www.amlett.com, www.vbripress.com/aml, DOI: 10.5185/amlett.2015.6138 Published online by the VBRI Press in 2015

Establishment of optimized metallic contacts on silicon for thermoelectric applications

Omar Abbes*, **Amer Melhem, Chantal Boulmer-Leborgne, Nadjib Semmar**

GREMI CNRS-Université d'Orléans, 14 Rue d'Issoudun, Orléans 45067, France

*Corresponding author. Tel: (+33) 238417123; E-mail: omar.abbes@univ-orleans.fr

Received: 30 September 2014, Revised: 27 March 2015 and Accepted: 05 April 2015

ABSTRACT

This communication describes the development of optimized metallic contacts on Si for thermoelectric applications. Thin solid films of Ni and Pt with the same thickness, were deposited on Si substrates. Two silicides were formed in a vacuum chamber and were studied. The EDX spectroscopy and electron microscopy have supported the presence of silicides in the surface of the samples. The thermoelectric study demonstrated that silicides could play a vital role in the enhancement of the electricity generated by thermoelectric materials that are made of Si. Pt silicide was found to be better candidate than three other metallic contacts (Pt, Ni and Ni silicide), but a comparison with other silicides is needed in the future, to get the best electronic contact on thermoelectric materials. Copyright © 2015 VBRI Press.

Keywords: Thermoelectricity; metallic contacts; silicon; seebeck coefficient.

Introduction

While the world's need of energy is rising with a decrease of fossil fuel supplies, it becomes crucial to develop smart materials that can supply clean and sustainable energy to meet the needs of the future. Thermoelectric materials are currently investigated as a promising pathway, they allow the conversion of temperature gradients into electricity, which provides power generation without refrigerant or moving parts. Cheaper electricity should hence, be obtained, since solar energy may insure a temperature gradient. During last years, nanostructured silicon demonstrated a great potential to ameliorate thermoelectric figure of merit ZT **[1]**. In addition, porous silicon (p-Si) exhibits interesting properties, such as good features of electroluminescence and photoluminescence in the visible and IR spectra **[2-4]**. A lot of effort has been devoted to boost the material's figure of merit, however, in a realistic device, metallic contacts are needed to extract electricity. Those contacts could gradually lower the resulting current, in the case of high electrical contact resistivity. Therefore, optimizing the metallic contacts grown on Silicon is of a high interest, toward their integration in thermoelectric applications. For example, in Complementary Metal-Oxide-Semiconductor (CMOS) technology, transition-metal silicides are used as contacts between metal interconnects and the Si (source, drain, and gate of the transistors) **[5].** Silicides offer major advantages such as contact resistance as well as excellent process compatibility with the standard Si technology. The production of silicides occurs during the reaction between a thin metal film and the Si thanks to the Salicide (Self-aligned silicide) process **[6-8]**. The contact used nowadays, is the Ni monosilicide (NiSi), but PtSi is presented as a very good candidate to be used as a contact in the Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETs); which could eventually lower the contact resistance **[9]**.

In this work, we investigate the fabrication of several thin metallic contacts on Si substrate, in order to establish a low resistive and a stable contact. Another objective of this novel study is opening the road for different thermoelectric materials to have the same metallic contact. Ni and Pt contacts were deposited using Precision Etching & Coating System (PECS), Ni and Pt silicides were formed by solid state reaction in a High vacuum chamber. All contacts were studied by stylus profilometer, scanning electron microscope (SEM) and micro ZT-meter.

Experimental

Preparation of materials

Materials were provided by ST Microelectronics. Si substrates were cleaved from Si(100) epi-ready wafers (manufactured by STMicroelectronics in France), the chemical cleaning of Si surfaces was done in two steps: the first was the rinsing in acetone and ethanol solvents to eliminate hydrocarbon contaminants due to storage of the substrates in air ambient. The next step was etching the contaminated Si native oxide layer in a diluted HF solution (10%) for several minutes. These cleaning steps of substrates was done prior to their introduction into the deposition chamber of the PECS set-up, exhibiting a base pressure better than 2.10^{-6} Torr, and equipped with high purity Ni and Pt charges (minimum of 99.99 wt. %).

Deposition of Ni and Pt

The Si substrates were cut into 25×25 mm^2 pieces. A mask covering the central part of the substrates, and containing four quadrants with a radius of ~ 3 mm at the four corners. The mask allowed the fabrication of contacts at the four corners, which is in adequacy with the distances between the pins of the micro ZT-meter. The set of substrate + mask, are introduced into the PECS chamber, where deposition of Ni and Pt took place at room temperature. The PECS package uses Ar beam to evaporate the targets, in our case the beam energy was set to 8 keV. Rotating the sample during deposition, permitted a better homogeneity of the thin metallic layers obtained. A film-thickness monitor improved the control of the film deposition process by providing a direct display of the deposition rate, plus the total deposition thickness. Hence, two samples of 50 nm thick Ni film on Si and two other samples of 50 nm thick Pt film on Si, were prepared. The deposition rate of Ni was 1 Å/s, while Pt one was 1.3 Å/s.

Characterizations

The profilometer analysis of all samples was conducted on a «Dektak» stylus profilometer. The samples' surface morphology was studied by Scanning Electron Microscopy (SEM, Carl Zeiss supra - 40 FEG - SEM) by using the secondary electron mode detection. The composition of the annealed samples was studied by Energy Dispersive X-ray spectroscopy (EDX, Bruker XFlash Detector 4010 coupled with the SEM), with an energy of ~ 5 keV. The Seebeck coefficient was determined for the prepared samples using a homemade micro ZT-meter (see supporting information below). Figure of merit could be obtained using the equation $ZT = \sigma S^2 T/\kappa$ in which S, σ, T and κ are respectively, Seebeck coefficient, electrical conductivity, operating temperature and total thermal conductivity **[10]**.

Results and discussion

In order to compare metallic contacts on Si, a good adhesion between the deposited layers and the substrate matrix is needed. Thus, microscopic analysis could give valuable insight of the material. Then, understanding of metal-silicon phase formation mechanisms during reactive diffusion would help to optimize fabrication process of the contact layers. It is, therefore, crucial to understand the thermally induced solid state reaction between the metallic films and Si substrate. Studies based on profilometer and EDX analysis should examine the reaction. In addition, thermoelectric characterization is very important to determine which contact would be a potential candidate for future applications.

Characterization of deposited films

The deposition process in PECS set-up chamber was monitored using a film-thickness monitor as mentioned above. A constant thickness of 50 nm was established for both Ni and Pt films, which is important for a better comparison. In **Fig. 1**, stylus profilometer measurements of the as deposited samples are shown. In **Fig. 1**(**A**), the stylus was moved on the surface from one corner (a quadrant where deposition took place), to the central part of the sample which was hidden by the mask (there was no deposition at this part). The distance covered by the stylus was about 700 µm, and the highness measured 0.05 µm, which corresponds to the 50 nm thick Ni layer.

The same highness was measured for the as deposited Pt film on Si substrate (**Fig. 1(B)**). In this case, the stylus covered 800 µm from the lower part (the substrate) to the quadrant (the as deposited Pt film). The profilometer analysis confirmed thus, the thickness of metallic films deposited, which is 50 nm for both Ni and Pt films. However, small peaks could be seen in **Fig. 1**, which may correspond to some impurities on the surface of the samples. Morphological investigations should reasonably confirm this hypothesis. In **Fig. 2** High Resolution SEM images of the surfaces of the as deposited metallic films on Si substrates are displayed. The surface morphology seems to be smooth and no visible structures are identified, a small number of impurity dots are meanwhile distinguishable, that should explain the peaks observed in **Fig. 1**.

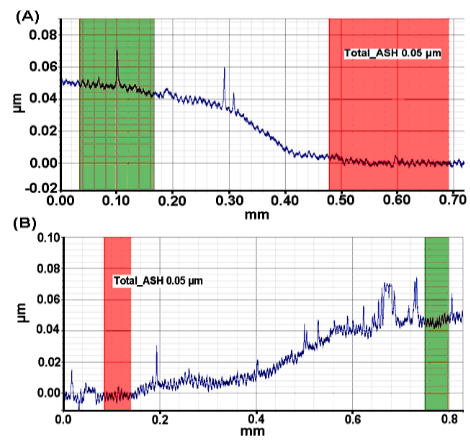


Fig. 1. Profilometer analysis of the as deposited (A) Ni film on Si substrate and (B) Pt film on Si substrate.

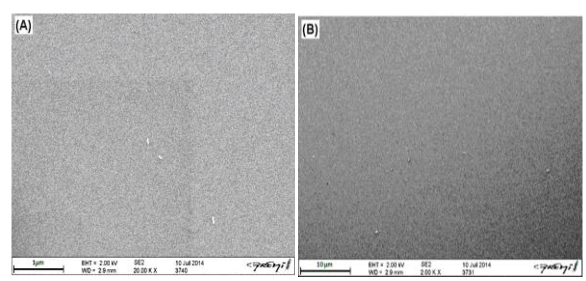


Fig. 2. SEM image of the surface of the as deposited (A) Ni film on Si substrate and (B) Pt film on Si substrate.

Silicides formation by reactive diffusion

As mentioned earlier, formation of silicide contacts was inspired from CMOS technology, to be able to compare Ni contact, Pt contact and silicides contacts on Si substrate. The formation of silicides is an example of reactive diffusion between a transition metal and a semiconductor. This microelectronic process includes the reaction of a thin metallic film with silicon, forming a silicide contact through a series of annealing and etching processes. In our study, the semiconductor would be Si reacting with Ni in one case, and with Pt in another, to form a low resistive Ni-silicide and Pt-silicide.

The phase diagrams of Ni-Si and Pt-Si include a large number of silicides: Ni_2Si, NiSi, $NiSi_2$ and Pt_3Si, Pt_2Si, PtSi **[11]**. However, in the case of a reaction between a submicrometric metal film and a silicon substrate, silicides appear sequentially and not simultaneously **[12]**. This fact permitted, in our study, the formation of the lowest resistive silicides. In the case of the reaction between the 50 nm thick Ni film with Si substrate, the best candidate is NiSi with a thin film resistivity of 14-20 μΩcm **[13]**. In order to form NiSi, the sample with Ni film on Si was introduced into a high vacuum chamber (pressure better than 10^{-6} Torr) and annealed at 500 °C for 30 minutes **[14]**. In the case of the 50 nm thick Pt film on Si substrate, the chosen silicide was PtSi with a thin film resistivity of 28-35 μΩcm **[13]**. To form PtSi, the sample was annealed 30 minutes at 350 °C under high vacuum too **[9]**. The formed films were first analyzed by the stylus profilometer, in order to determine the thickness of the resulting layers. The thicknesses of resulting silicides per nm of metal are 2.34 nm for NiSi and 1.97 nm for PtSi **[13]**. The profilometer analysis of the formed silicides (**Fig. 3**) are in agreement with that, since, the measured thickness is ~ 120 nm for Ni-silicide, and ~ 90 nm for Pt-silicide. Hence, the formed silicides should reasonably be: NiSi and PtSi. EDX spectroscopy was used in order to confirm the chemical composition of the formed silicides.

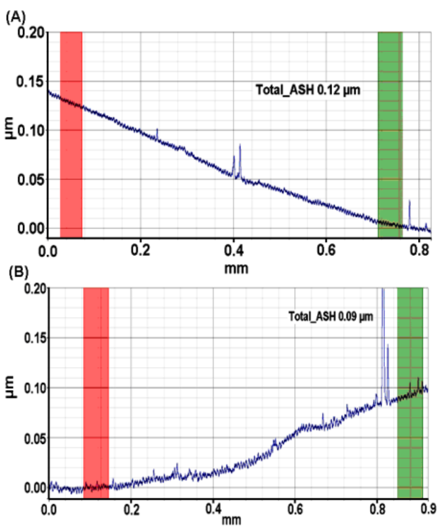


Fig. 3. Profilometer analysis of the formed (A) NiSi film and (B) PtSi film.

The chemical analyses of the obtained silicides are shown in **Fig. 4**. EDX spectroscopy of the Ni-silicide sample is presented in **Fig. 4(A)**. Two major peaks are present with one at 1.739 keV that corresponds to the Si peak and another at 851 eV corresponding to Ni **[15]**. In the case of the thermally induced solid state reaction between Pt film and Si, the EDX spectroscopy of the sample is presented in **Fig. 4(B)**. Three peaks could be noticed, one at 1.739 keV corresponding to Si, and two peaks at 270 eV and at 2.050 keV, which correspond to Pt **[15]**. The obtained percentages of the chemical composition of NiSi film were: 66% Si and 34% Ni, while they were 70% Si and 30% Pt, for PtSi film. The composition should be reasonably 50% of each element in both cases, however the substrate effect was note eliminated in our study.

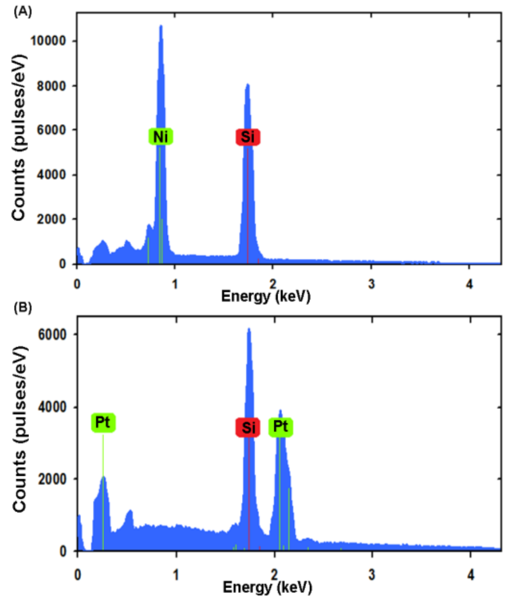


Fig. 4. EDX spectroscopy measured for the formed (A) NiSi film and (B) PtSi film.

The morphological study of both films was investigated by means of SEM, in **Fig. 5**. No porosity was detected by SEM observation, but after the thermal annealing, a different topography from the one observed in **Fig. 2**, could be noticed.

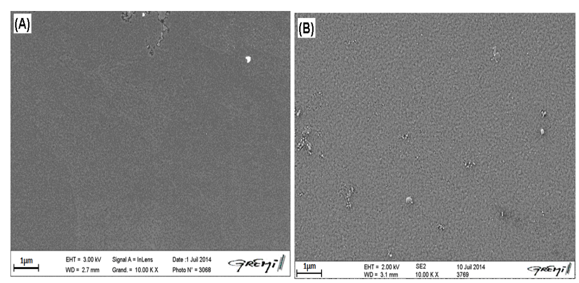


Fig. 5. Morphological investigation by SEM of the surface of the formed (A) Ni-silicide and (B) Pt-silicide.

Polycrystalline grain-boundaries were observed. The surface becomes much rougher after phases formation, and more impurity dots appear at the surfaces of NiSi as well as PtSi. Although a high vacuum annealing was insured, oxygen and carbon impurities should be present at the surface of the samples, which may explain such a result.

In order to determine which is the best contact among the four samples prepared: Ni/Si, Pt/Si, NiSi/Si and PtSi/Si thermoelectric characterization was led at standard temperature and pressure conditions using a micro ZT-meter, equipped with a sample holder and contacts joined to the voltmeter and thermometer, with an automatic acquisition to the computer.

Thermoelectric investigation using micro ZT-meter

The thermoelectric analysis of the samples was obtained, by determining the thermoelectric coefficient known as

Seebeck coefficient (S) named after Seebeck, who discovered the thermoelectric phenomenon in 1822, when he developed a voltage by joining two pieces of different materials together and placing a temperature difference to the couple. He also found that the voltage difference observed was proportional to the temperature gradient according to the next relation: $S = V/\Delta T$, in which S, V and ΔT are respectively, Seebeck coefficient, the voltage and the temperature difference. The Seebeck coefficient is very low for metals (only a few µV/K) and is much larger for semiconductors (typically a few 100 µV/K) **[16]**. In **Fig. 6** is presented the voltage measured of the samples as a function of the temperature difference. The calculated ratio of the linear fit of the voltage, on ΔT gave us the Seebeck coefficient of the four samples.

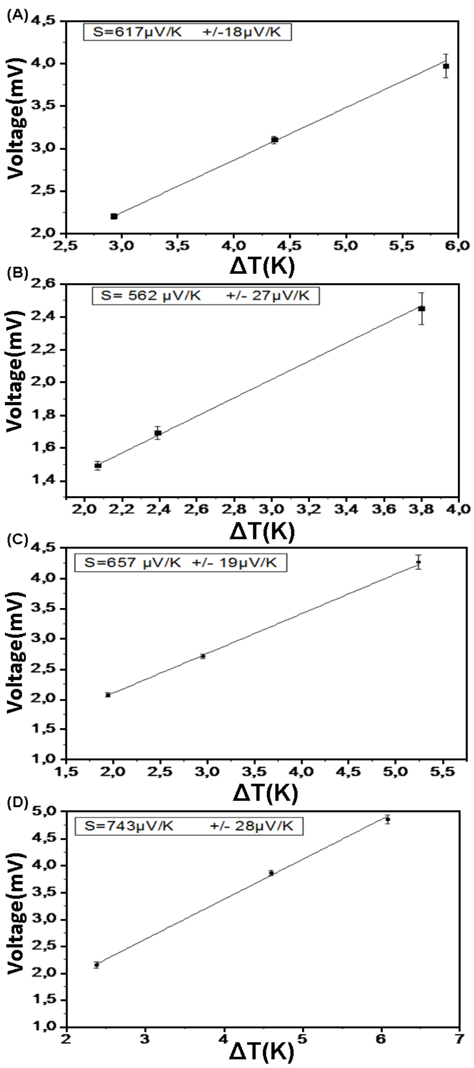


Fig. 6. Thermoelectric investigation of the four samples prepared: (A) Ni/Si, (B) Pt/Si, (C) NiSi/Si and (D) PtSi/Si.

Conclusion

In conclusion, four types of contacts were studied in this work. Ni and Pt films were first deposited on Si substrates; the films exhibited a smooth surface with no appearing impurities. The thickness of the deposited films was 50 nm. Only low resistive phases NiSi and PtSi, were formed by a sequential reactive diffusion between the metallic layer and Si substrate. The morphological investigation showed a homogenous film with grain-boundaries.

The thin film of PtSi formed on Si is the best contact among the metallic contacts tested with the micro ZT meter and S_{PtSi} = 743 µV/K is the highest coefficient obtained. However, a further study is still needed in order to test other silicides and establish an optimized electronic contact on all thermoelectric materials. Another future prospective is testing thermoelectric efficiency on the porous silicon using PtSi contact.

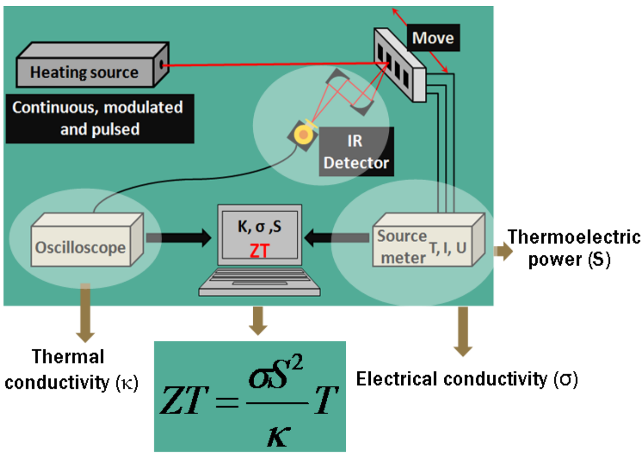
Reference

1. Lee, J.H.; Galli, G.A.; Grossman, J.C.; *Nano Letters,* **2008**, *8,* 3750. **DOI:** 10.1021/nl802045f
2. Hamadeh, H.; Naddaf, M.; Jazmati, A.; *J.Phys. D: Appl. Phys.*, **2008,** *41*, 245108. **DOI:** 10.1088/0022-3727/41/24/245108
3. Severiano, F.; García, G.; Castañeda, L; *Mater. Sci. Semicond. Processing*, **2014,** *27*, 326. **DOI:** 10.1016/j.mssp.2014.07.002
4. Fauchet, P. M.; *J. Lumin.* **1996,** *70,* 294. **DOI:** 10.1016/0022-2313(96)82860-2
5. Zhang, S.-L.; Ostling, M.; *Crit. Rev. Solid State Mater. Sci.*, **2003,** *28*, 1. **DOI:** 10.1080/10408430390802431
6. Hong, H.; Park, Y.K.; Kim, J.Y.; Song, K.; Choi, C.J.; *MATERIALS TRANSACTIONS*, **2012,** *53*, 1633. **DOI:** 10.2320/matertrans.M2012068
7. Tsaur, B.-Y.; Anderson, C.H.; *Appl. Phys. Lett.*, **1985,** *47*, 527. **DOI:** 10.1063/1.96115
8. Lepselter, M.P.; Andrews, J.M.; Ohmic Contacts to Semiconductors, B. Schwartz (Ed.), *The Electrochemical Society*, Princeton, NJ, **1969,** 159.
9. Abbes, O.; Hoummada, K.; Mangelinck, D.; Carron, V.; *Thin Solid Films*, **2013,** *542*, 174. **DOI:** 10.1016/j.tsf.2013.07.023
10. Pichanusakorn, P.; Bandaru, P.; *Mater. Sci. Eng. R: Reports*, **2010,** *67*, 19. **DOI:** 10.1016/j.mser.2009.10.001
11. Massara, R.; Feschotte, P.; Le système binaire Pt-Si, *Journal of alloys and compounds.* **1993,** *201*, 223. **DOI:** 10.1016/0925-8388(93)90888-T
12. Gas, P.; Girardeaux, C.; Mangelinck, D.; Portavoce, A.; *Mater. Sci. Eng. B.* **2003,** *101*, 43. **DOI:** 10.1016/S0921-5107(02)00709-2
13. Murarka; S. P.; Silicides for VLSI applications. *New York* : *Academic Press*, **1983**. **ISBN:** 978-0125112208
14. Mangelinck, D; Hoummada, K.; *Appl. Phys. Lett.* **2002,** *92*, 254101. **DOI:** 10.1063/1.2949751
15. Goldstein, J.; Newbury, D.E.; Joy, D.C.; Lyman, C.E.; Echlin, P.; Lifshin, E.; Sawyer, L.; Michael, J.R.; Scanning Electron Microscopy and X-ray Microanalysis. *Plenum Press, New York*, **2003**. **ISBN:** 978-1-4615-0215-9
16. Batal, M.A.; Nashed, G.; Haj Jneediu, F.; *Journal of the Association of Arab Universities for Basic and Applied Sciences*, **2014,** *15*, 15. **DOI:** 10.1016/j.jaubas.2012.09.005
17. Jae-Hwan Kim; Jung-Yeol Choi; Jae-Man Bae; Min-Young Kim; Tae-Sung Oh Liu; *Mater. Transact.* **2013,** *54*, 618. **DOI:** 10.2320/matertrans.M2013010
18. Yusuke Nakai; Kazuya Honda; Kazuhiro Yanagi; Hiromichi Kataura; *Appl. Phys. Express*, **2014**, *7*, 02510. **DOI:** 10.7567/APEX.7.025103

Supporting information

Experimental setups/schematics

The micro ZT-meter (**Supporting Fig. 1**) package includes a heating Laser source and a sample holder equipped with six pins, four of them are used to measure voltage with a Van der Pauw configuration, while two thermocouple pins are used to measure the temperatures at different places of the sample. The micro ZT-meter can also determine thermal and electrical conductivity, but in our study only the Seebeck coefficient was determined, which was sufficient to compare the contacts.



Supporting Fig. 1. Experimental micro ZT meter with simultaneous heating and measurement of voltage and temperature.