Nanostructured Reactive Metallic Multilayers

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Abstract. Metallic multilayers have been used in cross-sectional TEM specimen geometry to explore nanostructuring routes using ion and electron beams (top-down) as well as self-organised nanopatterning (bottom-up). Intermetallic alloy formation during heat treatment is studied for binary and ternary layer compositions. A choice of pillars (0D), 1D and 2D layer geometries are used to explore dimensionality effects.

1. Introduction

Metallic multilayer coatings have a wide range of applications in engineering as functional materials such as wear resistant coatings \cite{1}, magnetoresistive coatings \cite{2} and x-ray mirrors \cite{3}. The most recent applications are in the field of nanoscale layers for ignition devices or oxygen-free energy sources in nanolab experiments \cite{4, 5}. As reported in our earlier work for a binary Cu-Al system \cite{6, 7}, we found by both ex-situ and in-situ heating experiments that, starting at \( \approx 250-300^\circ \text{C} \) a tetragonal phase, \( \theta \)-CuAl\textsubscript{2}, is formed, whereas at high heating temperature \( \text{Cu}_9\text{Al}_4 \) is expected. However, it was found that due to the original layer thickness ratio between Cu and Al of 1:3, CuAl\textsubscript{2} remains the preferred phase up to the melting point with no occurrence of \( \text{Cu}_9\text{Al}_4 \).

In extension of our earlier work, we now characterize the reaction sequences and products of a Cu-Al-Cu-Ti multilayer system, fabricated by a combination of sputtering (Al) and evaporation (Cu,Ti), with respect to potential ternary alloy formation. Furthermore, we explore how further reduction in dimensionality of the system influences the reaction sequence, e.g. via preferred surface diffusion in hetero-nanowire or nanopillar specimens. Energy dispersive X-ray spectroscopy (EDX), Electron Energy Loss Spectroscopy (EELS), Selected Area Electron Diffraction (SAED) and High-resolution Electron Microscopy (HREM) are the preferred techniques to confirm the reacted phases.

2. Experimental procedures

All the TEM samples were prepared using conventional cross-sectional sample preparation, involving mechanical grinding and polishing followed by precision ion polishing system milling (PIPS-Gatan). The ion milling was conducted at 5 keV energy and between 3-6° milling angles. Two methods of nanopillar fabrication have been applied. Firstly, we use focused ion beam (FIB, JEOL 6500F dual-beam FEGSEM) and secondly we use e-beam drilling/cutting with a JEOL 3010 TEM at 300kV with LaB\textsubscript{6} source. In-situ heating experiments were performed using a Philips EM430T TEM at 300kV,
equipped with a Gatan single tilt heating holder. Heating increments were applied over 45 min. up to ~302°C with current step increments of 25mA. For the ex-situ heating approach, the sandwiched multilayer sample is annealed inside a tube furnace filled with argon gas with a two-step reaction process (to prevent Al melting), firstly at 400°C for two hours, then at 850°C for one hour. All the post-in-situ and ex-situ TEM micrographs were imaged using a JEOL JEM-2010F at 200kV equipped with Oxford Instruments ISIS energy dispersive X-ray (EDX)-mapping control and a Gatan GIF spectrometer for electron energy loss spectroscopy (EELS) chemical analysis.

3. Results and discussions
Figure 1 shows several contrast inverted bright field (BF) TEM images during in-situ heating up to 302°C of the cross-sectional Cu-Al-Cu-Ti layer system on Al₂O₃ substrate. Part of the specimen has been FIB milled into pillar shapes (JEOL/Orsay Fabrika dual beam; Ga beam of 3.5pA at 30kV and aperture #2 for ~3 min.). At room temperature (Fig 1(a)) all four metallic phases can be sorted by their scattering contrast in a grey level sequence of Cu – Ti – Al, according to their atomic number. At around 240°C the Cu-Al-Cu part of the layer system starts to react via interdiffusion, excluding the Ti layer. The transformation process at the nanopillars regions is completed at 285°C, and no further change to this region is observed at any higher temperature. On the other hand, the completion of the intermetallic reaction at the one-dimensional regime is slightly delayed to 302°C, as seen on the very top end of the image. The entire in-situ heating experiment took about ~ 1 hour.

Figure 1. (a-d) TEM micrographs (contrast inverted bright field) of the in-situ heating experiment from room temperature to 302°C for a Cu-Al-Cu-Ti multilayer sample (Philips EM430, 300kV).

Figure 2. Chemical mapping of the in-situ heat treated Cu-Al-Cu-Ti multilayer. (a) RGB chemical phase map of nanopillars with red = Ti-Kα, green = Cu-Kα and blue = Al-Kα and (b) EELS spectrum
image (linescan along red arrow of (a), total length ~300nm): second derivative plasmon map with corresponding phases: Cu-Al alloy at 15.6 eV, Ti at 17.1 eV and Al₂O₃ at 25 eV.

Figure 2 shows the post-processed results of an in-situ experiment, after return from ~300°C to room temperature and change to an analytical FEGTEM (JEM 2010F), using a different sample than for Fig. 1. Figure 2 (a) illustrates the EDX map of the three layer system (Cu-Al-Cu) which fully transformed into a homogeneous Cu-Al alloy. Along the line in Fig 2(a), an EELS spectrum imaging line scan in the plasmon energy range has been performed. To increase visibility of the three phases (alloy, Ti, substrate), the plasmon spectra have been converted into 2nd derivative maps (using IDL, see figure 2 (b)). The benefit of this technique is to enhance phase-to-phase contrast by means of resonance sharpness in addition to resonance position. The Cu-Al alloy appears to have a plasmon maximum at ~ 15.6 eV, whereas the Ti and Al₂O₃ are at ~ 17.1 and 25 eV respectively.

**Figure 3.** TEM micrograph of Cu-Al-Cu-Ti multilayer sample before (a) and after drilling (b-c).

Figure 3 (a-c) shows an alternative nanofabrication method for metal nano-pillars using e-beam instead of FIB. For the cutting of lines to convert the metallic layers into pillars, the condenser astigmatism is changed to produce an ultra-astigmatic line-focus. The continued irradiation with this line-focus over ~ 2 hours resulted in full cuts through all metal layers with Ti being the last one to separate. The diameter of the final nanopillars is ~ 80-150 nm which depends on the size of condenser aperture (CA) and specimen thickness. Since the size of the cut is given by the total multilayer length of 390 nm, the largest CA with mean convergence angle of ~ 32.0 mrad (~ 120 µm in diameter) became necessary. A beam drift problem caused some curvature in the produced nanopillars (fig 3(b)). However, this process could be minimised by reducing the drilling length for every session.

One motivation for e-beam cutting is the prospect of less damage (e.g. no Ga implantation) than with FIB. However, we also found beam induced transformations along the drilling area, mainly in Ti (Figure 3 (c)). Apart from some carbon contamination effects at the border of the drilling area in Cu we find that the original Ti layer has reacted into ultra-fine round Ti multi-grains with ~ 5 nm in diameter (e.g. red circle). This could possibly be due to irradiation induced “quasi-melting” and re-solidification, a process occurring far below the bulk melting temperature under high e-beam irradiation.

As the upper temperature limit of in-situ heating prevented the Ti layer from participating in any reaction, we extended our study by ex-situ heat treatment of the cross-sectional prepared TEM specimen of the original Cu-Al-Cu-Ti system. Figure 4 shows the Cu-Al-Cu-Ti sample after furnace heat treatment up to 850°C. Figure 4 (a) illustrates via EDX chemical mapping (JEM 2010F) that the original 4 layer system has been transformed into an ordered alternation layer of two different phases, presumably via spinodal decomposition of an intermediate metastable ternary high-temperature phase. The EDX point measurement quantification from both phases indicated a preliminary result for a binary Cu-Al alloy and a ternary Cu-Al-Ti alloy phase. By investigation using HREM plus EDX and diffraction analysis (not included here) we found consistent identification of the binary alloy as Cu₉Al₄.
and the ternary alloy as Cu₂AlTi. The HREM image of the interface separating the two phases gives an orientation relationship with parallel zone axes of <1 1 1> and <0 1 1> for Cu₉Al₄ and Cu₂AlTi alloys respectively (figure 4 (b)).

Figure 4. (a) RGB image of the Cu-Al-Ti sample after ex-situ heat treated up to 850°C with red = Ti-Kα, green = Cu-Kα and blue = Al-Kα. (b) HREM micrograph of Cu₉Al₄ – Cu₂AlTi interface with O.R. <1 1 1> (1 0 1) Cu₉Al₄ and <0 1 1> ~ 14° off (2 0 0) Cu₂AlTi.

4. Conclusions
We have demonstrated nanopillar fabrication using both FIB and electron beam cutting starting from a conventional cross-sectional TEM specimen of a multi-layer metal system. It was found that annealing induced transformations of the multilayer and the intermetallics formation can then be studied in parallel within the layered and pillared structures. Formation of functional metallic nanodots would be one application of this top-down nanofabrication route. Alternatively, appropriate choice of the layer-thicknesses inside the multi-layer system to avoid coincidence with a single intermetallic phase could be used for self-organised nanostructuring into alternating nano-phases inside a TEM specimen by means of phase separation following high-temperature annealing. Possible applications for such reactive multilayer films include joining and packaging and also ignition devices.

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