A SIC METALLIZATION SCHEME USING AN ALD PROTECTIVE LAYER FOR HARSH ENVIRONMENT DEVICES

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ABSTRACT

This paper reports on the development of a silicon carbide (SiC) metallization scheme, capable of surviving high temperatures (450°C) in air for an extended time (>100h). The interfacial reactions between the SiC and the metal contact are mitigated via a carbon diffusion barrier and the whole metallization is protected with a thin alumina layer deposited by atomic layer deposition (ALD) to prevent oxygen penetration and degradation of the carbon barrier layer. A demonstrated lifetime in excess of 100h at 450°C in air is presented and the contact interface is carefully characterized.

INTRODUCTION

Silicon carbide is a material of choice for fabricating sensors able to operate in harsh environments [1]. In particular, its mechanical and electrical stability and its chemical inertness make SiC well suited for designing devices for operation in high temperature and corrosive environments like geothermal well logging or gas turbines monitoring. SiC sensors able to operate at high temperature in air have already been demonstrated but their lifetime has not been investigated thoroughly. The main reason for this is the difficulty to develop an ohmic metallization scheme which remains stable at high temperature for extended periods [1, 2].

SiC is a wide bandgap semiconductor which makes the realization of ohmic contacts difficult. Theoretically, the deposition of any metals on single-crystalline SiC leads to a Schottky contact. The transition from Schottky to ohmic is observed only after a high temperature annealing under protective atmosphere. The most studied material to fabricate ohmic contacts to SiC has been nickel for n-type SiC and aluminum for p-type SiC. In the case of Ni, an annealing at 900-950°C is necessary to obtain an ohmic behavior. Thermodynamics studies are in agreement with the experiments and have attributed this transition to the appearance of the Ni_2Si phase. However, later studies challenge this theory [3-6] and show that the transition is probably more complex and involves the appearance of vacancies, defects or roughness modification at the interface [1, 6-9, 11]. In the case of polycrystalline SiC (polySiC), commonly used in MEMS devices, we have already demonstrated ohmic contacts with as-deposited Ni and Pt [2, 11]. The high doping level of the thin films used and their polycrystalline nature are probably the reasons for this behavior.

However, in the case of operation at high temperature, SiC reacts with the contact metal, resulting in increase in contact resistivity. When brought in contact with a metal at high temperature, SiC becomes less stable and reacts more easily, creating intermetallic species and releasing carbon. To avoid the formation of carbon at the contact interface, a solution is to add a Si-rich interfacial layer like $TaSi_2$ [12, 13]. The use of materials chemically stable with SiC, like TiW, is also a solution [14]. However, in most cases these materials can oxidize, so a gold or platinum layer is commonly added on top. Diffusion barriers like Ta-Ru are another solution to avoid oxygen penetration into the contact interface [15]. Eventually these different strategies lead to very complex multi-layer metallization schemes. The best metallization scheme for high temperature reported so far [12, 13] follows this path and is composed of Ti/$TaSi_2$/Pt with carefully chosen thicknesses to control the kinetics of the interfacial reactions involved during its use at high temperature.

In contrast to these complex approaches, we previously demonstrated an ohmic metallization scheme for polySiC that exhibits a very stable resistivity from room temperature to 540°C [2]. The improvement came from the growth of a nanocrystalline graphitic (NCG) layer between the SiC thin film and the metal contact (Pt), acting as a thermal barrier to prevent interfacial reactions. However, more extended lifetime studies revealed a contact resistivity increase after a few hours at high temperature in air. In this paper, an improved scheme is presented which exhibits a stable contact resistivity, exceededing 100h in air at 450°C.

EXPERIMENTAL

Silicon wafers are cleaned and thermally oxidized (1µm) to isolate the SiC thin film from the substrate. SiC thin films (1.7µm) are deposited via low pressure chemical vapor deposition (LPCVD) at 850°C with methylsilane (MS) and dichlorosilane (DCS) as precursor gases and H_2 as a carrier gas [16]. Ammonia is used to n-dope the films to a resistivity of 0.01 Ω.cm. Some samples are then annealed at 1300°C for 5 min in ultra-high vacuum (UHV, 10^{-9} Torr) to create a layer of NCG on the SiC, as characterized by Raman spectroscopy. Circular transmission line method (CTLM) test structures [11] are defined by lift-off of a Ti (5nm) / Pt (25nm) metal layer deposited by vacuum evaporation (Thermoionics VE-100) on all the samples (cf. figure 1 a-b). After lift-off, a low power oxygen plasma is used to remove the NCG layer on the exposed areas and its removal is confirmed by Raman spectroscopy. After fabrication of the metal contacts, an additional thin (10nm) protecting layer of Al_2O_3 is deposited by atomic layer deposition (Picosun Sunale R150) on top of some samples to act as a passivation layer.

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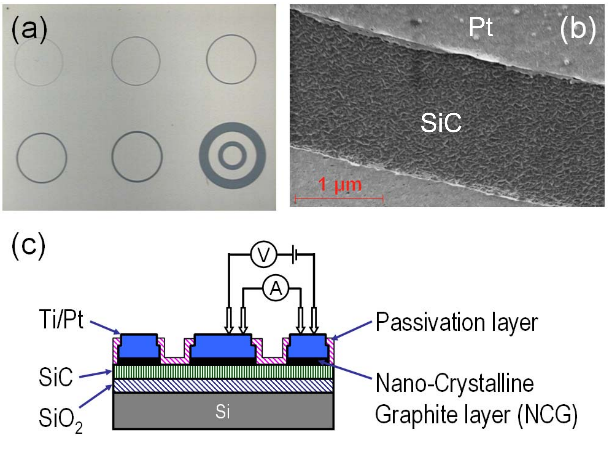


Figure 1: CTLM test structures.
(a) Optical image of the patterned CTLM structures and (b) SEM close-up view, tilted 45°.
(c) Schematic side view of the 4-point probe test setup.

Four samples of each metallization scheme, namely (a) Ti-Pt/SiC, (b) Ti-Pt/NCG/SiC and (c) Ti-Pt/NCG/SiC passivated with Al_2O_3 (cf. figure 2), are annealed on a hotplate at 450°C in air. Heating is regularly stopped and resistivity measurements are performed on each sample using a 4-point probe method (cf. figure 1-c), employing a Signatone S-1160 probe station equipped with a Keithley Multimeter 2400.

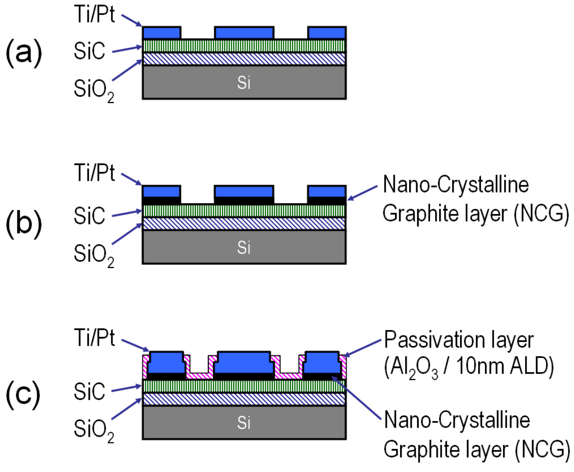


Figure 2: The three studied metallization schemes. (a) Ti-Pt / SiC, (b) Ti-Pt / NCG / SiC and (c) Ti-Pt / NCG / SiC + ALD protective coating.

RESULTS AND DISCUSSIONS

I-V measurements on the CTLM patterns allow the extraction of the contact resistivity between the SiC and its metallization. For the three tested metallization schemes, the initial contact resistivity varies between 1.8 and 3.5 mΩ.cm^2, slightly higher than our previously reported results. This difference may be attributed to the metal deposition technique used in this work (vacuum evaporation instead of sputtering) which provides less energy to the metal atoms during the deposition process. Consequently the contact interface is less dense and of lower quality. For the three metallization schemes, evolution of the contact resistivity as a function of the annealing time (450°C in air) is presented in figure 3.

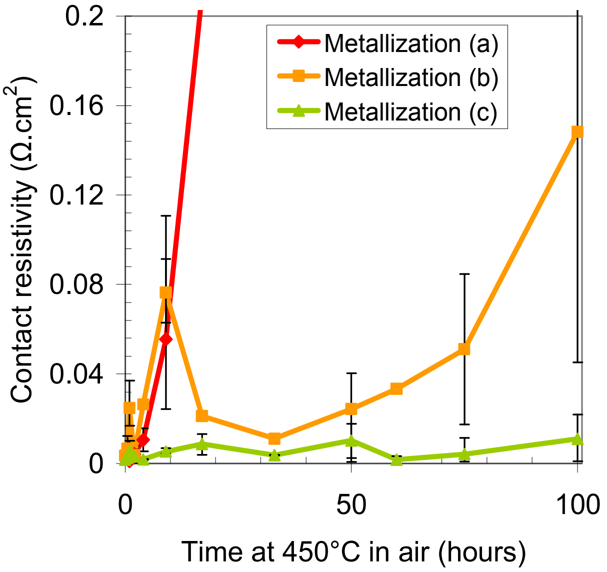
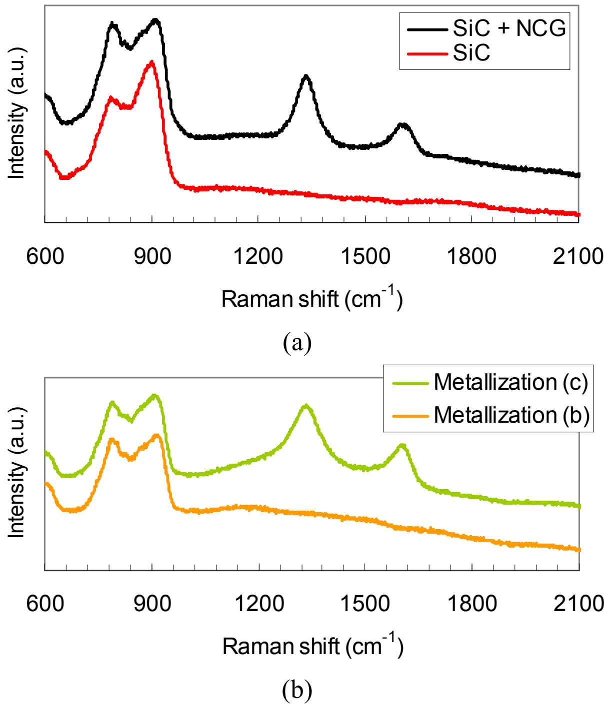


Figure 3: Evolution of the contact resistivity as a function of the annealing time (450°C in air).

The data reveal that the contact resistivity of the metallization (a) increases gradually and becomes too high to be measured after 10h. Metallization (b) presents a similar behavior during the first 10h but recovers rapidly before degrading severely towards of the end of 100h test. Possible degradation mechanisms involved will be discussed later. Metallization (c) presents a very stable contact resistivity which never exceeds 10.9 mΩ.cm^2 during the whole 100h testing.

In order to characterize the contact interface, the metal contact layer is etched at the end of the 100h testing. Samples are dipped for one minute in a 49% hydrofluoric acid (HF) solution to remove surface oxides and the Al_2O_3 layer in the case of the metallization (c). The Pt layer is then etched on each sample in a HNO_3:HCl (3:1) solution (aqua regia) heated at 85°C for 10 minutes. After these etching steps, some metallic residues are still visible on the metallizations (a) and (b) but not on the metallization (c).

To characterize the presence of a NCG layer on the SiC thin film after the annealing step at 1300°C in UHV, Raman spectroscopy is used [2] and is reported on Figure 4-a for our samples. The two characteristic peaks of disordered (D, 1345.5 cm^{-1}) and graphitic carbon (G, 1595.8 cm^{-1}) appear after this annealing step, confirming the growth of a NCG layer on top of the SiC. The two characteristic peaks of 3C-SiC are still visible at 796 cm^{-1} (TO) and 972 cm^{-1} (LO).



(a)

(b)

Figure 4: Raman characterizations of the contact interface.
(a) NCG layer before metal deposition.
(b) After 100h exposure at 450°C and removal of the metal layer.

Figure 4-b presents the Raman characterizations performed on the metallizations (b) and (c) after the 100h testing and removal of the Pt layer. Metallization (b), which initially had a NCG layer in between the SiC and the Ti-Pt, does not exhibit any carbon peak. On the other hand, metallization (c) still exhibits the two characteristic carbon peaks and no noticeable change can be observed. It is known that oxygen degrades the NCG layer at high temperature [17] and additional experiments have been carried showing that after a few minutes at 450°C in air the NCG is removed. Thus, it clearly appears that the NCG layer has been degraded by the oxygen which penetrated either through the Ti-Pt layer or more probably via the exposed sidewalls of the CTLM patterns on metallization (b). On metallization (c), the Al_2O_3 protective layer acted as an effective protective layer to avoid the NCG layer to be exposed to oxygen and damaged.

To further analyze the contact interface, X-Ray photoelectron spectroscopy (XPS, Omicron EA125) characterizations have been performed on each sample and spectra are reported on figure 5.

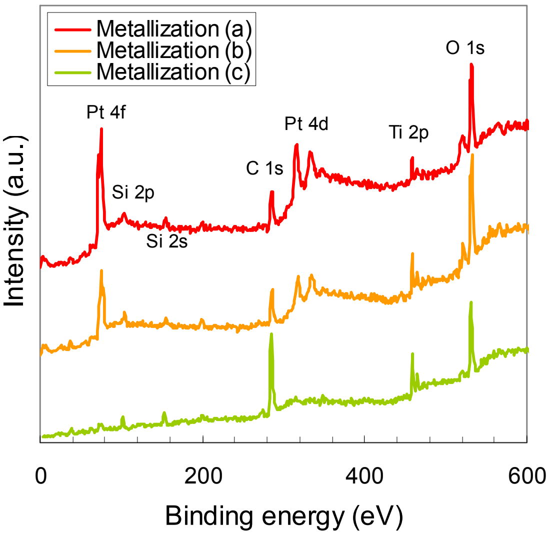


Figure 5: XPS characterizations of contact interface for each metallization after removal of the metal layer.

The spectra for metallizations (a) and (b) look similar, with the presence of Pt peaks, confirming the visual observations of metallic residues on the surface made previously. The signal is lower for metallization (b), probably revealing less residues. Pure Pt is rapidly etched in hot aqua regia but it is known that a thin oxide film grows at the Pt/Pt-silicides interface during silicidation and prevents etching of Pt silicides [18]. The presence of the Pt peaks on these two metallizations clearly indicates that Pt reacted with SiC during the 100h testing at 450°C, generating Pt silicides. Pt silicides can be formed at temperature as low as 350°C; thus this observation is not surprising for metallization (a) and has been reported in our previous work [2].

The presence of silicides for metallization (b) and not for metallization (c) indicates that the NCG layer acts as an efficient diffusion barrier to prevent the silicidation, even during extended operation at high temperature. However, this confirms our Raman characterizations, namely, the NCG layer has been damaged on metallization (b) during the high temperature exposure testing, due to the penetration of oxygen.

Finally, these characterizations help to explain the contact resistivity evolution presented in figure 3. As previously reported, metallization (a) degrades rapidly due to the formation of Pt silicides at the contact interface. Metallization (b) presents a two-step degradation involving the destruction of the NCG layer by oxygen followed by the formation of Pt silicides. On the other hand, metallization (c) exhibits a very stable contact resistivity which can be attributed to the mitigation of Pt silicides formation thanks to the NCG layer and the protection of this NCG layer by the Al_2O_3 capping layer.

CONCLUSIONS

We presented in this paper an ohmic metallization scheme for n-type polySiC able to operate more than 100h in air at 450°C. The metallization material is platinum and a nanocrystalline graphitic layer is grown in between the SiC and the Pt to mitigate interfacial reactions. For operation at high temperature in air, this graphitic diffusion layer is protected with a thin passivation layer (Al_2O_3) capping the metallization stack. Testing at 450°C in air for 100h revealed an extremely stable contact resistivity and characterizations of the contact interface confirm the efficiency of our approach in mitigating interfacial reactions and oxygen penetration. Further work will focus on applying this metallization scheme to single crystalline and p-doped SiC for electronics applications.

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