



# Chemical and electrical characterisation of the segregation of Al from a CuAl alloy (90%:10% wt) with thermal anneal



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## ABSTRACT

A copper–aluminium (CuAl) alloy (90%:10% wt) has been investigated in relation to segregation of the alloying element Al, from the alloy bulk during vacuum anneal treatments. X-ray photoelectron spectroscopy (XPS) measurements were used to track the surface enrichment of Al segregating from the alloy bulk during in situ ultra-high vacuum anneals. Secondary ion mass spectroscopy (SIMS) indicates a build-up of Al at the surface of the annealed alloy relative to the bulk composition. Metal oxide semiconductor (MOS) CuAl/SiO<sub>2</sub>/Si structures show a shift in flatband voltage upon thermal anneal consistent with the segregation of the Al to the alloy/SiO<sub>2</sub> interface. Electrical four point probe measurements indicate that the segregation of Al from the alloy bulk following thermal annealing results in a decrease in film resistivity. X-ray diffraction data shows evidence for significant changes in crystal structure upon annealing, providing further evidence for expulsion of Al from the alloy bulk.

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## 1. Introduction

Reduction of critical dimensions in integrated circuit components as predicted by Moore's law poses major challenges in the areas of materials growth, deposition and characterisation in order to meet the demands of decreasing feature sizes [1]. Copper (Cu) has replaced aluminium (Al) as the interconnect metal of choice in current IC production due to the benefits of lower resistivity, reduced RC time delay, decreased power consumption and increased resistance to electromigration failure [2]. With the advantages due to the change to Cu also came a number of disadvantages, most notably the diffusion of Cu into any surrounding silicon based inter layer dielectric (ILD) materials, which causes device degradation and ultimately device failure [3,4]. The current mechanism for containment of Cu within the interconnect line utilises a barrier layer composed of Ta/TaN. As future iterations of IC production shrink dimension sizes, high aspect ratio structures pose a problem for continuous barrier layer deposition using the current physical vapour deposition (PVD) approach. As such, alternative mechanisms for barrier layer formation are required.

Self-forming barriers have emerged as a possible candidate to replace the current relatively bulky Ta/TaN barrier layer deposited via PVD. In order to form a self-forming barrier, a metal is alloyed with Cu in the

interconnect line. Post metallization annealing results in the expulsion of the alloying material from the bulk interconnect line towards all surrounding surfaces of the interconnect line, including the interface with the inter layer dielectric (ILD) [5]. As the alloying element reaches the Cu/ILD interface, it chemically reacts with the top few nanometres (~3 nm) of the dielectric to form a stable metal silicate or metal oxide barrier [6,7]. Aluminium has emerged as a possible alloying element to use in self-forming barrier layer applications due to its high solubility in Cu [8] and thermodynamic favourability to form a stable metal oxide layer [9].

In this study, a CuAl alloy (90%:10% wt) is characterised as to its potential application as a self-forming barrier candidate by studying the segregation of Al from the alloy bulk during anneal treatments, which is the prerequisite step for a self-forming barrier to be realised.

## 2. Experimental details

Blanket Cu and CuAl alloy (90%:10% wt) layers approximately 100 nm thick were sputter deposited onto 100 nm thermally grown silicon dioxide on n-type <100> Si substrates, from dedicated sputter targets. In addition to blanket layers, a number of metal oxide semiconductor (MOS) structures were fabricated via patterned lift off lithography using n-type <100> Si which had 100 nm plasma enhanced chemical vapour deposited (PE-CVD) SiO<sub>2</sub>. Metal gates with areas of 200 μm × 200 μm were used consisting of the same CuAl alloy in addition to pure Cu and pure Al reference gate materials in order to study the effect of the Al alloying element during electrical testing of the CuAl alloy.

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X-ray photoelectron spectroscopy was used to study the segregation of Al from the CuAl alloy bulk during in situ anneal treatments within an ultra-high vacuum (UHV) system at a base pressure of  $1 \times 10^{-9}$  mbar. Samples were held at their target temperature for 60 min with the pressure not exceeding  $5 \times 10^{-8}$  mbar during annealing. The photoelectrons were excited using a conventional Mg K $\alpha$  ( $h\nu = 1253.6$  eV) X-ray source and an electron energy analyser operating at 20 eV pass energy, yielding an overall resolution of 1.2 eV. The XPS core level spectra were curve fitted using a combination of Voigt profiles in a 3:1 ratio and Doniach Sunjic asymmetrical line shapes, all using a Shirley–Sherwood type background. The full width half maximum (FWHM) of the metal components ranged from 0.64 eV (metal Al) to 1.16 eV (metal Cu) and from 1.64 eV (Al oxide) to 1.94 eV (Cu oxide) for metal oxide species. The O 1s FWHM peak components ranged from 1.2 eV (Cu oxide) and 1.7 eV (Al oxide). All curve fitting analysis presented in this study was performed using AAnalyzer curve fitting software programme. In addition to conventional XPS, hard X-ray photoemission spectroscopy (HAXPES) measurements with an energy resolution of 0.25 eV were performed on the CuAl alloy, both as deposited and annealed at 500 °C in vacuum at a pressure  $\sim 1 \times 10^{-9}$  mbar, at the National Synchrotron Light Source at Brookhaven National Laboratory. The higher photon energy of the synchrotron light source (2200 eV) enabled the acquisition of chemical information from further into the bulk alloy than conventional XPS with the Mg K $\alpha$  anode (1254 eV).

Thermal treatments, secondary ion mass spectroscopy (SIMS) and XPS measurements were all performed in-situ. The SIMS setup included a Hiden Analytical IG20 ion gun operating with a positive argon ion beam of 5 keV. Secondary Al (27 amu) ions were detected using a Hiden Analytical mass spectrometer EQS quadrupole analyser. Capacitance–voltage measurements were performed on the MOS structures using a Boonton model 72b 1 MHz capacitance metre interfaced to a Keithley 4200 electrometer with voltage sweeps ranging from +20 V/–20 V. Four point probe analysis was performed on blanket metal layers which were subjected to vacuum anneal treatments (held at target temperature for 60 min at pressures better than  $1 \times 10^{-6}$  mbar) using a Jandel Rm3-AR general purpose four point probe system. X-ray diffraction (XRD) measurements were performed using a triple-axis Jordan Valley Bede D1 X-ray diffractometer using a copper K $\alpha$  ( $\lambda = 1.5405$  Å) radiation, operated at 45 kV and 40 mA.

### 3. Results & discussion

Fig. 1 displays the Cu 3p/Al 2p XPS core level spectra both as loaded and following in situ thermal anneal treatments for the CuAl alloy. The Cu 3p and Al 2p photoemission peaks overlap, requiring careful peak fitting analysis relative to metallic Cu and Al and Cu and Al oxide reference spectra (not shown).

As indicated by the peak fitting analysis, the as loaded state of the CuAl alloy is composed mainly of metal Cu, with the addition of a small quantity of Cu oxide and a limited quantity of Al, mainly in a sub oxide state. Following annealing treatments, it is apparent that the Al 2p signal increases by way of increased metal Al and Al oxide within the sampling depth of XPS, reflecting the upward diffusion and segregation of the alloying element Al from the CuAl alloy bulk. Oxidation of the metallic Al is likely a combination of reduction of surface Cu oxide, as seen in previous studies [10], and also oxidation during anneal treatments which result in a rise in the background chamber pressure. This observation is supported by the reduction in Cu oxide signal after thermal anneal. The oxidation of Al at the surface in effectively a UHV environment is consistent with the high thermodynamic stability of Al oxide. It should also be noted that residual metallic Al, seen within the alloy following anneal treatments, has been suggested as a means of improving electromigration behaviour of Cu within the interconnect line [11,12]. A decrease in Cu oxide within the alloy not only serves to decrease the resistance of the alloy as seen in previous studies [13], but as suggested by Willis et al. [14] could also lead to a reduction of Cu ion diffusion into any surrounding dielectric materials.

Fig. 2 displays the XPS O 1s core level spectra, for the as loaded and annealed CuAl alloy. The peak fitting analysis indicates two species of oxide present at the surface of the CuAl alloy, attributed to both Cu oxide and Al oxide, in agreement with the Cu 3p/Al 2p spectra in Fig. 1. Following an in situ anneal at 200 °C, it is noted that the Cu oxide peak is reduced to below the detection limits of XPS, with the concurrent growth of the Al oxide peak. Further in situ annealing at a temperature of 500 °C causes the O1s peak area to increase, consistent with additional oxygen incorporation within the film from within the UHV environment, thereby further oxidising the Al which has segregated from the alloy bulk towards the surface. This result is consistent with the known thermodynamic favourability of Al to form a stable oxide, which could potentially act as a Cu diffusion barrier layer [15].

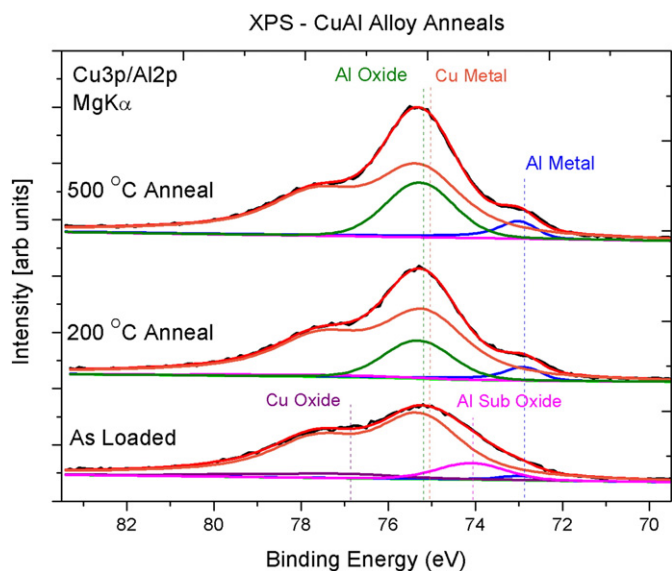


Fig. 1. XPS Cu 3p/Al 2p core level spectra both as deposited and following in-situ anneal treatments of the CuAl alloy showing the increase in Al metal and oxide signals consistent with surface segregation.

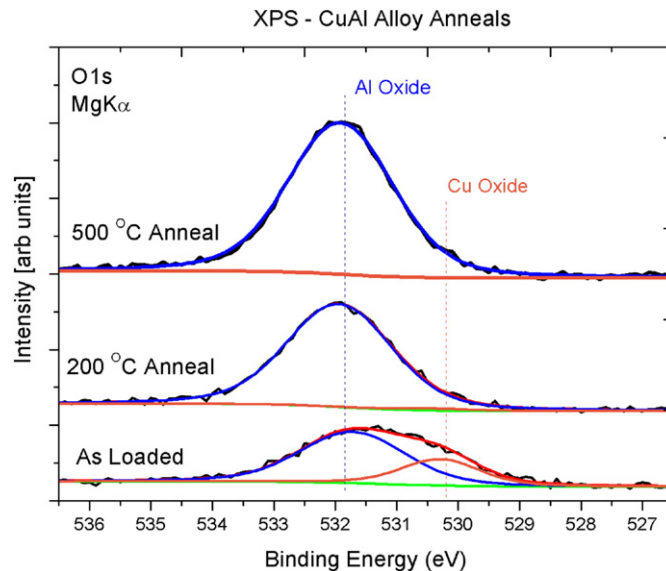


Fig. 2. XPS O 1s core level spectra of the CuAl alloy for the as deposited and following in-situ anneal treatments displaying the reduction in the Cu oxide signal and an increase in the Al oxide signal consistent with surface localized oxidation of the segregating Al.

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