Ni, Pt, and Ti stanogermanide formation on $Ge_{0.92}Sn_{0.08}$

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***Abstract* — the aim of this work is to provide a systematic and comparative study on the material characteristics and electrical contact performance for a germanium-tin (GeSn) alloy with a high percentage of Sn (8%). Thin metal films (10 nm) of Nickel (Ni), Titanium (Ti), or Platinum (Pt) were deposited on $Ge_{0.92}Sn_{0.08}$ layers and subsequently annealed at different temperatures ranging from 300°C up to 500°C.**

Various experimental techniques were employed to characterize the metal morphology and the electrical contact behavior, with the intention of identifying the most promising metal candidate, in terms of low sheet resistance and low surface roughness, considering a low formation temperature.

The investigations carried out show that for nano-electronic contact applications, nickel-stanogermanide (NiGeSn) turns out to be the most promising candidate among the three different metals analyzed. NiGeSn presents low sheet resistance combined with low formation temperatures, below 400 °C; PtGeSn shows better thermal stability when compared to the other two options while, Ti was found to be unreactive below 500°C, resulting in incomplete TiGeSn formation.

Keywords— GeSn, sheet resistance, stanogermanide

I. Introduction

In recent years many technological innovations have facilitated the transistor shrinkage rules according to Moore's law. Breaktroughs, such as the use of the high-k gate dielectric technology [1], 3D structures such as the trigate/FinFET [2][3], and the introduction of embedded stressors in source and drain to enhance the performance of the device [4], have produced substantial advantages for advanced Complementary Metal Oxide Semiconductor (CMOS) technologies. Although giant steps have been taken in recent decades, the constant pursuit of Moore's law and the trend of continuous power reduction , lead us to investigate new alternatives which enable further device reduction [5].

Consequently, a feasible and interesting solution to advanced Silicon (Si) CMOS scaling might be found in the transition metal di-chalcogenides (TMD), Germanium (Ge), GermaniumTin ($Ge_{(1-x)}Sn_{(x)}$) alloys, and III-V compounds; nevertheless, the integration processing and development costs of these new semiconductor materials are huge and not straightforward. Therefore in the last decade Ge and its alloy, GeSn, show promise over the other candidates due to their intrinsic characteristics as well as easier integration on Si platforms [6]. As a result, extensive study on Ge and GeSn has been made in order to explore the possibility of integration of this material into the CMOS process [7].

Furthermore, as the channel dimensions trend points towards shrinking, the source/drain resistances have become relatively more significant in the overall parasitic resistance of the transistor; then in many cases, the contact resistance becomes the bottleneck for many technologies. Therefore analogously with Si, where the silicides are used to create the metal contacts, germanides and stanogermanidation seem to be the natural candidates for metal contacts respectively for Ge and GeSn alloys.

Although the Ge solutions proposed have a strong appeal, studies of contacts to GeSn are still immature; consequently an intensive investigation on the contacts is essential to ensure good GeSn device performances.

Judging from recent literature, it seems that several research groups have focused their attention on the contact analysis using different metals with the aim to extrapolate the performance and point out the best candidate in terms of resistance and thermal stability. In this regard, from the up-to-date work on GeSn, a lot of activity has been focused on Nickel-stanogermanide (NiGeSn) contacts [8][9][10][11] and a possible mix of different metals to increase the thermal stability of the Ni [12][13][14]; for these reasons, the purpose of this work is to show a systematic and comparative study, using three different metals Ni, Ti, and Pt, on $Ge_{0.92}Sn_{0.08}$.

II. Experiments

Fig.1 summarizes the process flow carried out in this work. The starting material is comprised of a nominally un-doped epitaxial layer of $Ge_{0.92}Sn_{0.08}$, (nominally 28 nm thick), obtained using chemical vapour deposition (CVD), on a nominally un-doped virtual substrate layer of Ge used to reduce the lattice mismatch of the structure.

Prior to deposition of the metal, all the coupons were subjected to a cleaning process; the samples are first dipped in acetone, isopropyl alcohol, and deionized water respectively for 30 seconds.

Afterwards, a 10 nm layer of three different metals was deposited on the samples. The deposition was carried out using the FC2000 electron beam evaporator at a pressure of 5×10^{-7} Torr. Ni and Pt were evaporated with a rate of 0.2 nm/s while the Ti was evaporated at a rate of 0.1 nm/s. The samples were then subjected to a 30 s rapid thermal annealing (RTA) in N_2 ambient at different temperatures; ranging from 300 - 500 °C with in steps of 50 °C. The ramp rate used for each RTA was 100 °C/min and the cool down time was 15 minutes. Several characterization techniques were employed to describe both morphological and electrical aspects.

We characterized the material features through Scanning electron microscopy (SEM), performed by Zeiss Supra 55VP machine; atomic force microscopy (AFM) carried out by Veeco Multimode V AFM in tapping/non-contact mode over an area of 5 µm × 5 µm. Cross-sectional transmission electron microscopy (XTEM) was done using a JEOL 2100 HRTEM operated at 200KV and the lamella was produced by a Dual Beam Helios Nanolab 600i, using Ga ion beam. Furthermore, energy dispersive X-ray Spectroscopy (EDX) was done using FEI a dual Beam Helios Nanolab equipped with Oxford Instruments' X-MAX-50 EDX detector.

Finally, for the electrical characterization a 4 point probe measurement was performed using a LUCAS LABS-S-302 4 manual probing station.

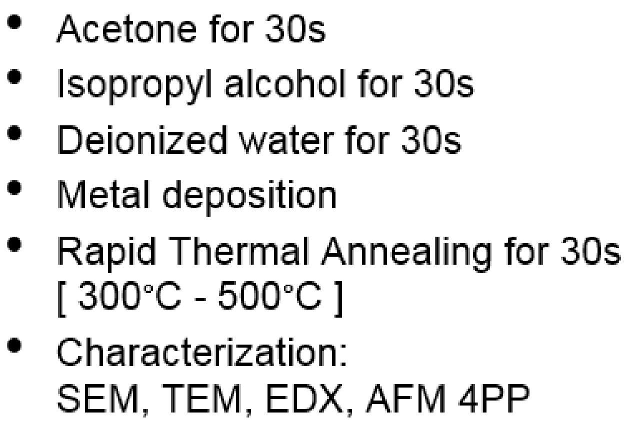

Figure 1. Summary of the experimental process flow**.**

III. Results and Discussion

All the analysis previously reported, was done as a function of the annealing temperature and of the different metals used, with the aim of reporting the most promising material to create metal contact for GeSn alloy.

In Fig. 2 the morphological evolution for samples annealed to the thermal range extremes (300°C and 500°C) is reported. From the study, all the metals show a smooth and homogeneous surface at 300°C, while at 500°C, Ni and Ti exhibit a discontinuous layer compared with Pt, that preserves its integrity.

Moreover, from further SEM analysis (not showed in this work), we noticed that NiGeSn and TiGeSn contacts begin to depict some surface imperfections respectively from 400°C and 450°C, while PtGeSn showed continuous surface structures over the entire temperature range.

Therefore, the degeneration at high annealing temperature is remarkable for Ni and Ti and may depend on the relatively high Sn content involved in the alloy (8%) or from the metal precipitations, that could lead to the surface agglomeration and degradation.

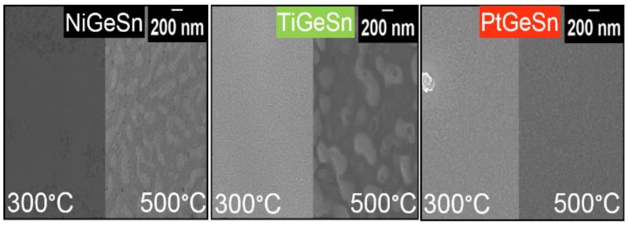

Figure 2. Representative SEM images of stanogermanides formed at different annealing temperatures. The pictures depict respectively NiGeSn , TiGeSn and PtGeSn surfaces annealed at 300°C, always show on the left side, and 500°C always on the right side.

Continuing the study the AFM investigation (Fig. 3) confirms the data previously found in the SEM study (Fig. 2), namely an increasing trend in roughness as a function of the annealing temperature. On all samples, the analysis was carried on a central area in order to avoid edge effects.

Fig.3 shows the 3D images with the root-mean-square (RMS) values found for the extreme temperature considered; it is noteworthy that the roughness increases significantly for NiGeSn and TiGeSn annealed at 500°C while for PtGeSn the RMS value slightly changes.

Indeed from the investigation we found that the surface roughness of the samples increased due to the agglomeration effects as expected and was further confirmed from the cross-sectional TEM analysis below.

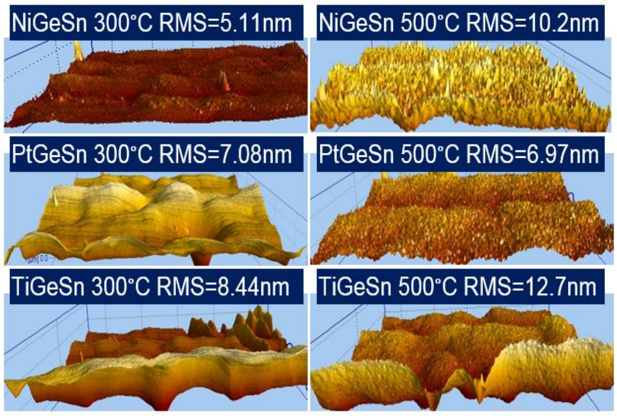

Figure 3. RMS value and 3-D images derived from AFM analysis of NiGeSn, TiGeSn and PtGeSn annealed at 300 °C and 500 °C.

To provide further details about the morphology of the metal-GeSn layers a cross-sectional TEM inspection was done for the contacts formed respectively at 300 °C and 500 °C (Fig. 4). As shown in Fig. 4(a), 4(c) and 4(e) the cross-sectional analysis of the sample annealed at 300°C confirmed that surface layer alloys were formed only with Ni and Pt in the temperature range taken into account; while the Ti did not appear to react with the underlying GeSn, which displayed a superficial layer of 10 nm.

Comparable results were found for the sample formed at 500°C as highlighted in Fig. 4(b), 4(d) and 4(f), in which Ni and Pt form stanogermanide layers while Ti does not yet react with the GeSn alloy.

The solid-state growth process for the 30 s anneal resulted in structures with different thickness variation, depth, and grain size depending on the annealing temperature. Briefly, all Ni and Pt structures were composed of crystal grains with specific size and orientation, justified by observing the variation of the diffraction contrast in the TEM images.

In accordance with the top-down SEM analysis (Fig. 2), it was also seen that the continuity of the NiGeSn layers has degraded at 500 °C, resulting in the formation of well-defined island-type regions, as shown in Fig. 4(b). In comparison, the PtGeSn structures appeared continuous at both temperatures.

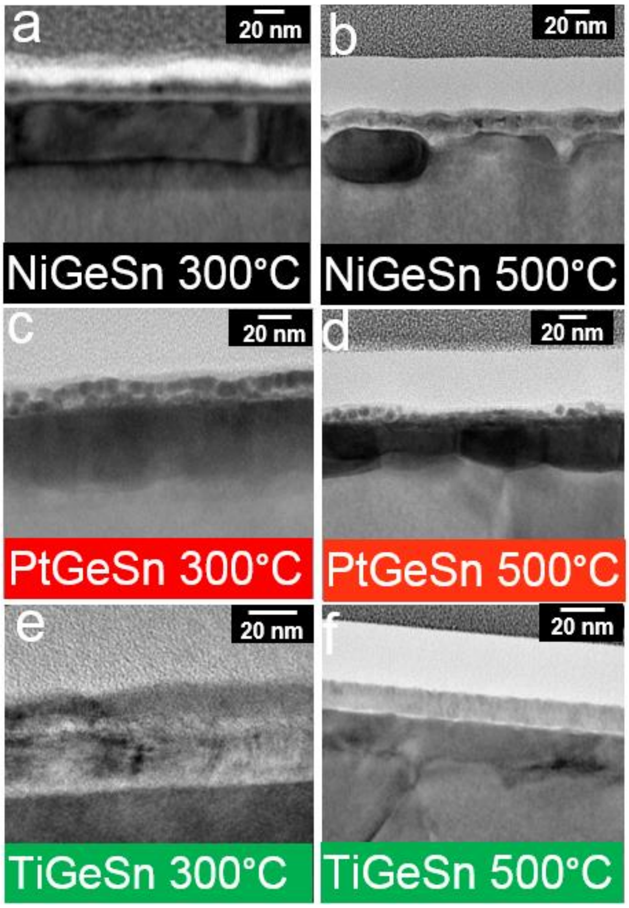

Figure 4. TEM images at the same magnification for all the metals at the two different extreme annealing temperature; a) NiGeSn at 300 °C, b) NiGeSn at 500 °C, c) PtGeSn at 300 °C, d) PtGeSn at 500 °C, e)TiGeSn at 300 °C, f) PtGeSn at 500 °C.

To obtain further details on the metal structures, we used EDX line scans to obtain compositional profiles for all samples (fig.5 and fig.6). Figure 5 provides STEM imaging and EDX line scans for two Ni samples respectively annealed at 300°C and 500°C (fig. 5(a) - fig. 5(c). From the graph below the pictures (fig 5(c) and fig. 5(d)) it can be seen that the Sn content (both averaged values across the stanogermanide layer and point measurements within the layer) decreased to about 4.0 and 6.0 at. % for the Ni samples while Sn content for the non-annealed sample measured under similar EDX condition showed Sn content of about 8.0 at.%.

Looking at the Sn EDX profile in the underlying Ge substrate, highlighted in the picture and in the graph with light green region, we can see that the Sn signal is at the limit-of-the detection of the measurement (about 0.1 at.%). It is worth mentioning that the compositional profiles for all NiGeSn and PtGeSn structures were relatively uniform both across (perpendicular) and along (parallel) the layer surface.

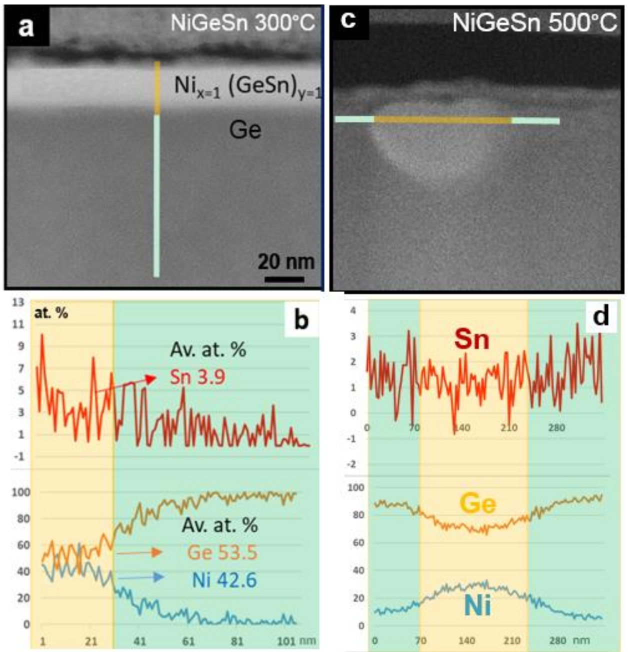

Figure 5. STEM imaging and corresponding EDX line scans for the regions marked with golden and light blue measured for the Ni(GeSn) sample formed at 300°C (a) and 500°C (c) Graphs below report respectively the line scan of the respective sample above; b) Ni(GeSn) at 300°C d) Ni(GeSn) at 500°C

Furthermore all the other EDX line scans are reported in figure 6. As a consequence of what has been mentioned and depicted previously, for Pt samples annealed at 300°C and 500°C (respectively Fig. 6(c) and 6(d)) it is possible to see that the blue curve peak, always used to highlight the metal, fit with the other two peaks, red used for Ge and green for Sn. While for the Ti samples, as pointed out in Figs. 6(a) and 6(d), the blue curve peak is positioned outside the green and red peaks; essentially meaning that the metal does not react with the GeSn alloy beneath to form TiGeSn.

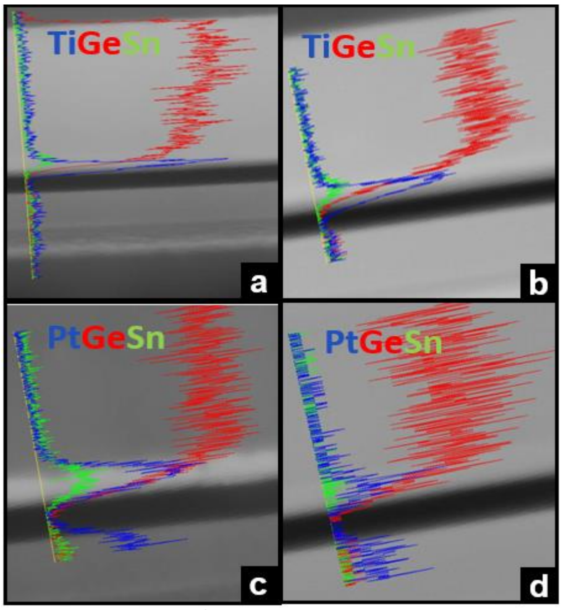

Figure 6. EDX analysis of the other metals. Figure (a) and (b) represent respectively TiGeSn at 300 °C and 500 °C; while figure (c) and (d) represent PtGeSn annealed respectively at 300 °C and 500 °C. In all the last four images (a), (b), (c) and (d), the blue curve is always related to the metal used, the red curve at Ge while the green one to the Sn.

With regards to the electrical testing, a 4PP measurement was performed on all the samples developed.

Each coupon was tested 3 times, in 3 different places, respectively on the two opposite corners and in the center of the coupon in order to extract an averaging resistance.

In fig.7 it is possible to see the sheet resistance values measured by following the four-point probe methodology [15]; the graph display the result achieved as a function of the annealing temperature. Nickel shows the lowest values up to 450°C; point where Platinum overtakes Nickel performance showing the lowest resistance values. While for Titanium the data are always at least one order of magnitude higher compared with the other two materials.

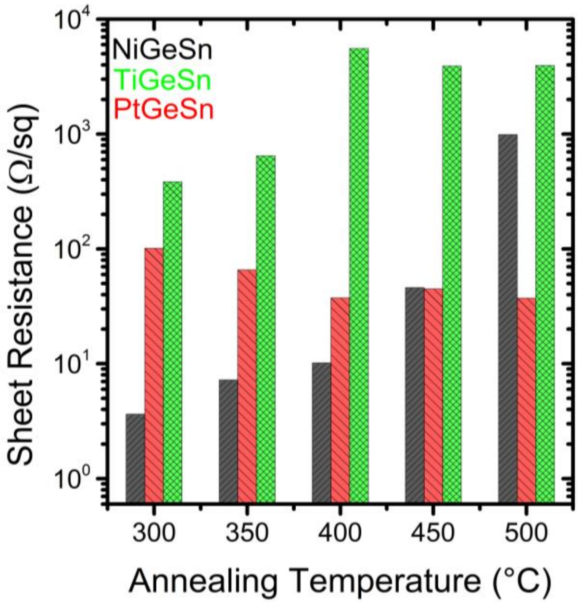

Figure 7. Sheet resistance for all the metal material take into account as a function of the formation temperature. The black curve will highlight Ni data , the red curve will show the Pt and the green the Ti ones

Conclusion

The aim of this work was to show the best metal candidates for stanogermanide contacts on $Ge_{0.92}Sn_{0.08}$ thin films in the formation temperature range selected.

We pointed out the sheet resistance trends, for three different metals, respectively Ni Ti and Pt subjected at various annealing temperatures.

Relating to the morphological aspects, in the thermal range selected, Ni and Ti were found to be the more sensitive materials for the agglomeration as showed in the SEM analysis; further confirmed also by TEM detection which showed that Ni and Pt are able to form continuous stanogermanide layers while Ti does not react with the underlying GeSn layer.

In addition, we performed a roughness study that depicts an increasing trend as a function of the annealing temperature.

Finally, from the electrical data investigation, NiGeSn shows best low-resistance performance up to a formation temperature of 435 °C, above which PtGeSn outperforms the NiGeSn in terms of sheet resistance.

Therefore, the most attractive solution to increase the thermal stability, as long as good contact performance is required, is represented by mix of Ni and Pt. This alternative could be used in future to develop GeSn devices with higher performance avoiding the contact problems due to the higher Sn concentration.

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