VERY HIGH TEMPERATURE (800^{O}C) OHMIC CONTACT OF AU/NI$_2$SI ON N-TYPE POLYCRYSTALLINE SILICON CARBIDE AGED IN AIR

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ABSTRACT

Ohmic and low-resistance electrical contacts on silicon carbide have been demonstrated for the first time up to very high temperature (800°C) in an oxidizing environment. A specific contact resistance of about $2 \times 10^{-4}\,\Omega.\mathrm{cm}^2$ was achieved after silicidation at 900°C. Long term aging tests in an oxygen atmosphere were performed, demonstrating ohmic behavior up to 1000 h at 550°C and over 4 h at 800 °C. The aging mechanism has been explained, suggesting that polycrystalline 3C-SiC is not as stable as expected at very high temperatures, acting as a source for Si out-diffusion. Also, *in-situ* electrical measurements at very high temperatures in air using the transmission line method (L-TLM) have been achieved demonstrating good performance of the proposed metallization at representative operating conditions for harsh environments.

KEYWORDS

SiC, ohmic contact, transition metal silicides, formation mechanism, oxidation, silicon diffusion

INTRODUCTION

Instrumentation that can operate in harsh and high temperature environments is required to meet the measurement needs in the energy, transportation and industrial sectors. Monitoring coal gasification or natural gas production, increasing fuel efficiency or decreasing pollutant emissions need new in-situ high temperature sensors [1]. In the last decade, some materials have been developed and improved to remain stable in very high temperature environments. Among them, silicon carbide is a promising semiconductor due to its electrical and mechanical properties for operating at high temperature. Compared with Si, single- and poly-crystalline SiC have extreme hardness, chemical inertness, high wear resistances, and radiation resistances [1]. Though SiC has promissing mechanical properties up to 900°C, the metal/SiC electrical contacts are a main limitation. Metal contact on SiC has been intensively studied at room temperature, but very rarely during representative operating conditions [2]. Up to now, multilayer Ti/TaSi$_2$/Pt metallizations have achieved the highest temperature of 600°C for long term aging in air [2]. These multilayers were designed with a top layer (Pt) to prevent oxidation and a lower layer (Ti) for a good electrical contact. A diffusion barrier is however required to prevent non-ohmic Pt-silicide formation. Unfortunately, classical TiN and TaSi$_2$ barriers oxidize beyond 600°C [3;4]. Since diffusion mechanisms are greatly enhanced at very high temperature (Arrhenius dependence), this multilayer approach is fundamentally limited. In this work, we have identified Ni$_2$Si as a candidate metallization that resists oxidation while providing a good ohmic contact up to very high temperatures. In this paper, we will present the method to create the Ni$_2$Si contact, followed by its characterization from room temperature to 800°C in air. Chemical composition as a function of depth is also studied to identify the life limiting factor.

MATERIAL AND EXPERIMENTAL SETUP

The experimental approach consists of measuring the contact resistance of Ni$_2$Si pads on SiC films using L-TLM structures. These test structures consists of a row of rectangular pads (500 µm × 1500 µm each) spaced from 100 to 500 µm in increments of 100 µm.

The 3.1 µm thick poly-3C-SiC films were grown on silicon wafer by low-pressure chemical vapor deposition (LPCVD) at 900°C using SiH_2Cl_2 (100%) and C_2H_2 (5% in H_2) precursors. In situ nitrogen was doped using NH_3 (5% in H_2) for n-type conductivity [5]. The SiC films were grown at the Case Western Reserve University microfabrication facilities (M. Mehregany). Sample surfaces were cleaned in Piranha solution, and L-TLM patterns were defined by photolithography for lift-off. In an e-beam evaporator, pure 5 nm thick chromium and 200 nm thick nickel layers were deposited over the photoresist patterns with a very low deposition rate. To remove the native oxide, the samples were etched with HF immediately before being loaded into the evaporation chamber. The photoersist was removed to lift-off the metal (Microposit Remover 1165 at 80°C) and leave it only in the L-TLM patterns. Nickel silicide was obtained by heating the sample in a commercial rapid thermal annealing (RTA) chamber during 120 seconds at 900°C under 100 sccm flow of forming gas (90% N_2-10% H_2).

Temperature dependence of metal-semiconductor contact behavior was investigated on Au/Si$_2$Ni/SiC samples placed in a tube furnace, and electrically monitored with wires to measuring instruments.

The available metals operating at high temperature without oxidation are gold and platinum. As gold is easily wire-bondable, it has been chosen for electrical connection even if its lifetime should be more limited than platinum connections. A 200 nm thick evaporated gold cap layer enabled the bonding of Au wires on the Ni2Si surface. The samples were then mounted onto alumina jigs (37 mm × 37 mm × 5 mm). They were connected to gold pads on alumina plates by ball-bonding with 35 µm thick gold wires. Two wires were welded on each TLM pad to reproduce the four-terminal method between two successive pads selected by a switch control. The alumina plate must be well polished with a low roughness (< 30 nm) to have a good welding with wires. Alumina plates were therefore polished with Materpolish II on Microcloth PSA from Buehler, and 200 nm thick gold pads were evaporated on its surface through a stencil mask. High temperature cables were inexpensive mineral insulated cables (1.57 mm thick Omegaclad XL from Omega) with nickel-chrome based wires. These cables have an excellent oxidation resistance at temperatures up to 1150°C. Each cable was insulated with an alumina tube. Electrical connection between the wires of the high temperature cables and the pads on the alumina plates was performed by compression, with alumina washers, screws and nuts. Because various materials with different work functions are in contact, thermoelectric potentials may develop at each cable-pad and pad-wire junction. But since two electrical connections on each TLM pad are completely symmetric and at the same temperature, this effect should be cancelled. Furnace and jig temperature were calibrated with a thermocouple before contact resistance measurements.

Current-Voltage measurements between each contact pad of the L-TLM structures are done by an Agilent 34970A with a switching unit. At each operating point, specific contact resistance (Ni_2Si – SiC interface) and sheet resistance (SiC film) are extracted. Measurements are taken during 4 minutes every 25°C, after reaching a stable temperature. Between each step, temperature increased with a rate of 2°C/min up to 800°C. At 800°C, always under dry air flow (100 sccm), sample characterization is done every 15 minutes.

Moreover, elemental composition through the depth of the contacts was performed with X-ray photoelectron spectroscopy (XPS) with Mg and Al Kα sources and an argon ion gun (analysis area 110 µm × 110 µm).

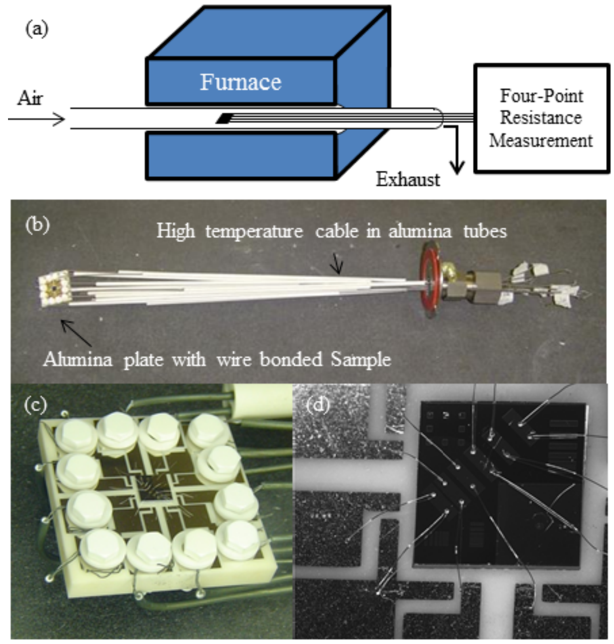

Figure 1: (a) Drawing of set up for taking linear transmission line method (L-TLM) measurement at high temperature; (b) Mounting of 12 insulated cables screwed on the alumina plate, connected to the measurement instrument through a hermetic pressure feedthrough; (c) Close-up of the packaging with sample at the center and screwed nickel-chromium cables compressed with alumina screws, washers and nuts; (d) Close-up picture of sample with ball-bonded Au wires.

RESULTS AND DISCUSSION

Phase formation of the contacts

The silicidation-carburization process of nickel on poly-3C-SiC is a critical step in the reliability of metal-semiconductor contact, above all in high temperature applications. It must slow down the interdiffusion of various materials, and prevent oxidation of the contacts. After annealing, contact resistance has to show an ohmic behavior. For 3C-SiC, Schottky-ohmic transformation begins at 900°C with the dominant phase being Ni_2Si [1]. Since the degradation of nickel contacts increases rapidly with temperature, annealing temperature of Ni/SiC samples has been set at 900°C. To confirm the silicidation of the entire thin film, x-ray diffraction structural analysis was taken in glancing incidence. The dominant peak of pure Ni at 44.6° from as-deposited samples completely disappeared after RTA. Orthorhombic δ-Ni_2Si polycrystalline is well defined in the spectrum and seems to be the dominant phase. There is also oxidized nickel after annealing. Oxidation is inevitable even under forming gas. Forming gas simply limits surface oxidation of nickel and prevents diffusion in the layer. Without forming gas, surface oxidation is more important and increases the thermal degradation of the contacts by formation of grain boundaries in the nickel silicide layer. Contact resistance after annealing shows an ohmic behavior around 200 $\Omega.cm^2$. Surface morphology of contacts after annealing presents a homogeneous layer with some dark spots (~ 100 nm) at the surface. These spots correspond to chromium that has migrated at the surface and oxidized when exposed to air.

Temperature dependence

The values of sheet resistance (SR) extracted from the TLM measurements remain stable at 5.3 Ω/sq up to 400°C, and then decreases to 0.4 Ω/sq at 800°C (Fig. 2). Meanwhile, specific contact resistance (SCR) decreases with temperature from $294 \pm 16\ \Omega/sq.cm^2$ to $6.4 \pm 0.8\ \Omega.cm^2$ at 800°C. Evolution of the contacts shows a conservation of ohmic characteristics of the metallization. A hump around 500°C is representative of all measured samples corresponding to a SCR increase of 40%. Even with a slow temperature ramp, atomic diffusions in the contacts are negligible and cannot explain the two regimes at intermediate temperatures. The electronic behavior of the contacts can explain the hump, without indicating any thermal deterioration of the contact. According to the Schottky model, the barrier height at a metal/semiconductor interface and semiconductor doping govern the different mechanisms of current transport. Thermoionic emission (TE), thermoionic field emission (TFE) and field emission (FE) from the Schottky model [6] have been fitted on the experimental data of SCR, and only the TFE model fits well using the Pearson's chi-square test and the anticipated physical parameters of the Schottky barrier. Temperature dependence of the specific contact resistance is then defined by [6]:

$$\rho_c = \left(\frac{1}{qA^*}\right)\frac{k^2}{\sqrt{\pi(\varphi_B + u_F)}}\cosh\left(\frac{E_{00}}{kT}\right) \times \left[\sqrt{\coth\left(\frac{E_{00}}{kT}\right)}\exp\left(\frac{\varphi_B + u_F}{E_0} - \frac{u_F}{kT}\right)\right] \quad (1)$$

where q is the elementary electron charge, k the Boltzmann constant, A^* the modified Richardson constant (49.3 $A.cm^{-2}.K^{-2}$ for 3C-SiC [7]), φ_B the Schottky barrier height, u_F the energy difference between Fermi level and the upper level of valence band, E_0 the tunneling probability ($E_0 = \frac{E_{00}}{\coth\left(\frac{E_{00}}{kT}\right)}$ with $E = \frac{q\hbar}{2\sqrt{\frac{N_D}{m^*\varepsilon}}}$ the characteristic energy, $\hbar$ the reduced Planck constant, N_D the semiconductor doping concentration (2.6×10^{20} atoms per cm^{-3} [5]), m^* the effective mass of tunneling electron, ε the dielectric constant of semiconductor ($9.72\varepsilon_0$, with ε_0 permittivity of free space [8]). The characteristic energy E_{00}, the energy difference u_F, and the Schottky barrier height φ_B are floating parameters.

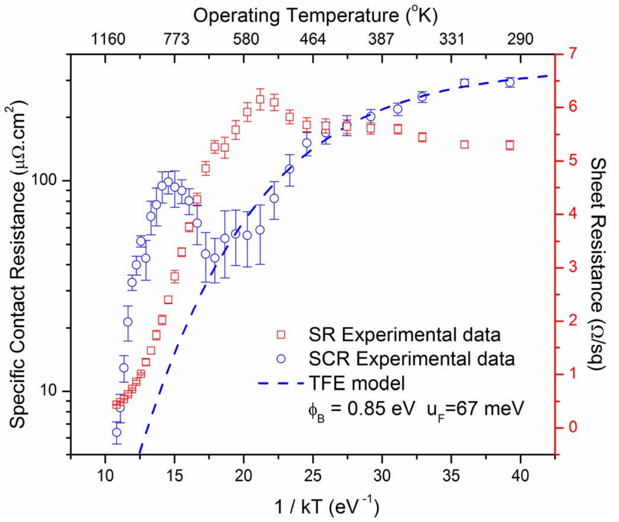

Figure 2. Temperature dependence of SCR and SR for Au/Ni_2Si contact in air. The curve fitting of SCR uses the TFE model.

Figure 2 presents the extrapolation of TFE model on SCR experimental data. Only the low temperatures until 400°C can be correctly fitted by TFE model with a small Schottky barrier height (0.80 ± 0.10 eV). The work function of undoped Ni_2Si is estimated [9] at 4.7 eV (Ni 5.15 eV) and 3C-SiC electronic affinity [10] at 4 eV. The barrier is then evaluated in the Schottky limit as 0.7 eV close to the extracted value. The characteristic energy E_{00} is constant at 68 ± 4 meV, corresponding to an effective mass of tunneling electron $m^*=0.51m_0$ for a doping concentration 2.6×10^{20}atoms per cm^{-3}. Also, the energy difference between the Fermi level and the upper level of valence band is small $u_F=67 \pm 7$ meV. In this regime, the TFE model with those parameters is validated by the criterion [6]:

$$\frac{\cosh^2\left(\frac{E_{00}}{kT}\right)}{\sinh^3\left(\frac{E_{00}}{kT}\right)} < \frac{2(\varphi_B + u_F)}{3E_{00}} \quad (2)$$

At high temperature, above 400°C, SCR experimental data diverge from the TFE model. No models of transport mechanisms gave satisfactory parameters. In all of them, the carrier transport is defined by the fundamental quantities: Schottky barrier height and the carrier concentration. If we assume that the TFE model governs again the transport mechanism, SCR can be higher than theoretical values with a higher barrier and/or a lower carrier concentration. In this model, field and thermoionic emissions cohabit. With a higher barrier, field emission will dominate, but not enough to compensate thermoionic emission. SCR increases then between 400°C and 500°C. Above this temperature, electrons seem to have enough thermal energy to jump again over the barrier, and SCR decreases.

Time dependence

Heated to 800°C, specific contact resistance and sheet resistance were measured during 4h30min under dry air flow as shown in Figure 3. After 15 min, SCR and SR increase slightly probably with an incorporation of oxygen. After, sheet resistance increases gradually during 3 h. Inversely, specific contact resistance decreases by a factor 2. Contrary to Kuchuk's works [11], there is no thermal degradation of the electrical contacts. An ohmic behavior was maintained up to 18 h at 800°C. After the aging tests, the metallization thickness increased to around 300 nm and exhibits a higher roughness. Over longer periods of time, an oxide layer formed over the pads, which was removed by HF etching. Endurance tests were also done at 550°C, demonstrating similar values of SCR and SR, and no degradation after more than 1000 h.

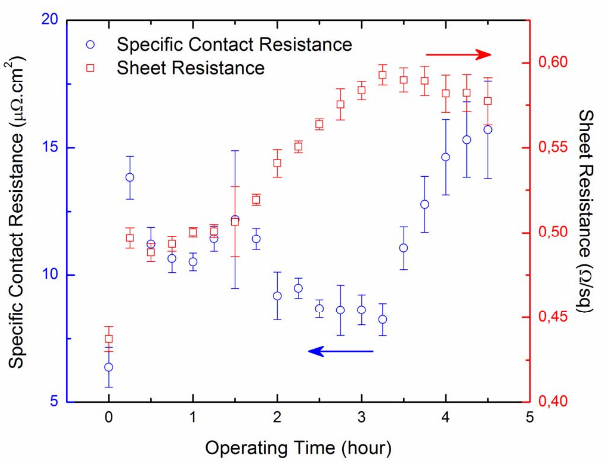

Figure 3: Time dependence of SCR and SR for Au/Ni_2Si contact at 800°C in air.

Depth profiles of the elemental composition, on a metallization without gold but having the same aging at 800°C, clearly shows silicon out-diffusion from the SiC underlayer to the surface of the metallization (Figure 4). SiC is not an inert material at high temperature, dissociating to liberate Si atoms. The contact structure has three clearly separated regions:

1. Close to the surface, enriched of Si and O;
2. Swelling zone enriched of Si, O and Ni with some C;
3. Interface between contact layer and SiC containing O, Si, C and Ni.

Oxygen concentration is high throughout the metallization, and is counterbalanced by carbon concentration. XPS analysis showed that silicon at the surface is completely thermal oxidized. Ni traces in region 1 are also oxidized as NiO. The high concentration in oxygen (region 2) shows chemical bonds with a mixture of metallic Ni and indefinite nickel silicide, but not SiO_2. The atomic concentration ratio of Si:O is 1:1.85, indicating other atomic bonds with Si. Region 3 is the original Ni_2Si contact layer on SiC. As the film is aged after annealing, Ni_2Si concentration decreases with its partial dissociation and the Ni-Si out-diffusion. In the SiC film, there is a silicon shortage in comparison of C concentration (~5% difference), suggesting that silicon out-diffusion comes from the depth of the SiC film: dissociation of SiC. Time dependence of SCR and SR in Figure 3 is the result of the competition between oxidation and silicon out-diffusion from SiC through the metallization and to the wires.

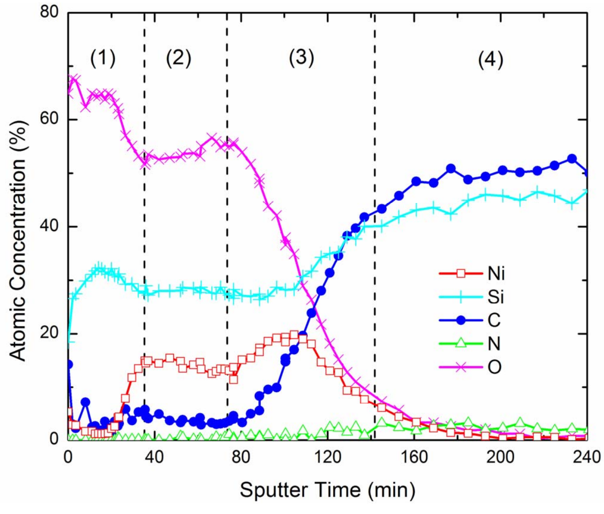

Figure 4: Element depth profiles of Ni_2Si/SiC after 22 h of aging in air (1) SiO_2 crust, (2) $Ni\text{-}Si\text{-}SiO_2$ swelling layer, (3) $Ni_2Si\text{-}SiC$ contact layer, (4) SiC layer.

CONCLUSION

This work proves a good thermal stability of Au/Ni_2Si contacts on polycrystalline 3C-SiC in air at very high temperatures, suggesting a metallization approach for harsh environment SiC MEMS. Low resistance ohmic contacts were maintained at 800°C in air for more than 4 h, with in-situ measurements, and up to 18 h with ex-situ measurements. SCR as a function of temperature was well captured by a thermoionic field emission model, but a yet unexplained behavior of SCR was measured above 400°C. Degradation of contacts follows two sequential mechanisms: Si out-diffusion and oxidation. Si atoms emanate from the SiC layer and diffuse through the Ni_2Si layer, suggesting that SiC is not as stable as commonly expected. The Si atoms that reach the exposed surface of the metallization oxidize in contact with air, which eventually limits the ability to make electrical measurements. To improve sensor lifetime, silicon out-diffusion must be taken into account in oxidizing environments. Its lifetime could then be predicted by a modified Deal-Grove model.

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