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From solid solutions to fully phase separated interpenetrating networks in sputter deposited "immiscible" W–Cu thin films

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ABSTRACT

W–Cu alloys are typically used for heat sinks, radiation shielding or high performance contact materials. Their immiscibility leads to interpenetrating structures, with typically smallest microstructural length scales on the order of several micrometres. This work focusses on tuning this length scale from the atomic level to the nanometre and submicron range. This is made possible by exploiting the two constituents' immiscibility in thermodynamic equilibrium as well as the lack of Cu segregation to W grain-boundaries, thus allowing for the growth of the two phases. The system is studied in the complete concentration range and microstructure is related to both mechanical and electronic properties.

1. Introduction

The immiscible binary W–Cu (tungsten–copper) system is extremely interesting from an application point of view with desirable property combinations, as a result of the good electric conductivity, high melting point (3420 °C), hardness, thermo-mechanical stability and radiation shielding capabilities of tungsten [1–4] paired with the excellent thermal conductivity (1401 W/(mK) [1]) and electrical performance ($1.678 \cdot 10^{-8}$ Ωm [1,4]) of copper. Possible applications thus include thermal management, high power, high voltage, plasma and nuclear appliances [5–8]. W–Cu composites have further shown promising results as radiation shielding in medical applications [2]. Additionally, the system exhibits complete immiscibility, stemming from its very high heat of mixing of 16–24 kJ/mol [9], 35.5 kJ/mol [10,11] up to 121 kJ/mol (at 1100 °C) [12,13]. A simple consideration of a systems enthalpy of mixing ΔH^{mix}, atomic size and structure differences, however, is insufficient to allow for a complete tunability of microstructural length scale. While a positive enthalpy of mixing is prerequisite for phase separation, it needs to be related to the enthalpy of segregation, ΔH^{seg}, via $\Delta H^{seg}/(\Delta H^{mix})^a > c$, with temperature dependent constants a and c to determine whether a stable nanocrystalline microstructure can be achieved or not. In the former case, tunability is limited by the equilibrium grain, respectively phase size. Thus, a nanocrystalline, segregation stabilised microstructure can be achieved for W–Cu up to 453 °C. Above this temperature, microstructural evolution commences via a metastable, followed by an unstable region, as reported by the group around Schuh [12–14]. At higher temperatures, the phase separating tendencies of the system can therefore be exploited to achieve full microstructural tunability.

Due to the high hardness of tungsten, the systems immiscibility and the large difference in melting temperature W–Cu composites are generally fabricated by powder metallurgic means, on which extensive research regarding powder sizes and morphologies, configurations, sinter parameters etc. has been undertaken [8,15–22]. Sintered parts, however, are susceptible to several kinds of inherent defects and restrictions. Examples are process intrinsic inhomogeneities and the inclusion of pores, limitations regarding obtainable compositions and restrictions on minimum microstructural length scales [8,15–22]. Sputter deposition in contrast presents the opportunity to homogeneously distribute several elements simultaneously [9,23]. Exploiting this metastable synthesis route in combination with thermal treatment then allows for a precise microstructural tuning from an as-deposited solid solution state up to fully phase separated post annealing interconnected networks. Thus, materials properties can be engineered to meet very specific requirements by exploiting mutual solubility and microstructural refinement in metastable configuration as well as phase separation and coarsening behaviour [23,24].

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The presented investigation aims to investigate the evolution of microstructural and physical properties of co-sputtered W–Cu thin films. Solid solution W–Cu thin films were therefore produced from the vapour phase. Thermal treatment is then performed on deposited thin films to tune the microstructural evolution between the metastable as-deposited and the equilibrium phase separated state. The resulting microstructures and accompanying thin film properties are investigated by conducting cross sectional scanning electron microscopy, X-ray diffraction, nanoindentation and resistivity measurements. Experiments were carried out prior and posterior to thermal treatment to characterise thin films across the entire compositional spectrum with respect to developing microstructures. Results thus acquired for monolithic thin films are then used to combine the high hardness of W with the good conductivity of Cu in a multilayer thin film with compositional gradient perpendicular to its surface.

2. Experimental methods

The experimental methods described in the following chapter are similar to and adapted from an earlier study [25] and, thus, are only shortly described in the following.

2.1. Deposition

Preceding deposition of thin films, a 10 h bake-out at 120 °C was performed. Subsequently, titanium (Ti) and each target intended for use, copper and/or tungsten (99.95% and 99.999% purity, respectively; 76.20 mm diameter; target and substrate surface normals at 35°, 130 mm throw distance) were sputtered into the chamber (5 min, 300 W, 0.667 Pa) for gettering of residual oxygen and target surface purification. This allowed an average base pressure of $3.48 \cdot 10^{-5}$ Pa to be reached. Subsequently, a Ti adhesion layer (15 or 50 nm) and the co-sputtered W–Cu thin film were deposited (PVD Products Inc., USA) onto Si (100) substrates (50 nm each SiO_2 and SiN_x diffusion barrier, Si-Mat Silicon Materials, Germany). For additional surface cleaning, target plasma was ignited 2 min before opening target and substrate shutters. Stated deposition times are durations with opened shutters. All W–Cu thin films were deposited from both targets simultaneously at 0.667 Pa (5 mTorr), 100 sccm Ar flow (99.998% purity) and 20 rpm substrate rotation, to achieve uniform deposition. Magnetron power fraction was varied between separate depositions to achieve different compositions. For layered structures, an out-of-plane compositional gradient was achieved by variation of magnetron fraction during deposition, resulting in sublayers of alternating W- and Cu contents.

2.2. Thermal treatment

Annealing of as-deposited (ad) thin films was performed in a laboratory furnace (Model: 1100-4080-M1, Thermal Technology Inc., USA). Representative temperature profiles are depicted in Fig. 1. Prior to heating, the furnace chamber was evacuated and subsequently flushed (Ar, 99.999%) three times to achieve a vacuum of better than $2.45 \cdot 10^{-2}$ mbar, which was kept constant at roughly $2.0 \cdot 10^{-2}$ mbar during annealing. The nominal annealing temperature in all experiments was 750 °C with durations under thermal influence of 10 min, 1, 5 and 10 h. After annealing, heating coils were shut off to achieve maximum passive cooling rates.

2.3. Characterisation

Cross sectional microstructure and surface morphology analysis was performed by broad ion beam (BIB) milling with a Hitachi IM 4000 (Hitachi High-Tech, Japan) and subsequent imaging with an extra high resolution scanning electron microscope (FEI Magellan 400 FEG XHR-SEM; FEI Company, USA) according to [25] (see Fig. 2).

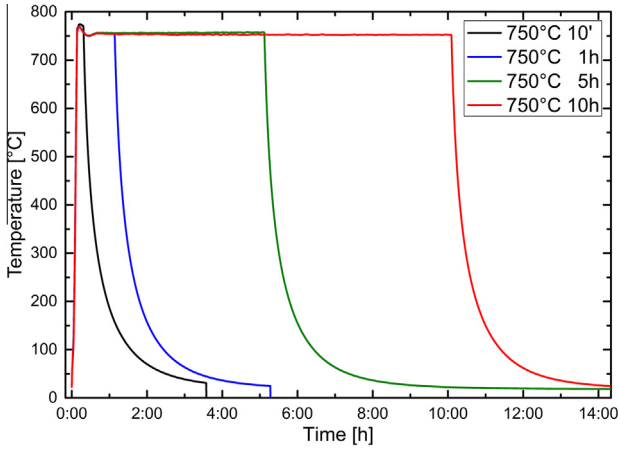

Fig. 1. Temperature profiles of annealing processes. Process temperature for all treatments was kept constant at 750 °C. Heating duration from RT to nominal temperature was 10 min. Durations at 750 °C were 10 min, 1 h, 5 h and 10 h. Displayed profiles show the temperature in sample vicinity.

Further microstructural as well as crystallographic analysis was performed utilising X-ray diffraction (XRD). Analysed ω-2θ diffraction profiles were recorded on an Empyrean X-ray diffractometer (PANalytical, Netherlands) in the 2θ range of 20–100° (step size 0.026°, 77.265 s time per step, Cu-Kα radiation $\lambda = 0.154056$ nm). ω was set at an offset of 5° to avoid excessive substrate diffraction peaks. Texture in the deposited thin films results in a limited number of reflections obtained from one dimensional XRD measurements. Thus, linear fits in Williamson–Hall plots [26] are unreliable, rendering this extremely useful method non-applicable. Instead, a rather simple estimation of grain sizes, or rather crystallite sizes, was chosen by applying Scherrer's equation [27,28] $D = (K\lambda)/(\beta_{hkl} \cos\theta)$ directly to the residual broadening β_{hkl} with $\lambda = 1.5406$ Å and shape factor $K = 0.9$. Instrumental peak broadening was accounted for by deducting 0.1° from the observed FWHM (full width half maximum)

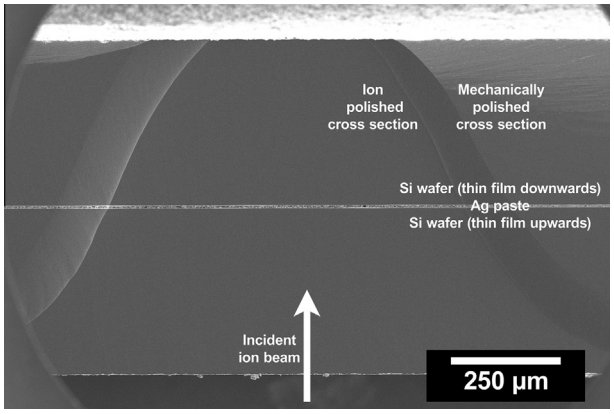

Fig. 2. Overview of sample sandwich structure after conventional metallographic grinding (grit 500 and 4000) and broad ion beam cross section cutting (1.5 h at 6 kV, ~140 µA ion beam current, 0.09 sccm Ar, ±40° swing angle at 23 reciprocations/min). The image shows 2 $Si/SiO_2/SiN_x$ substrates with thin film deposits facing each other. Adhesion is achieved with conductive silver paste applied between thin films. Ion beam incidence direction is from bottom to top. The bell shape of the ion beam polished surface is a result of the bell shaped distribution of beam intensity and swing motion.