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Improvement of Ni/Si/4H-SiC ohmic contacts by VLS grown sub-contact layer

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ABSTRACT

This work presents results of using VLS epitaxial Si–Ge-type structure as a sub-contact layer designated for Ni/Si ohmic contacts. The epitaxial growth was performed at 1240 and 1414 °C in various types of atmosphere in a processing chamber. The prepared layers had mostly smooth surface. XPS analysis showed that germanium escape from the structure occurred during the process of the epitaxial growth. An important result is that silicon and carbon bind in the form of SiC already at the surface of the structure, which proves silicon carbide formation during the epitaxial growth. Ni/Si-type contact metallization was deposited onto all epitaxial structures. After annealing we received ohmic contacts with contact resistivity equal or lower compared to the standard contact structure Ni/Si/SiC prepared on the same substrate. The best value of contact resistivity was $4 \times 10^{-5}\ \Omega\,cm^2$. The doping concentration in the VLS epitaxial layers is reaching the value $(6–7) \times 10^{18}\ cm^{-3}$.

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1. Introduction

Outstanding properties of silicon carbide make it a promising material for manufacturing of many semiconductor devices. Its properties like wide band gap (3.2 eV for 4H polytype), high breakdown electric field, thermal conductivity, saturated drift velocity and chemical stability are ideal, e.g., for high temperature and high power/frequency applications [1]. It is also used as a substrate for an epitaxial growth of some III–V semiconductors.

Nickel is very frequently used for the fabrication of ohmic contacts on n-type SiC [1,2]. The annealing process of Ni/SiC structure is performed at temperature around 1000 °C, resulting in low specific contact resistivity ($\sim 10^{-4}$–$10^{-6}\ \Omega\,cm^2$). This annealing process is accompanied by the reaction of Ni with SiC and silicides are created – mainly Ni_2Si phase [3]. Once a certain region of SiC is decomposed, the excess carbon in the contact layer should be considered as well; there is substantial carbon segregation to the top region of the contact [3]. Despite the excellent electrical properties of Ni/SiC metallizations, the presence of free carbon does not promise a long-term stability of ohmic contacts. A possible solution can be seen in Ni/Si multilayer [4]. The addition of silicon into nickel metallization can reduce the reaction with SiC during annealing and minimize the decomposition of SiC; also the homogeneity and conductivity should be superior to nickel contact.

It is known that contact resistivity depends on the charge carrier concentration in a sub-contact area [5]. For formation of ohmic contacts, it is advantageous to use highly doped layer of semiconductive material localized in the area below the contact structure. This is usually performed by masking followed by diffusion or ion implantation of desired doping elements. In the case of SiC, standard diffusion techniques cannot be used because of the small diffusion coefficients of doping elements. Ion implantation is generally used even if some problems still remain unsolved, especially concerning p-type doping (high-temperature subsequent annealing). Selective epitaxial growth (SEG) is common technique for semiconductor materials such Si, GaAs or GaN. Application of SEG to SiC is more difficult because of the higher growth temperatures under H_2. In these conditions, the classic materials used as mask are not stable. Very perspective is a more recent work [6] describing vapor–liquid–solid (VLS) mechanism without any mask. Si-based solutions with lower melting point and higher carbon solubility than silicon are used. The metal additives to Si to lower the melting point are Al for p-type layer and Ge for n-type. The liquid phase is fed by an alkane in order to grow the SiC layer on a seed (SiC substrate). C supersaturation in the melt is achieved by cracking the alkane on the top of the liquid. The dissolved C then migrates to the seed due to the C activity gradient between the top end the bottom of the liquid and SiC finally nucleates on the seed surface.

The goal of this article is to demonstrate the possibility of VLS epitaxial growth on SiC for preparation of sub-contact layers for ohmic contacts of the Ni_2Si type. The VLS epitaxial growth was done by thermal annealing of Si and Ge layers in methane atmosphere. The Ni/Si metallization is then evaporated onto the prepared structure and thermally processed in a standard manner.

2. Experimental

N-type 4H-SiC on-axis substrate wafers with doping level $4.2 \times 10^{18}\ cm^{-3}$ (supplied by SiCrystal AG) were used in our experiments. Si-face of SiC substrate was chosen in our experiments.

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2.1. VLS epitaxy

The first step in the preparation of a Si–Ge VLS epitaxial layer was the vacuum depositing of Si and Ge layers in the evaporating apparatus UNIVEX 450. The substrates were chemically cleaned by the standard process [5]. Then the substrates were blown dry by nitrogen and transferred into the evaporation apparatus. The deposition of layers was done by an electron gun, at pressure of 2×10^{-6} mbar, substrate temperature was kept at 135 °C during deposition.

The thermal forming of Si–Ge structures is an important technological operation at preparation of the VLS epitaxial layer. The forming was done in the chamber of the evaporating apparatus at temperature of 1240 or 1414 °C for 10 min. The annealing environments were atmosphere of methane, mixture of methane and nitrogen and pure nitrogen.

Composition of the prepared layers was studied by means of XPS analysis (X-ray photoelectron spectroscopy). Analyses were performed in ESCAProbeP apparatus produced by Omicron Nanotechnology Ltd. equipped with Al Kα (1486.6 eV) X-ray source and a hemispheric analyzer. The size of the analyzed area was approximately 1 mm^2. Ar ions (energy of 5 keV) were used for ion sputtering.

2.2. Contact metallization

In our experiments, we used well-known metallization of the Ni/Si type [7], whose structure Ni(13)/Si(12)/Ni(13)/Si(12) corresponds to formation of the Ni_2Si-type silicide during the annealing process. The data in brackets by the individual elements mean thickness of the respective layer in nm. The individual layers of the metallization were again deposited in the evaporating apparatus UNIVEX 450, using the electron gun. The procedure used for surface cleaning was the same as for the VLS epitaxial layer deposition. After that the samples were placed into the evaporating apparatus and pumping was started. Prior to the evaporation, the surface of substrates had been cleaned with plasma in argon atmosphere (pressure of 0.1 mbar, voltage at auxiliary electrode 1 kV, and current 60 mA). After depositing the structures were annealed in vacuum at temperature of 960 °C for 10 min.

The electrical characterization was performed by measuring contact resistivity r_C with the modified four-point method [8]; 150×200 μm^2 contact pads with the distance of 1 mm were used. The measuring current was 10 mA and the precision of voltage measurements using an A/D converter was in the order of 10 μV.

3. Results and discussion

3.1. VLS epitaxial growth

Three types of structures were prepared: the first with composition Si(11)/Ge(39)/SiC, the second with modified sequence of layers – Ge(39)/Si(11)/SiC and the third with composition Si(111)/Ge(393)/Ni(7)/SiC. Thicknesses of the layers were chosen in such a way, that the atomic ratio of silicon to germanium in the structure was 1:3. The Si–Ge system of this composition is completely melted at temperature higher then approximately 1160 °C. The third structure was used for the specification of a doping concentration in the VLS epitaxial layers.

The substrates with deposited metallization were cut to pieces of approximately 5×5 mm. The individual samples were annealed in different environments at temperatures of 1240 and 1414 °C. In the original works (see for example [6]) related to preparation of VLS epitaxial structures, annealing was done in propane atmosphere. In this work we tested methane at two pressure levels in the apparatus (1×10^{-1} mbar and $1 \times 10^{+1}$ mbar). Several samples were annealed in the atmosphere of pure nitrogen at above mentioned pressures and finally we did one experiment, where the annealing atmosphere was a mixture of nitrogen and methane in 1:1 ratio at the pressure of 2×10^{-1} mbar. Methane within the VLS process supplies carbon necessary for the epitaxial growth into the Si–Ge structure. The nitrogen atmosphere was tested, since nitrogen is a doping element for N-type SiC. A control annealing was done in vacuum as well. Survey of all experiments is in Table 1. The first column represents the structure composition for the VLS epitaxial growth. The second column describes the growth conditions (atmosphere, pressure and temperature). The third column shows the surface quality of the produced layer. Majority of the structures exhibits smooth and glossy surface. Among all, those are the structures of the Ge(39)/Si(11)/SiC type. An example of the surface morphology of the Si(11)/Ge(39)/SiC structure annealed in methane atmosphere at pressure of $1 \times 10^{+1}$ mbar and temperature 1240 °C is shown in Fig. 1. The size of the depicted area is 200×300 μm. The surface shows minor imperfections which emerged during the epitaxial growth.

Composition of the VLS structures was studied by means of the XPS analysis. Fig. 2a shows the concentration profile of the Si(11)/Ge(39)/SiC structure after deposition. From the graph it is obvious that individual layers are separated from each other as well as from the substrate. The boundary between the substrate and the Si–Ge structure was reached after approximately 7 min of ion etching,

Table 1
Survey of experiments within the VLS process.

Structure composition	Annealing process	Surface morphology	Contact resistivity r_C (Ω cm^2)	Surface morphology of metallization
Si(11)/Ge(39)/SiC	Vacuum, 1240 °C	Smooth	$(7.08 \pm 2.07) \times 10^{-5}$	Poor
Si(11)/Ge(39)/SiC	CH_4, 1×10^{-1} mbar, 1240 °C	Smooth	$(7.05 \pm 1.27) \times 10^{5}$	Poor
Si(11)/Ge(39)/SiC	N_2, 1×10^{-1} mbar, 1240 °C	Small defects	$(1.50 \pm 0.28) \times 10^{-4}$	Poor
Si(11)/Ge(39)/SiC	$CH_4 + N_2$, 2×10^{-1} mbar, 1240 °C	Small defects	$(5.32 \pm 0.32) \times 10^{-5}$	Fair
Si(11)/Ge(39)/SiC	N_2, $1 \times 10^{+1}$ mbar, 1240 °C	Small defects	$(7.32 \pm 0.69) \times 10^{-5}$	Fair
Si(11)/Ge(39)/SiC	CH_4, $1 \times 10^{+1}$ mbar, 1240 °C	Small defects	$(6.60 \pm 0.62) \times 10^{-5}$	Fair
Si(11)/Ge(39)/SiC	N_2, 1×10^{-1} mbar, 1414 °C	Smooth	$(7.31 \pm 0.76) \times 10^{-5}$	Smooth
Si(11)/Ge(39)/SiC	CH_4, 1×10^{-1} mbar, 1414 °C	Small defects	$(6.65 \pm 0.95) \times 10^{-5}$	Smooth
Ge(39)/Si(11)/SiC	Vacuum, 1240 °C	Smooth	$(5.85 \pm 1.38) \times 10^{-5}$	Poor
Ge(39)/Si(11)/SiC	CH_4, 1×10^{-1} mbar, 1240 °C	Smooth	$(6.92 \pm 1.40) \times 10^{-5}$	Poor
Ge(39)/Si(11)/SiC	N_2, 1×10^{-1} mbar, 1240 °C	Smooth	$(1.94 \pm 0.54) \times 10^{-4}$	Poor
Ge(39)/Si(11)/SiC	$CH_4 + N_2$, 2×10^{-1} mbar, 1240 °C	Smooth	$(6.45 \pm 0.69) \times 10^{-5}$	Fair
Ge(39)/Si(11)/SiC	N_2, $1 \times 10^{+1}$ mbar, 1240 °C	Smooth	$(6.74 \pm 0.99) \times 10^{-5}$	Poor
Ge(39)/Si(11)/SiC	CH_4, $1 \times 10^{+1}$ mbar, 1240 °C	Small defects	$(6.76 \pm 0.55) \times 10^{-5}$	Poor
Ge(39)/Si(11)/SiC	N_2, 1×10^{-1} mbar, 1414 °C	Smooth	$(7.94 \pm 1.07) \times 10^{-5}$	Smooth
Ge(39)/Si(11)/SiC	CH_4, 1×10^{-1} mbar, 1414 °C	Smooth	$(6.90 \pm 0.64) \times 10^{-5}$	Smooth
Si(111)/Ge(393)/Ni(7)/SiC	$CH_4 + N_2$, $1 \times 10^{+1}$ mbar, 1240 °C	Small defects	$(4.02 \pm 0.64) \times 10^{-5}$	Fair
Si(111)/Ge(393)/Ni(7)/epiSiC	$CH_4 + N_2$, $1 \times 10^{+1}$ mbar, 1240 °C	Small defects	$(3.3 \pm 0.74) \times 10^{-3}$	Fair

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