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_2/Si structures show a shift in flatband voltage upon thermal anneal consistent with the segregation of the Al to the alloy/SiO_2 interface. Electrical four point probe measurements indicates 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.

Keywords

Aluminium, Copper, Self-forming barrier, CuAl alloy, XPS, XRD

Introduction

Reduction of critical dimensions in integrated circuit components as predicted by Moore's law pose 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 surrounding inter layer dielectric (ILD)[5]. As the alloying element reaches the Cu/ILD interface, it chemically reacts with the top few nanometres (~ 3nm) 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.

Experimental details

Blanket Cu and CuAl alloy (90%:10% wt) layers approximately 100nm 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 deposition (PE-CVD) SiO_2. Metal gates with areas of 200 μm x 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.

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 1×10^{-9} mbar. Samples were held at their target temperature for 60 minutes with the pressure not exceeding 5×10^{-8} mbar during annealing. The photoelectrons were excited using a conventional Mg Kα (hν = 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 (metal Al) to 1.16 (metal Cu) and from 1.64 (Al oxide) to 1.94 (Cu oxide) for metal oxide species. The O 1s FWHM peak components ranged from 1.2 (Cu oxide) and 1.7 (Al oxide). All curve fitting analysis presented in this study was performed using AAnalyzer curve fitting software program. In addition to conventional XPS, hard x-ray photoemission spectroscopy (HAXPES) measurements with a resolution of 0.25 eV were performed on the CuAl alloy, both as deposited and annealed at 500 ^{O}C in vacuum at a pressure ~1x10^{-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 form further into the bulk alloy than conventional XPS (1254 eV).

Thermal treatments, secondary ion mass spectroscopy (SIMS) and XPS 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 meter 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 minutes at pressures better than 1x10^{-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_{α} (λ = 1.5405Å) radiation, operated at 45 kV and 40 mA.

Results & Discussion

Figure 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. As can be seen from Figure 1, the Cu 3p and Al 2p photoemission peaks overlap, requiring careful peak fitting analysis relative to metal Cu, metal Al, Cu oxide 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 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 according to Willis et al [14] reduction of Cu oxide could prevent Cu ion diffusion into any surrounding dielectric materials.

Figure 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 Figure 1. Following in situ anneal treatments, 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 ^{O}C causes the O1s peak area to increase, consistent with 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].

Figure 3 displays HAXPES survey spectra acquired at a photon energy of 2200 eV of the CuAl alloy both as deposited and following annealing treatments. The Al 1s photoemission peak at a binding energy of 1556 eV increases in intensity from the as deposited to annealed states confirming the segregation that occurs at elevated temperatures. SIMS measurements were used to depth profile the CuAl alloy both before and after the UHV anneal treatments. Figure 4 displays an increase in Al signal in the vicinity of the surface of the annealed samples, relative to the as deposited sample in agreement with photoemission data.

Metal oxide semiconductor (MOS) structures were fabricated to track electrical changes in the CuAl alloy following vacuum anneal treatments. Figure 5 displays the capacitance-voltage (CV) measurements obtained at 1 MHz for Cu, Al and CuAl alloy MOS structures fabricated on PECVD SiO_2 for both as deposited layers and following a 500 ^{O}C vacuum anneal for one hour. As deposited MOS structures exhibit sputter damage, from deposition of metal gate contacts, as seen by a stretch out of the CV profile from accumulation to inversion regions. When the as deposited CV measurements are examined, it is apparent that a difference in flatband positions exists between the pure Cu and Al metal gate MOS structures, attributed to the difference in workfunction between the two metals, as reported in previous studies [16]. The flatband position of the CuAl alloy is noted to be more Cu like due to the large amount of Cu within the sample (Cu 90%:Al 10% wt). Following vacuum anneal treatment at 500 ^{O}C, a change in the CV profiles which now display an abrupt transition between accumulation and inversion is detected which is attributed to the removal of sputter damage. Additionally, a flatband voltage shift is noted for the CuAl alloy from a more Cu like value in the as deposited CV sweeps, to a more Al like value following anneal treatment. This transition to a more Al like state for the CuAl alloy is attributed to the migration of Al from the alloy bulk to the surrounding surfaces including the interface with the underlying SiO_2 dielectric. As the Al migrates to the metal/SiO_2 interface, it modifies the workfunction of the alloy at the metal/SiO_2 interfacial region , resulting in a flatband voltage shift to more Al like values, similar to results reported in previous studies of binary alloys [17]. These measurements suggest that the CuAl alloy could have a more thermally stable metal/oxide interface than that exhibited by pure Cu metal [18].

Four point probe measurements were conducted on blanket CuAl alloy layers following vacuum anneal treatments and compared with similar measurements on pure Cu blanket layers as a reference and the results are displayed in Figure 6. These measurements indicate that the resistance of the reference Cu layer drops by ~ 25% from as deposited to the 500 ^{O}C anneal stage. This change in resistance is consistent with the crystallisation of the Cu layer, increasing conductivity and thus decreasing resistance by reduction of electron scattering sites [19]. When the resistance measurements of the CuAl alloy are examined, a fall of ~50% in resistance is noted, although the absolute values are much higher than for the copper layer, which may be due to excess Al still residing in the bulk of the material. This larger drop in resistance relative to the pure Cu reference can be explained both as crystallisation of the film, acting to decrease resistance but also due to expulsion of the Al alloying material from the alloy bulk. As the alloying material is expelled, it no longer acts as an impurity in the bulk and thus the resistance of the film drops, as seen in previous studies of Cu alloys [5].

In order to obtain additional information as to the segregation mechanism of the Al from the CuAl alloy bulk, XRD measurements were performed on both Cu and CuAl alloy in the as deposited and vacuum anneal states as shown in Figure 7 (a) and (b) respectively. As can be seen from the as deposited Cu film, both Cu (111) and Cu (200) peaks are evident, consistent with the deposited Cu layer. Analysis of the as deposited CuAl film shows a broadened structure with peaks at 40.4^{o} and 42.7^{o}. The peak at 42.7^{o} may possibly be related to the Cu (111) peak in a CuAl alloy. However the absence of a peak close to the Cu (200) position casts some doubt on this. Another possibility is that the peaks seen in the as deposited CuAl sample are associated with one of the phases in the complex Cu-Al phase diagram at Al concentrations ~ 10% wt. Given the positions of the XRD peaks, one possibility is a metastable martensitic phase (variously called β'_1 and β' in the literature), and some of the reflections we see match very well with those seen for this phase (the peaks at 40.4^{o} and 42.7^{o} correspond to lattice spacings of 0.223 nm and 0.212 nm; reports for the metastable martensitic phase give spacings of 0.224 nm and 0.212 nm [20]. Following vacuum annealing at 500 ^{o}C, no notable change is seen in the Cu reference film however a considerable change is noted in the CuAl alloy film. As can be seen from Figure 7(b), the annealed CuAl alloy diffractogram changes to a form very similar to that seen for the Cu reference film, with two peaks close to the Cu (111) and Cu (200) peak positions, although slightly shifted and broader compared to the Cu reference counterpart, which is consistent with a random alloy of Al in Cu (α phase). Behaviour of this type has been seen in previous CuAl alloy studies [15], and is consistent with incorporation of Al *via* the grain boundaries of the Cu film [12], thereby increasing the lattice constant. The discussion above in respect of the unannealed CuAl samples and the metastable martensitic phase must be regarded as tentative, given the complexity of the CuAl phase diagram in this Al concentration region and the absence of detailed local crystallographic studies using e.g. selected area electron diffraction. Nonetheless the dramatic changes seen in the XRD data upon annealing the CuAl film (and the α phase behaviour seen for the annealed samples) strongly indicate a significant change in crystal structure of the alloy following annealing in vacuum. This is consistent with the other measurements reported here indicating the expulsion of Al from the alloy bulk, since the formation of the α phase of Al in Cu occurs only for Al wt % values < 10% (i.e. less than the nominal wt % value of the as deposited samples) [21].

Conclusions

In summary, XPS and SIMS measurements have been used to show that a CuAl alloy (90% : 10% wt) annealed in vacuum exhibits segregation of the Al alloying element from the alloy bulk. Reduction in Cu oxide and growth of Al oxide at the surface as a function of thermal anneal indicates that this anneal alters the surface chemistry. MOS structures consisting of the CuAl alloy, pure Cu and pure Al were studied via capacitance-voltage measurements and a change in flatband position of the CuAl alloy structures was noted following vacuum annealing, consistent with the expulsion of Al from the alloy bulk towards the metal/ILD interface. Four point probe measurements show a larger drop in resistance of the CuAl alloy relative to a pure Cu reference sample, which again has been attributed to expulsion of Al from the alloy bulk. Finally XRD data show dramatic changes in crystal structure of the alloy upon annealing, again consistent with the expulsion of Al from the alloy bulk. These studies all suggest that a CuAl alloy could have significant potential applications as an interconnect metal.

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References

[1] "International Roadmap For Semiconductors - Interconnects," p. 6, 2006.

[2] B. Li, T. D. Sullivan, T. C. Lee, and D. Badami, "Reliability challenges for copper interconnects," *Microelectron. Reliab.*, vol. 44, no. 3, pp. 365–380, Mar. 2004.

[3] Y. Shacham- Diamand, "Copper transport in thermal SiO2," *J. Electrochem. Soc.*, vol. 140, no. 8, pp. 8–13, 1993.

[4] J. D. McBrayer, "Diffusion of Metals in Silicon Dioxide," *J. Electrochem. Soc.*, vol. 133, no. 6, p. 1242, Jun. 1986.

[5] J. Koike and M. Wada, "Self-forming diffusion barrier layer in Cu–Mn alloy metallization," *Appl. Phys. Lett.*, vol. 87, no. 4, p. 041911, Jul. 2005.

[6] J. Bogan, A. P. McCoy, R. O'Connor, P. Casey, C. Byrne, and G. Hughes, "Photoemission study of the identification of Mn silicate barrier formation on carbon containing low-κ dielectrics," *Microelectron. Eng.*, vol. 130, pp. 46–51, Nov. 2014.

[7] P. Casey, J. Bogan, J. G. Lozano, P. D. Nellist, and G. Hughes, "Chemical and structural investigation of the role of both Mn and Mn oxide in the formation of manganese silicate barrier layers on SiO2," *J. Appl. Phys.*, vol. 110, no. 5, p. 054507, Sep. 2011.

[8] A. I. Oliva, J. E. Corona, and V. Sosa, "AlCu alloy films prepared by the thermal diffusion technique," *Mater. Charact.*, vol. 61, no. 7, pp. 696–702, Jul. 2010.

[9] A. P. McCoy, J. Bogan, L. Walsh, C. Byrne, P. Casey, and G. Hughes, "The addition of aluminium to ruthenium liner layers for use as copper diffusion barriers," *Appl. Surf. Sci.*, vol. 307, pp. 677–681, Jul. 2014.

[10] T. N. Taylor, "Reaction of vapor-deposited aluminum with copper oxides," *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, vol. 9, no. 3, p. 1840, May 1991.

[11] S. Yokogawa, H. Tsuchiya, Y. Kakuhara, and K. Kikuta, "Analysis of Al Doping

Effects on Resistivity and Electromigration of Copper Interconnects,” *IEEE Trans. Device Mater. Reliab.*, vol. 8, no. 1, pp. 216–221, Mar. 2008.

[12] K. Maekawa, K. Mori, N. Suzumura, K. Honda, Y. Hirose, K. Asai, A. Uedono, and M. Kojima, “Impact of Al in Cu alloy interconnects on electro and stress migration reliabilities,” *Microelectron. Eng.*, vol. 85, no. 10, pp. 2137–2141, Oct. 2008.

[13] W. L. Prater, E. L. Allen, W.-Y. Lee, M. F. Toney, J. Daniels, and J. a. Hedstrom, “Reduction of resistivity in Cu thin films by partial oxidation: Microstructural mechanisms,” *Appl. Phys. Lett.*, vol. 84, no. 14, p. 2518, 2004.

[14] B. G. Willis and D. V. Lang, “Oxidation mechanism of ionic transport of copper in SiO2 dielectrics,” *Thin Solid Films*, vol. 467, no. 1–2, pp. 284–293, Nov. 2004.

[15] D.-C. Perng, J.-B. Yeh, K.-C. Hsu, and S.-W. Tsai, “Self-forming AlOx layer as Cu diffusion barrier on porous low-k film,” *Thin Solid Films*, vol. 518, no. 6, pp. 1648–1652, Jan. 2010.

[16] I. Fisher and M. Eizenberg, “Copper ion diffusion in porous and nonporous SiO2-based dielectrics using bias thermal stress and thermal stress tests,” *Thin Solid Films*, vol. 516, no. 12, pp. 4111–4121, Apr. 2008.

[17] B. Tsui, S. Member, C. Huang, and S. Member, “Wide Range Work Function Modulation of Binary Alloys for MOSFET Application,” *IEEE Electron. Device Lett.*, vol. 24, no. 3, pp. 153–155, 2003.

[18] A. Kohn, E. Lipp, M. Eizenberg, and Y. Shacham-Diamand, “Copper-related degradation of SiO[sub 2] in metal–oxide–semiconductor capacitors subjected to bias thermal stress: Leakage of the minority charge carriers in the inversion layer,” *Appl. Phys. Lett.*, vol. 85, no. 4, p. 627, 2004.

[19] S. Lagrange, S. . Brongersma, M. Judelewicz, a Saerens, I. Vervoort, E. Richard, R. Palmans, and K. Maex, “Self-annealing characterization of electroplated copper films,” *Microelectron. Eng.*, vol. 50, no. 1–4, pp. 449–457, Jan. 2000.

[20] N. Nakanishi, “The Crystal Structure of β prime; Martensite in Cu-Al Binary Alloys,” *Trans. Japan Inst. Met.*, vol. 2, no. 2, pp. 79–85, Jul. 1961.

[21] T. B. Massalski, *Binary Alloy Phase Diagrams*, Vol 1. OH: American Society for Metals, 1986.

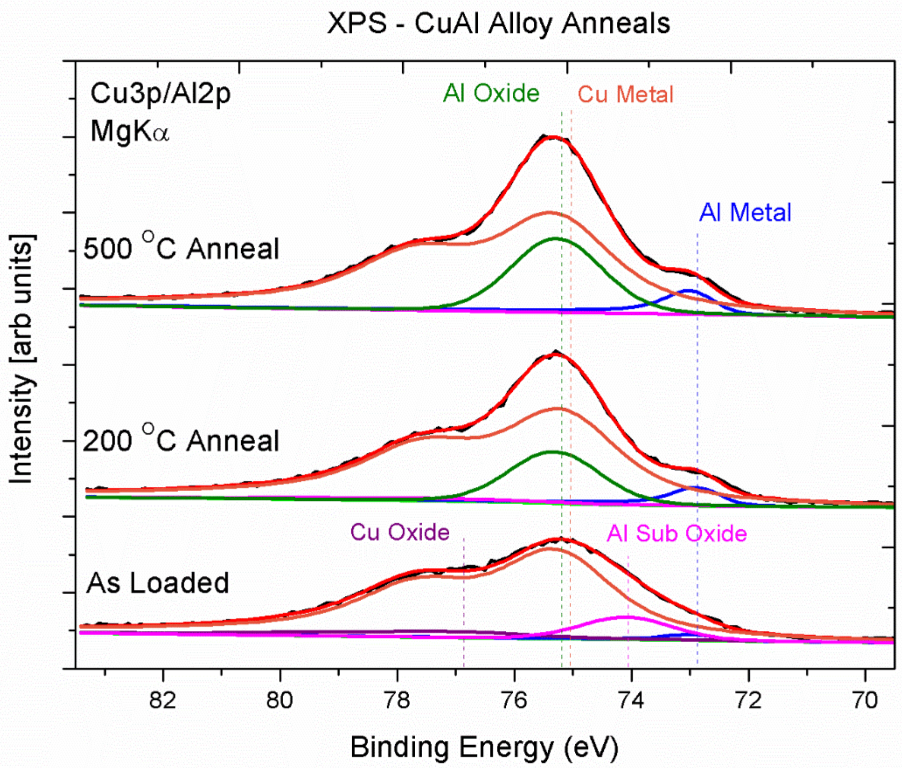

Figure 1: XPS Cu 3p/Al 2p core level spectra both as deposited and following in-situ anneal treatments of the CuAl alloy.

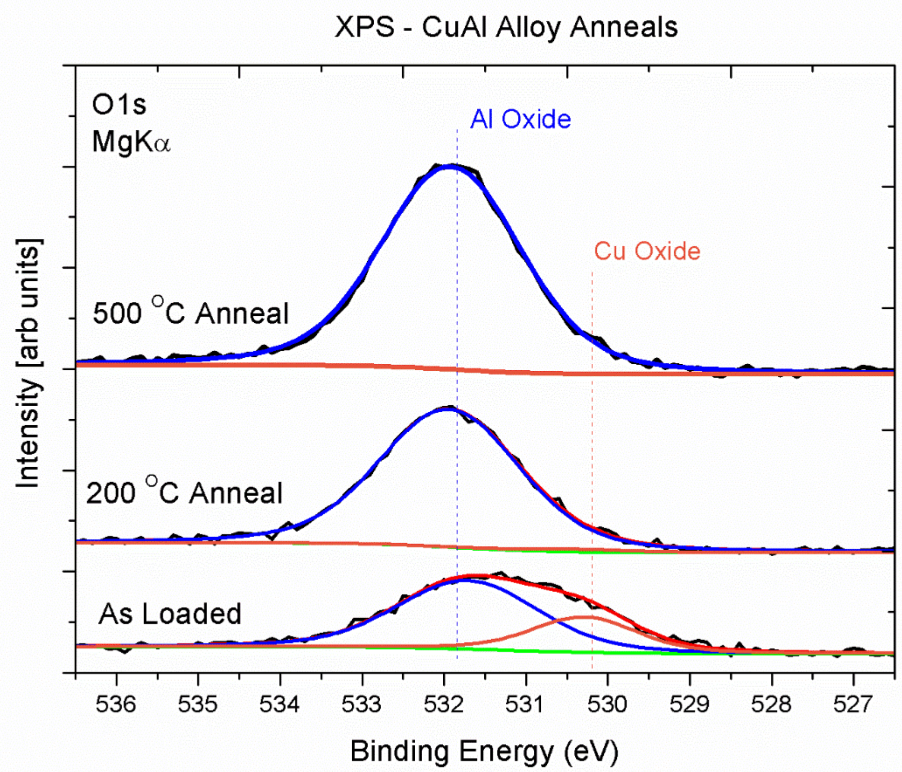

Figure **2**: XPS O 1s core level spectra of the CuAl alloy for the as deposited and following in-situ anneal treatments displaying the reduction in the Cu oxide signal.

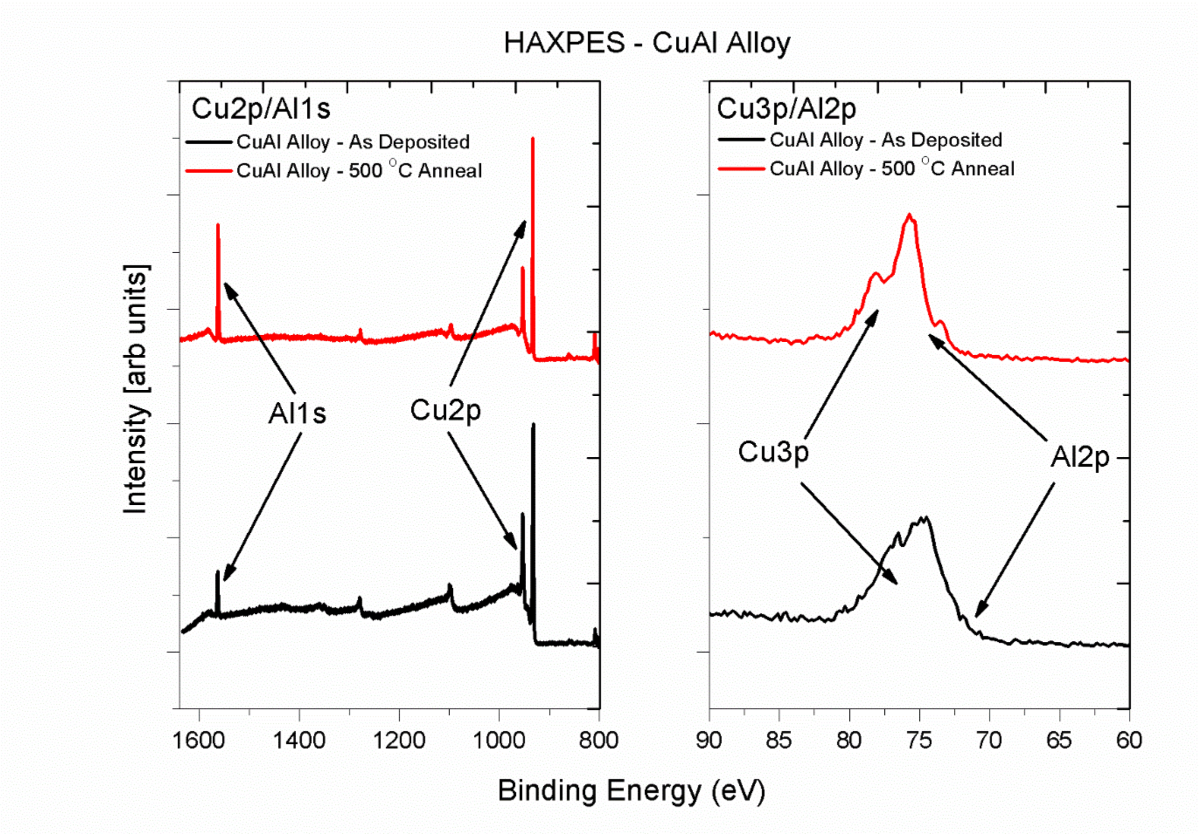

Figure 3: HAXPES Cu 2p/Al 1s and Cu 3p/Al 2p spectra of the CuAl alloy showing increase in Al 1s and Al 2p signal following anneal treatment.

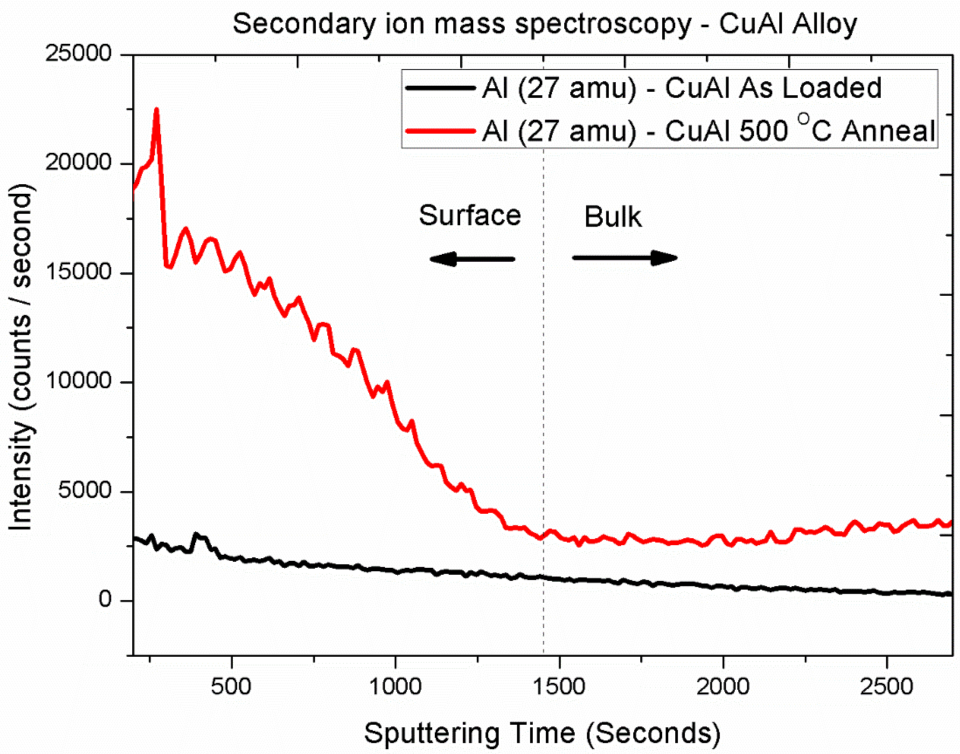

Figure 4: SIMS analysis of CuAl alloy before and after 500 ^{O}C UHV anneal.

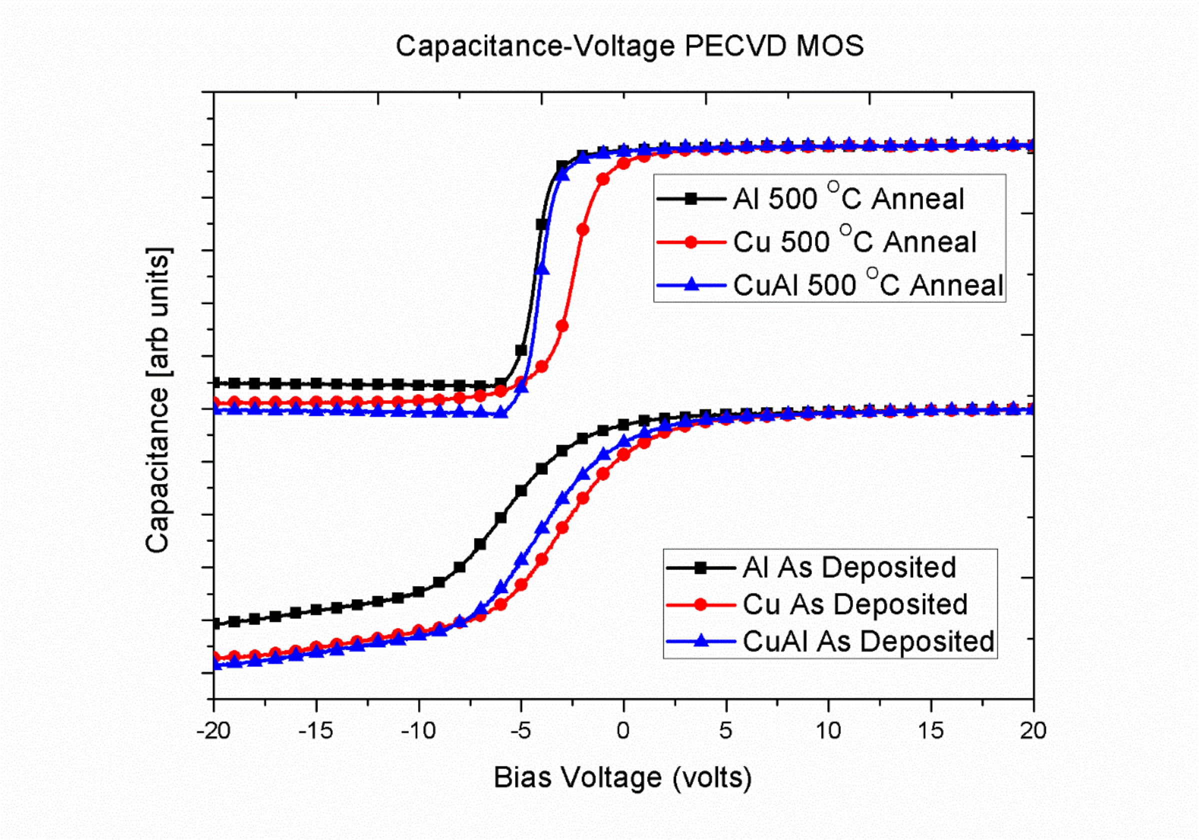

Figure 5: Capacitance-voltage sweeps of Cu, Al and CuAl alloy gate MOS structures both as deposited and following 500 ^{O}C vacuum anneal treatment.

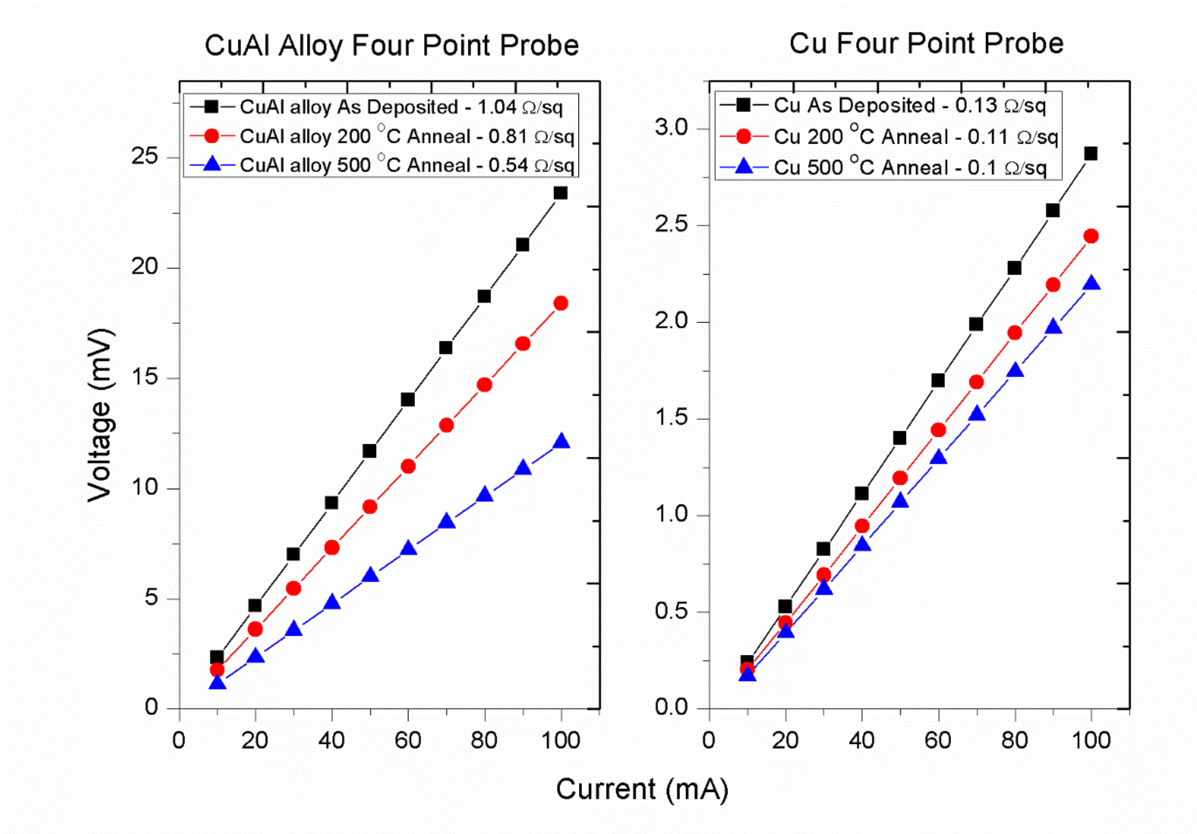

Figure **6**: Four point probe measurements of CuAl alloy and reference pure Cu following vacuum anneal treatments.

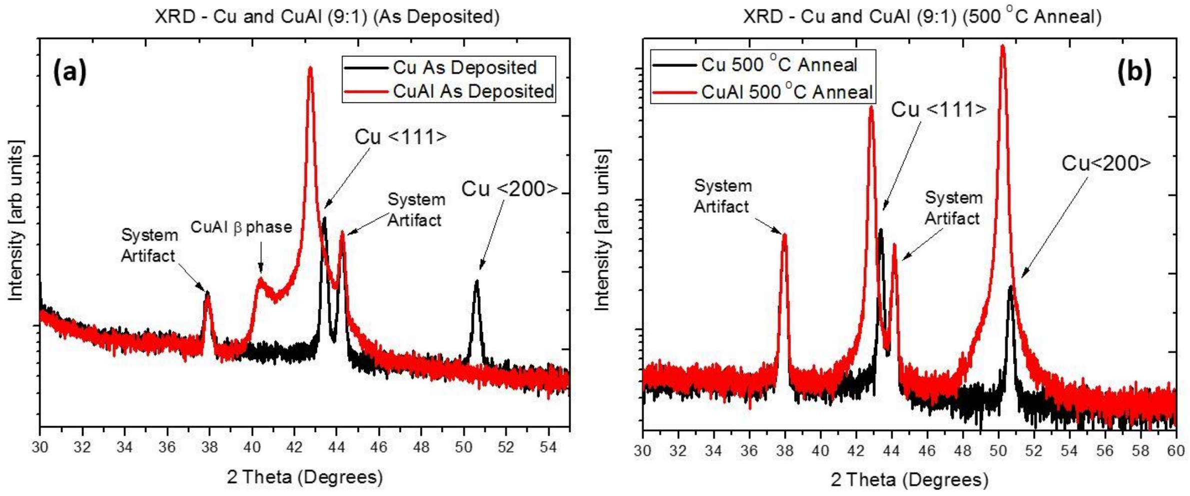

Figure 7: XRD data for (a) as deposited and (b) 500 ^{O}C vacuum annealed Cu and CuAl alloy films.