperature it would display only Schottky behavior. Many studies dealing with Ni/SiC contacts have been conducted and a high level of knowledge of the processes and mechanisms in this contact structure has been reported [1,3,4]. In the annealing process, Ni reacts with SiC forming Ni silicide and carbon phases. Ohmic behavior of this contact structure may be caused by carbon vacancies which should form at the contact/SiC interface and which should support the tunneling current, or by a layer of graphitized carbon at the SiC surface or by various other defects at the contact/SiC interface [3–5].

Several authors have already dealt with contact structures where the Ni silicide contact on SiC has not been formed by reaction of Ni and SiC [6–10]. Further, ohmic contacts have been prepared from materials that should not react with SiC, such as TiC, TaC and others [11–14]. At the Ni/SiC contacts, in spite of good electrical features, the contact/SiC interface may cause trouble with reliability of the contacts due to its strong structural as well as chemical heterogeneity [15]. This heterogeneity is represented by a disordered layer of various reaction products in the form of carbon and Ni silicides coming from the reaction of Ni with SiC during annealing. Another motivation for preparation of non-reactive contact structures has been an intention to examine what the significance of an interaction, in a general sense, of the contact material with SiC is, in relation with the mechanism of electrical behavior of the contact. Several authors prepared pure annealed Ni silicide contacts without SiC decomposition and they have obtained very good results of contact resistivities, reaching the values of the Ni contacts [7,16,17]. Authors of [9] have even reached ohmic behavior of the NiSi silicide contact after annealing it at a temperature as low as 300 °C.

Possible reactions between a contact material and a semiconductor are deduced from both experimental and calculated phase diagrams. On the basis of experiments and calculations the Ni–Si–C ternary phase diagram for high temperatures has been created [18–21]. When looking at the diagrams one can easily notice that Ni is not in equilibrium with SiC and that there is a reaction present where Ni silicides and carbon are formed. This is completely in accordance with results of experiments where annealed Ni/SiC contacts

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were prepared. In contrast, Ni_2Si, NiSi and $NiSi_2$ are stable phases with SiC.

There are however no experimental data for evaluation of the Ni–Si–C system at lower temperatures, where different phases may be stable. When the annealing of a contact structure is finished the contact structure cools down to room temperature and there may be changes taking place in the contact structure during cooling. Assuming the Ni–Si–C diagram for lower temperatures to be the same as for high temperatures could lead to erroneous conclusions even when taking into account the fact that diffusion is suppressed at the lower temperatures. The Ni–Si binary diagram [19,22] describes Ni_2Si, NiSi and $NiSi_2$ silicides as stable phases at low temperatures. We have used the FACTSAGE database [23] for obtaining information about the Ni–Si–C system at lower temperatures. Fig. 1 shows a calculated ternary phase diagram of the Ni–Si–C system at 500 °C. We have found that there are no major changes in the diagram from room temperature up to 500 °C, with only slight changes in the solubility of Si in Ni in the region of low concentrations of Si. The experimental and theoretical diagrams are concurrent at high temperatures. The only difference is that Ni_5Si_2–C–SiC invariant equilibrium transforms into Ni_2Si–C–SiC equilibrium.

When comparing diagrams at lower and at high temperatures, it is evident that Ni_2Si, NiSi and $NiSi_2$ are in equilibrium with SiC in the whole range of temperatures from room temperature up to the higher temperatures that are used for annealing. So when the contact structure cools down there are very probably no changes or reactions taking place. Also, during a prolonged operation of a device comprising Ni silicide contact structures on SiC, even at elevated temperatures, no changes or reactions are expected.

Analysis of the contact structures by means of Raman spectroscopy provides a lot of information about phase and chemical composition and therefore it is a highly useful method [24,25]. Using AFM (Atomic Force Microscopy), it is possible to examine how a contact material interacted/reacted with SiC after etching-off of the contacts. From the AFM images we can read the way in which the SiC surface was morphologically modified.

In this work we prepared Ni and Ni silicide contact structures on n-type 4H– and 6H–SiC(0001) with medium doping levels; these structures were further annealed at high temperatures. For these structures we measured contact resistivity and I–V (current–voltage) characteristics, the structures were submitted to Raman spectroscopy analysis and AFM analysis. The goal was to investigate reactivity of these contact materials with the underlying SiC, to observe the progress of formation of silicides, determine evolution of electrical parameters with annealing temperature, and in particular to correlate the observed chemical and electrical parameters of the structures. Comparison of Ni and Ni silicide contacts was expected to provide further valuable results due to their similarity. Significant attention was paid to comparing the experimental knowledge with thermodynamic assumptions.

In this work we prepared Ni contact structures as well as individual Ni_2Si, NiSi and $NiSi_2$ structures. It was our intention that the observed silicides should not originate from a reaction with SiC. The silicide structures were prepared by annealing of deposited Ni and Si layers on SiC in the respective ratios. This is highlighted in order to clearly distinguish between silicides formed by reaction between Ni and SiC from those formed by reaction between deposited Ni and Si. As a result, Ni and Si were deposited in such sequences and quantities that free Ni would not come into contact with SiC.

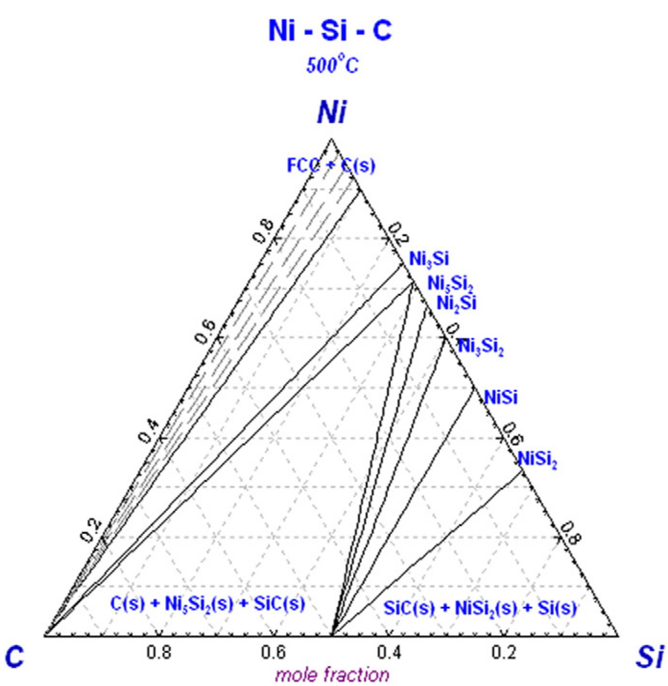

Fig. 1. Calculated ternary phase diagram of the Ni–Si–C system at 500 °C and standard pressure using FACTSAGE.

2. Experimental details

Two types of substrate were used for the experiments, both obtained from SiCrystal AG. The first one was n-type 4H–SiC(0001) doped with nitrogen, with concentration of carriers of 4.2×10^{18} cm^{-3}. The second was n-type 6H–SiC(0001), doped with nitrogen with concentration of carriers of 5.5×10^{17} cm^{-3}. The individual samples were cut from a plate, 0.5 mm thick, and their size was roughly 0.5×0.5 cm. The samples were subjected to a modified RCA type treatment prior to deposition of the contact material. The samples were then dried in a stream of clean nitrogen and placed into the deposition apparatus. Deposition was carried out by evaporation using an electron gun in a vacuum of 2×10^{-4} Pa. Deposited materials were Ni of 4 N purity and Si of 4 N or better purity. The pattern of the contacts was created by deposition through a metal mask. The size of the contact pads was 150×200 μm with 1 mm spacing. The samples were heated up to 135 °C during deposition. Determination of layer thickness was conducted through the use of a calibrated oscillating crystal placed in the deposition apparatus. Table 1 below summarizes thicknesses and sequences of the individual layers of Ni and Si for each contact structure.

Annealing of the samples was carried out in a vacuum of 3×10^{-4} Pa for various periods of time at various temperatures in resistively heated

Table 1
Thicknesses and sequences of the individual layers of Ni and Si for each contact structure.

Contact material	1. layer	2. layer	3. layer	4. layer	Total thickness [nm]
Ni	50 nm Ni	/	/	/	50
Ni_2Si	a) 12 nm Si	13 nm Ni	12 nm Si	13 nm Ni	50
	b) 48 nm Si	52 nm Ni	/	/	100
NiSi	18 nm Si	9.75 nm Ni	18 nm Si	9.75 nm Ni	55.5
$NiSi_2$	a) 20 nm Si	5.4 nm Ni	20 nm Si	5.4 nm Ni	50.8
	b) 40 nm Si	21.6 nm Ni	40 nm Si	/	101.6