Aluminide intermetallics for advanced interconnect metallization: thin film studies

Jean-Philippe Soulié
Imec
Leuven, Belgium
Jean-Philippe.Soulie@imec.be

Zsolt Tőkei
Imec
Leuven, Belgium
Zsolt.Tokei@imec.be

Johan Swerts
Imec
Leuven, Belgium
Johan.Swerts@imec.be

Christoph Adelmann
Imec
Leuven, Belgium
Christoph.Adelmann@imec.be

***Abstract*— AlNi, Al_3Sc, AlCu, and Al_2Cu thin films have been investigated as potential alternatives for Cu in interconnect metallization schemes. Stoichiometric NiAl thin films of 56 nm thickness show a resistivity of 13.9 μΩ cm after post-deposition annealing at 600ºC. Different capping layers were tested to overcome the formation of an oxide top layer. Al_3Sc presents a resistivity of 12.5 μΩ cm after post-deposition annealing at 500ºC (for 24 nm thick films). AlCu and Al_2Cu outperform Ru films at 20 nm thickness and above (9.5 μΩ cm for 28 nm films). Challenges and integration feasibility are discussed.**

Keywords—Aluminides; alternative metals; thin films; resistivity; interconnect

I. Introduction

Due to challenges to metallize interconnect lines below 10 nm half pitch in the near future, new alternative metallization schemes have recently been explored to replace Cu, which has been the traditional choice for interconnect metallization during the last 20 years. After an initial focus on alternative elemental metals such as Co, Mo, or Ru, research has lately evolved to include also binary and ternary compounds [1, 2], targeting improved reliability and resistivity at small dimensions. Transition metal aluminides are amongst the intermetallics with potential as alternative metals in scaled interconnects. Some of these intermetallics show low bulk resistivities (below 10 μΩ cm), high melting points, and good oxidation resistance [3]. Specifically, AlNi has already shown promise [4] although ultrathin AlNi layers or scaled interconnect lines may require O and Al diffusion barriers to obtain low resistivities [5]. Recently, Al_2Cu has also been proposed as an interconnect metal [6]. With good wettability and a favourable resistivity size effect, Al_2Cu might become an alternative to Cu as it may not require additional liner or barrier layers for future technology nodes.

In this paper, the properties of AlNi, Al_3Sc, AlCu, and Al_2Cu ultrathin films with thicknesses between 4 and 56 nm will be evaluated with respect to their potential for interconnect metallization. We discuss the dependence of the resistivity on film thickness as well as post-deposition annealing (PDA) conditions for AlNi, as well as the need for capping layers. The resistivity of Al_3Sc compound shows a complex dependence on thickness and composition, reaching 12.5 μΩ cm after PDA at 500°C for a 24 nm thick film. Finally, AlCu and Al_2Cu thin films possess a lower resistivity than Ru at 20 nm and above. Intrinsic *vs.* extrinsic limitations of resistivity are one of the challenges and it will be discussed as well as the feasibility of technology integration.

II. Experimental Details

All aluminide films have been deposited on 300 mm SiO2 (100 nm)/Si (100) wafers by physical vapor deposition (PVD) using co-sputtering from Al and Ni or Sc or Cu targets. PDA was performed in H_2 for 20 minutes. The crystal structure was examined by grazing-incidence x-ray diffraction (GIXRD) using Cu-Kα radiation. The film thicknesses were determined by a combination of x-ray reflectance (XRR) and transmission electron microscopy (TEM). The film resistivities were determined from four-point sheet resistance measurements in combination with the film thickness corrected for the thickness of the surface oxide, which was assumed to be insulating.

III. Results

A. AlNi films

Recently, we have shown that stoichiometric 56 nm thick AlNi films can reach resistivities down to 13.9 μΩcm after PDA at 600°C, in combination with the observation of an ordered B2 phase (*Pm*-3*m* structure) and low stress [5]. The resistivity increased however strongly when the film thickness was reduced below 15 nm due to the formation of a non-stoichiometric (strongly Al-rich) surface oxide layer. While AlNi films with thicknesses down to 3 nm showed a stable native Al-oxide at the top of the films, this led to an off-stochiometric (Ni-rich) AlNi layer underneath, with strongly increased resistivity. To avoid the non-stoichiometric surface oxidation, capping layers were deposited onto AlNi films. While both TiN and TaN were ineffective, Si capping led to a decrease of the AlNi resistivity for films below 10 nm. Yet, the phase separation between Ni and Al was still present after 600°C PDA, as shown in Figure 1. In addition, 5 nm of Si was deposited *in situ* as capping layer after AlNi deposition and then annealed *ex situ* at 500°C in H_2. Extending the wafer cooling after PDA in the furnace before air exposure to lower temperatures (LCD, Low Cool Down) further reduced the resistivity of thin AlNi films (see Fig. 1, ~36 μΩcm for a 6 nm

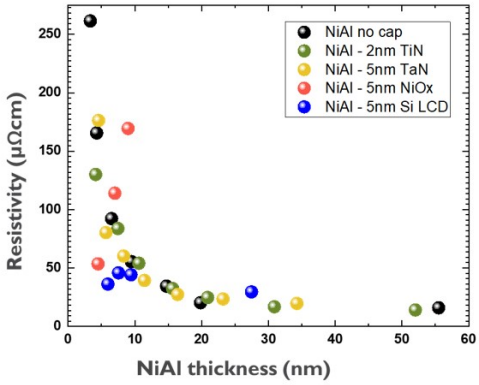

Figure 1: Resistivity *vs.* thickness for stoichiometric AlNi films with different capping layers after PDA at 500°C. For some samples, a low cool down (LCD) procedure was used after PDA.

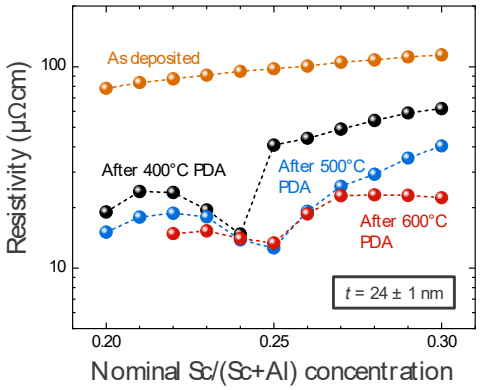

Figure 2: Composition dependence *vs.* resistivity for Al-Sc films (thickness ~24nm).

thick AlNi film), which is comparable to values of PVD Mo in this thickness range. The GIXRD pattern of these "5 nm Si-LCD" samples showed a (110) peak for all the thicknesses. However, the (100) peak, which indicates B2 order, was only observed for the thickest film of 30 nm (data not shown), suggesting large disorder in the thinnest films. All sample surfaces were smooth after PVD deposition and PDA. The AFM rms surface roughness varied from 0.25 nm for a 6 nm thick AlNi film, via 0.34 nm at 9.4 nm, to 0.83 nm for a 30 nm thick film. Further work optimizing the Si capping process will be dedicated to establishing the resistivity scaling potential of AlNi films in the thickness range below 10 nm.

B. Al_3Sc films

Al_xSc films were deposited with Sc concentrations in the range between 20 and 30 at.% and annealed up to 600°C in H_2. With respect to as deposited films, a clear drop in resistivity was observed after PDA at 400°C (Fig. 2). A resistivity minimum at 25 at.% Sc suggests the presence of order in the films. The lowest resistivity was found to be 12.5 μΩcm for 24 nm thick stoichiometric Al_3Sc after 500°C PDA. As deposited, the films were x-ray amorphous to nanocrystalline (data not shown). After annealing, they crystallized with XRD patterns consistent with the expected $L1_2$ (*Pm*-3*m*) structure. No secondary phase was observed although a secondary Al phase may be difficult to observe due to peak overlaps.

Figure 3 depicts the resistivity of Al_3Sc as a function of film thickness, both as deposited and after PDA. The thickness dependence of as deposited films was very weak and the resistivity remained high (~100 μΩcm). After PDA, two regimes could be distinguished (similar to the Al-Ni system [5]): for films with thicknesses above about 10-15 nm, the resistivity decreased strongly upon annealing and showed little dependence on film thickness. However, for thinner films, the resistivity increased strongly with decreasing thickness, and the effect of PDA was weak. TEM found a 4 to 4.5 nm thick Sc-rich surface oxide layer, rather independent of the Al_3Sc film thickness, as seen in Figure 4. The chemical profile of the surface oxide was quite complex, due to the formation of interface layer with the underlying SiO_2, and the total layer

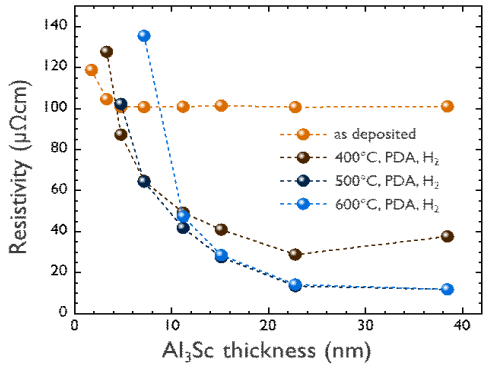

Figure 3: Resistivity *vs.* film thickness of stoichiometric Al_3Sc films, both as deposited and after post-deposition annealing in H_2.

structure could be approximated by the following stack (bottom to top): Si (substrate)/SiO_2 / $AlScO_x$ / SiO_x / bulk Al_3Sc / thin Al_2O_3 / $AlScO_x$. For films with thicknesses below 7 nm, the remaining unoxidized Al_3Sc became very thin (about 2.6 nm for 7 nm nominal film thickness). The TEM images showed further that the center of the film remained crystalline, while the surface oxide and the interfacial layer were

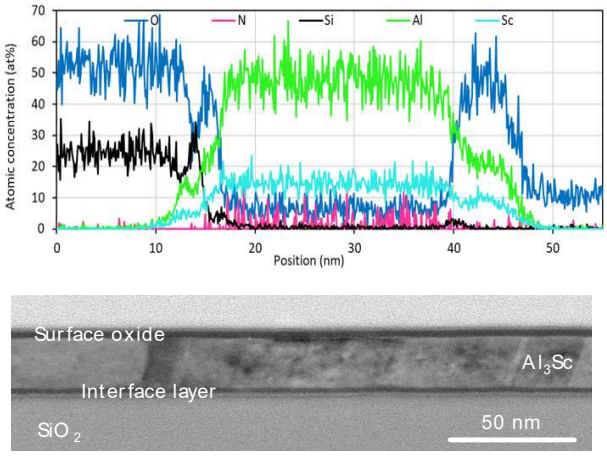

Figure 4: Composition profile (top) and cross-sectional TEM image (bottom) of a 30-nm-thick Al_3Sc film after 600°C PDA.

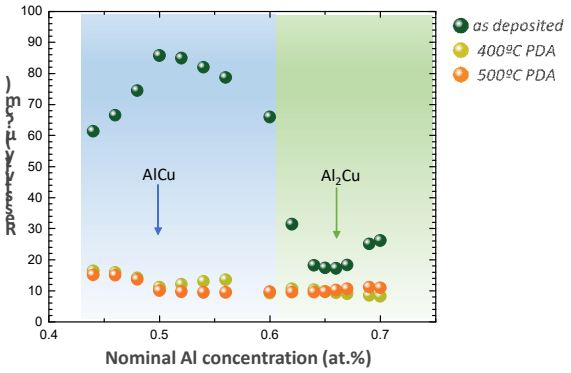

Figure 5: Resistivity of ~28 nm thick Al-Cu thin films *vs.* Al concentration, both as deposited and after PDA in H_2 at the indicated temperatures.

amorphous. The results show that effects of non-stoichiometric oxidation and interface formation are similar for Al_3Sc and AlNi, and possibly general features of (most) aluminide thin films. For interconnect applications, the effects will have to be prevented during processing, possibly encapsulating dielectric layers with O- and/or Al/Sc diffusion barrier properties.

C. Al-Cu films

Figure 5 shows the resistivity of ~28 nm thick Al_xCu films as a function of their composition. Both AlCu and Al_2Cu are line compounds in the phase diagram [7]. The resistivities decreased with PDA temperature, with a saturation observed at 400°C and above. The lowest resistivities obtained for 28 nm thick AlCu and Al_2Cu films were around 9.5 μΩcm. Around Al_2Cu, only a weak dependence of the resistivity on the composition was observed after at high temperature PDA.

XRD patterns (not shown) were consistent with the bulk phases: monoclinic AlCu (*C2/m*) and tetragonal Al_2Cu (*I4/mcm*). At compositions between stoichiometric AlCu and Al_2Cu, XRD indicated a two-phase region with both AlCu and Al_2Cu present, as expected from the Al-Cu phase diagram.

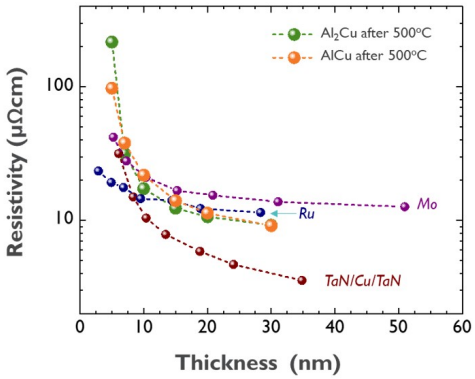

Figure 6: Resistivity of AlCu and Al_2Cu thin films *vs.* film thickness after PDA at 500°C in H_2 compared with elemental metals (TaN/Cu/TaN and Ru data after 420°C PDA).

After 400°C PDA, all ~28 nm thick films remained flat, according to AFM measurements. To assess the potential of Al_xCu for scaled interconnects, the resistivity was determined at thicknesses down to 4 nm (Fig. 6). Again, two regimes were observed, similar to AlNi and Al_3Sc, with a strong increase of the resistivity below 10 nm thickness. TEM images (not shown) indicated analogous effects of non-stoichiometric surface oxidation as well as interface layer formation. Nonetheless, AlCu and Al_2Cu films with thicknesses above 10 nm show resistivities below 20 μΩcm and approach 9 μΩcm around 30nm after 500°C PDA, which confirms the potential of Al_xCu as low-resistivity metals.

IV. Conclusions

In conclusion, the properties of AlNi, Al_3Sc, AlCu and Al_2Cu thin films deposited by PVD have been studied with a focus on the thickness dependence of the resistivity. All systems showed two regimes: (i) a strong resistivity increase with decreasing thicknesses below about 10 to 15 nm, and (ii) much less dependence on the resistivity of thicker films on their thickness. In the "thick film" regime, all studied intermetallics showed resistivities comparable or lower than Ru or Mo, with the lowest resistivities of 9.5 μΩcm for AlCu and Al_2Cu. However, the experiments also indicated challenges for the studied aluminides, *i.e.*, the control of the film stoichiometry, in particular in presence of non-stoichiometric surface oxidation as well as interface layer formation or the impact of crystallinity/grain structure on the resistivity. These challenges may be overcome by non-reactive *in-situ*-deposited dielectrics or capping layers as well as by reducing the thermal budget required to obtain low resistivity films. Such solutions will then ultimately allow to assess the intrinsic scaling potential of the resistivity of these intermetallics in ultrathin films and interconnect lines.

The authors would like to thank Patrick Carolan, Olivier Richard, and Hugo Bender for the TEM/EDS analysis. This work has been supported by Imec's industrial affiliate program on nano-interconnects.

References

[1] C. Adelmann et al., "Alternative metals: from *ab initio* screening to calibrated narrow line models", Proc. 2018 IEEE IITC, pp. 154–156, Sep. 2018.

[2] L. Chen et al., "Interdiffusion reliability and resistivity scaling of intermetallic compounds as advanced interconnect materials", J. Appl. Phys., 129, pp. 035301, Jan. 2021.

[3] J.A. Howell, S.E. Mohney and C.L. Muhistein, "Developing Ni-Al and Ru-Al intermetallic films for use in microelectromechanical systems", J. Vac. Sci. Technol., B29, pp. 042002, Aug. 2011.

[4] L. Chen, D. Ando, Y. Sutou, D. Gall and J. Koike, "NiAl as a potential material for liner- and barrier-free interconnect in ultra-small technology node", Appl. Phys. Lett., vol. 113, pp. 183503, Oct. 2018.

[5] J.Ph. Soulié et al., "Thickness scaling of NiAl thin films for alternative interconnect metallization", Proc. 2020 IEEE IITC, Oct. 2020.

[6] L. Chen, D. Ando, Y. Sutou and J. Koike, "$CuAl_2$ thin films as a low-resistivity interconnect material for advanced semiconductor devices", J. Vac. Sci. Technol., B37, pp. 031215, May 2019.

[7] A.I. Oliva, J.E. Corona and V. Sosa, "AlCu alloy films prepared by the thermal diffusion technique", Mat. Charac., 61, pp. 696, March 2010