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TITLE: Improved Thermal Stability Observed in Ni-based Ohmic Contacts to n-type SiC for High-Temperature Applications

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Abstract

The high-temperature stability of a Pt/TaSi₂/Ni/SiC ohmic contact metallization scheme was characterized using a combination of current-voltage measurements, Auger electron spectroscopy, and transmission electron microscopy imaging and associated analytical techniques. Increasing the thicknesses of the Pt and TaSi₂ layers promoted electrical stability of the contacts, which remained ohmic at 600°C in air for the extent of heat treatment; the specific contact resistance showed only a gradual increase from an initial value of $5.2 \times 10^{-5} \Omega\text{-cm}^2$. We observed a continuous silicon-oxide layer in the thinner contact structures, which failed after 36 h of heating. Meanwhile, thicker contacts with enhanced stability contained a much lower oxygen concentration that was distributed across the contact layers, precluding the formation of an electrically insulating contact structure.

Introduction

Chemical sensors that can be used to monitor and control unwanted emissions of pollutants into the atmosphere are in great demand. Examples include monitoring of hydrocarbons from automobile engines and monitoring of flue gases such as CO emitted from power plants. Many of the polluting processes and gases require sensors that can be operated at high temperatures ($\sim 300\text{--}800\text{ }^{\circ}\text{C}$) and in chemically aggressive environments. Therefore, the intrinsic properties of SiC, such as its wide band gap and chemical inertness, give it substantial advantages for use in these sensors.^[1, 2] Metal-insulator-silicon carbide (MISiC) sensors have been developed at the Swedish Sensors Centre (S-SENCE) and continues now at the Functional Nanoscale Materials, FunMat, Centre at Linköping University in Sweden; the sensors can operate in oxidizing ambients for short durations at temperatures up to $700\text{ }^{\circ}\text{C}$.^[3]

One of the critical limitations to long-term operation of SiC gas sensors at high temperatures, however, is the degradation of the metal-SiC contacts. This problem is associated with metal-SiC reactions to form silicides, carbides, and/or free carbon, and oxidation. Further complications are introduced by the requirements for high-temperature ohmic contacts: high resistance to oxidation, stable electrical conductivity and contact resistance, and the ability to be connected to the external circuitry (e.g. wire bonding). In order to meet all of these requirements, contact structures typically consist of multiple metal layers, any of which can introduce an additional thermodynamic instability to the system.^[4, 5]

In a previous study^[6], we investigated the high-temperature stability of Pt/TaSi_x/Ni/SiC ohmic contacts, which have been implemented in actual SiC-based gas sensors developed for applications in diesel engines and power plants. Successful operation of the contacts after heating at $300\text{ }^{\circ}\text{C}$ in air for 1000 h was demonstrated; however, the contacts lost ohmic behavior after much shorter times at 500 and $600\text{ }^{\circ}\text{C}$. The results of that study

showed that electrical failure corresponded with oxidation of the tantalum silicide layer. In this study, we attempted to control the stoichiometry of the TaSi₂ layer and increased the thicknesses of the Pt and TaSi₂ layers to equal those in Pt/TaSi₂/Ti/SiC contacts that showed electrical stability at 600 °C.⁷ Contact structures with thin and thick Pt and TaSi_x layers were compared via electrical measurements and a combination of Auger depth profiles, transmission electron microscope (TEM) images, electron energy loss spectroscopy (EELS), and energy dispersive x-ray spectroscopy (EDS) to identify morphological and chemical changes at key points during the heat treatment tests. The associated phases formed are discussed in terms of contact degradation.

Experimental

The electrical contacts in sample set A were fabricated on a N-doped substrate ($\sim 5 \times 10^{16} \text{ cm}^{-3}$) containing a 1 μm -thick n-type epitaxial layer with a nitrogen doping concentration of $1 \times 10^{16} \text{ cm}^{-3}$, as determined by secondary ion mass spectroscopy (SIMS) analysis. The fabrication and processing of the devices were performed at ACREO AB, Stockholm, Sweden and Linköping University. First, a 100 nm-thick Ni layer was deposited by thermal evaporation. A 5-minute anneal was performed in Ar at 950 °C to form ohmic contacts. Subsequently, a 50 nm-thick TaSi_x adhesion layer and a 150 nm-thick Pt capping layer were deposited by magnetron sputtering. Linear transfer length method (TLM) patterns, along with sensor devices (not used in this study), were fabricated using traditional photolithographic techniques; the former devices were used for calculations of specific contact resistivity. The TLM contact patterns consisted of 150 x 500 μm rectangles with the following contact spacings: 10, 20, 30, 40, and 50 μm . Each set of TLM patterns was isolated from one another by mesas.

The electrical contacts in sample set B were fabricated on a p-type single crystal 6H-SiC wafer containing a 0.5 μm -thick n-type epitaxial layer with a doping concentration of $8.1 \times 10^{18} \text{ cm}^{-3}$. The SiC surface was first solvent-cleaned in acetone and isopropanol, followed by a 10 minute etch in dilute hydrofluoric acid solution. The samples were rinsed in deionized water, dried with nitrogen, and immediately loaded into an ultra-high vacuum deposition chamber, where they were heated at 700°C for 15 min to remove surface contaminants. After cooling to room temperature, Ni (100 nm) was deposited onto the SiC surface using electron-beam evaporation. The contacts were then annealed *ex-situ* in vacuum (2×10^{-5} torr) at 950°C for 5 min. Following a 1-min. ozone treatment, TaSi₂ (400 nm) and Pt (200 nm) layers were deposited onto the Ni surface using magnetron sputtering at an operating pressure of 2 mTorr. Finally, circular transmission line method (CTLM) test patterns for determination of specific contact resistance were defined using standard photolithography techniques. The dimensions of the CTLM patterns were as follows: 100 μm diameter circles, separated from a field of metal by spacings of 5, 10, 15, 20, 25, 30, 35, 45, and 55 μm .

Thermal stability tests were conducted using a tube furnace to heat the samples to 600°C in a flow of synthetic air for various intervals of time. After the samples cooled to room temperature, current-voltage measurements were performed using a probe station and HP 4155B semiconductor parameter analyzer. Auger electron spectroscopy (AES) depth profiles were obtained from selected samples to observe the interfacial chemistry. The AES system used was a PHI 660 Scanning Auger Microprobe equipped with a coaxial LaB₆ filament electron gun and a single pass cylindrical mirror analyzer. The electron beam energy was 10 keV and the beam current was approximately 3 μA . A 3 KeV positive argon ion beam was used to obtain the depth profiles. Additional materials characterization included an FEI Tecnai F20 field emission transmission electron microscope (TEM) equipped with an energy

dispersive X-ray spectrometer (EDS). The TEM cross-section specimens were prepared using a focused ion beam system, equipped with scanning electron microscopy, to cut out and polish the desired section of the contact.

Results and Discussion

The metallization schemes and corresponding specific contact resistance values for both sets of contacts are given in Table 1. The initial difference in contact resistance is attributed to the difference in doping concentration in the SiC substrates. A summary of the electrical results is given in Figure 1, which shows a plot of average specific contact resistance as a function of time at 600°C for sets A and B of Ni-based ohmic contacts. While sample set A exhibited a significant increase in specific contact resistance followed by electrical failure after 36 h of heating at 600°C in air, the contacts with thicker TaSi₂ and Pt layers (set B) remained ohmic for extent of heating (312 h). It should be noted that the contact resistance remained relatively stable after heating for 6 h, and the contacts did not lose ohmicity even after 300 h of heating. Rather, the electrical measurements became difficult, and it was necessary to scratch through an oxide layer with the probes in order to make electrical contact. Examination by Auger electron spectroscopy (not shown) reveals the presence of silicon oxide near the surface.

Table 1. Layer thicknesses and doping concentrations in the underlying n-type SiC epilayers for Sample Sets A and B. Contact resistance values are given for contacts prior to heating and for the contacts heated for 24 h and 312 h at 600 °C.

Sample Set	Layer Thickness (nm)			SiC Doping Conc. (cm ⁻³)	ρ_c ($\Omega\text{-cm}^2$)		
	Pt	TaSi _x	Ni		0 h	24 h	312 h
A	150	50	100	1×10^{16}	8.7×10^{-4}	2.3×10^{-2}	not ohmic
B	200	400	100	8×10^{18}	5.2×10^{-5}	1.4×10^{-4}	3.3×10^{-4}

A series of AES depth profiles obtained from Set A contacts are given in Figure 2. Prior to heating in air at 600°C, a build-up of carbon and a small amount of oxygen are present at the nickel-silicide surface. The ‘free carbon’ is a product of the reaction between Ni and SiC to form Ni₂Si and C during the ohmic contact annealing step,^[7, 8] while the oxygen is a result of exposure to air between the ohmic contact anneal and the subsequent TaSi_x deposition. The AES depth profiles obtained from set A contacts shortly before electrical failure (24 h) and after electrical failure (36 h) show oxidation throughout the TaSi_x layer. It is noted that AES depth profiles are unable to distinguish lateral composition variations that may exist within the layers; furthermore, layer roughness, as shown below for the sample heated for 36 h (Fig. 3b), causes tailing in the elemental depth profiles. Therefore, to complement the AES depth profiles, we also characterized the sample interfaces using cross-sectional TEM with chemical analysis.

Figure 1. Average specific contact resistance of Pt/TaSi_x/Ni/SiC ohmic contacts as a function of time at 600 °C, as determined from current-voltage measurements that were taken at room temperature, after cooling the samples.

Figure 2. AES depth profiles obtained from Set A contacts (a) prior to heat treatment, (b) after 24h in air at 600°C, and (c) after 36h in air at 600°C.

Scanning transmission electron microscopy (STEM) images of contact set A cross-sections after 24 h and 36 h are given in Figure 3. The chemical elements within different

regions were identified using EDS and are labeled in the STEM images. Although the AES depth profiles in Figure 2 (a) and (b) indicated oxidation throughout the TaSi_x layers, EDS analysis showed that at 24h, regions of oxidized TaSi_x and regions of metal are intermixed; the non-oxidized regions should therefore serve as a pathway for electrical conduction. In contrast, EDS analysis at 36 h shows that a layer of silicon oxide approximately 50 –100 nm thick formed. The presence of this silicon oxide layer, which is electrically insulating, would account for the electrical failure after 36 h of heating in air at 600 °C.

Figure 3. STEM images of a contact cross-section from sample set A after (a) 24 h and (b) 36 h of heating in air at 600°C.

A second series of AES depth profiles obtained from set B contacts is given in Figure 4. Prior to heating in air, the depth profile for contact set B (Figure 4a) looks very similar to that of contact set A (Figure 3a). The minor differences, less free carbon and no oxygen at the nickel silicide surface in contact set B, are attributed to the fact that the contacts were fabricated at different facilities using slightly different procedures (see Experimental section). After heating in air at 600°C for 36 h, contact set B was still ohmic, while contacts from set A were not. Upon comparison of the Auger depth profiles at 36 h, Figures 2c and 4b, the contact chemistry appears to be similar, with a significant oxygen concentration across the TaSi_x layers. Again, STEM images with EDS analysis helps to distinguish between these two contacts. A significant difference between the cross-sections of contacts A (Figure 3b) and B

(Figure 5) at 36 h is the roughness: the contacts with thicker Pt and TaSi₂ layers displayed much more planar interfaces and smoother surfaces than those of set A. Energy dispersive spectroscopy was used to identify the chemistry within the different regions of the cross-sections. The layer of SiO_x in sample set A, which is believed to cause electrical failure in such contacts, is not observed in sample set B. Although regions of oxidized TaSi₂ were identified near the Ni₂Si and Pt interfaces, a significant amount of un-oxidized TaSi₂ remains. Quantitative information about the absolute oxygen concentration is not reported here, because the accuracy of oxygen detection with EDS is poor.

An AES depth profile obtained from a contact in set B after heating in air at 600°C for over 300 h is given in Figure 4c. Although the contacts are still ohmic with seemingly stable electrical characteristics, we observed significant changes in the interfacial chemistry. Such changes include Pt migration into the contact as well as Ni out-diffusion to the Pt/TaSi₂ interface: two layers of Ni silicide appeared to form on either side of the Ta silicide layer. Coincidentally with the interdiffusion of metal species and corresponding migration of the Ni silicide layer, the oxygen concentration profile appeared to spread out and remain relatively low throughout the contact layers. This behavior is in contrast to the increasing oxidation of the Ta silicide layer with time that occurred in sample set A.

The reduction in oxidation of the layers in sample set B relative to that observed in sample set A and the associated, dramatic improvement in electrical stability is attributed to the increased thicknesses of the TaSi₂ and Pt capping layers. Interestingly, Fig. 4c also indicates that a thin layer of silicon-oxide formed near the surface of the contact, a result similar to that reported by Okojie et al.^[9] on Ti-based contacts with identical capping layers. In that study, the migration of oxygen into the contact was contained by the presence of a

surface layer of Pt₂Si with a very slow rate of oxidation. This mechanism may also be operating in the contacts reported here.

Figure 4. AES depth profiles obtained from Set B contacts (a) prior to heat treatment, (b) after 36 h in air at 600°C, and (c) after 312 h in air at 600°C.

Figure 5. STEM image of a contact cross-section from sample set B after 36 hours of heating in air at 600°C.

Conclusions

The stability of Pt/TaSi₂/Ni/SiC ohmic contact structures was investigated after heating in air at 600 °C. An increase in the Pt and TaSi₂ layer thicknesses, and possibly small differences in the silicide stoichiometry or film quality, resulted in a dramatic improvement in the stability of the contact resistance. Electrical failure of the contacts containing thinner Pt and TaSi₂ layers was attributed to the formation of a silicon oxide layer within the contacts. In contrast, thicker TaSi₂ and Pt capping layers substantially reduced oxidation within the contact layers and prevented the formation of an electrically insulating contact structure.

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