Phase constitution and interface structure of nano-sized Ag-Cu/AlN multilayers: Experiment and *ab initio* modeling

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Nano-sized Ag-Cu_{8nm}/AlN_{10nm} multilayers were deposited by reactive DC sputtering on α -Al₂O₃(0001) substrates. Investigation of the phase constitution and interface structure of the multilayers evidences a phase separation of the alloy sublayers into nanosized grains of Ag and Cu. The interfaces between the Ag grains and the quasi-single-crystalline AlN sublayers are semi-coherent, whereas the corresponding Cu/AlN interfaces are incoherent. The orientation relationship between Ag and AlN is constant throughout the entire multilayer stack. These observations are consistent with atomistic models of the interfaces as obtained by *ab initio* calculations. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4761471>]

Nanostructured and ultra-fine grained materials with their characteristically high interface density often exhibit chemical and/or physical properties that differ significantly from those of the corresponding bulk materials; e.g., a much higher yield strength, a strikingly lower or higher melting point and/or specific electrical, magnetic and optical properties.^{1,2} These findings have intensified developments of nanostructured materials with targeted properties for advanced nanotechnologies.³ A common approach in the design of functional nanomaterials is to arrange the constituents in a composite fashion by depositing alternating nanometer-thick sublayers of materials with different complementary properties on a bulk substrate^{4,5} using physical and/or chemical vapor deposition techniques under high vacuum conditions.^{6–9}

Using a multilayer approach and employing the fact that many metals and alloys exhibit a significant melting point depression (MPD) (as compared to the bulk melting temperature) when confined to nanoscale size,^{10–12} our present research aims at the development of nanostructured Ag-Cu-based brazing filler materials for low-temperature joining applications. Within the same research framework, a melting point depression of about 230 K, well-applicable to low-temperature joining technologies, was previously demonstrated for nano-sized Al-Si/AlN multilayers.^{13,14} Ag-Cu binary alloys are routinely used as base for brazing fillers to join different solid materials.¹⁵ The Ag-Cu system displays an eutectic phase diagram: Ag and Cu are practically immiscible below 650 K, and the eutectic melting point of 1051 K occurs at a (bulk) composition of Ag-40 at. % Cu.¹⁶ Conventionally, the melting point of the eutectic Ag-Cu alloy is further reduced by alloying with foreign elements, which is

often accompanied by detrimental side effects, such as increased toxicity (Cd), higher costs (In), or a reduced corrosion resistance (Zn and Sn).

Our research strategy instead aims at a reduction of the eutectic melting point of the Ag-40 at. % Cu alloy by scaling its dimension down to the nanometer range. To this end, we design a multilayer stack by alternating each nano-sized Ag-40 at. % Cu sublayer with a thin AlN sublayer, which serves as a chemically inert diffusion barrier to confine the alloy to the nanoscale up to its melting point. Evidently, below a certain thickness of the alloy sublayer, its thermodynamic stability (i.e., the total Gibbs energy) becomes dominated by the excess Gibbs energy contributions resulting from the interfaces and high-angle grain boundaries in the system.² The resulting destabilization of the *solid* state of the alloy sublayer(s) with respect to the corresponding *liquid* state is expected to induce the targeted size-dependent MPD.

As a first step in the development of nanostructured Ag-Cu-based brazing filler materials for low-temperature joining applications, this study addresses the preparation and microstructural characterization of the Ag-Cu_{8nm}/AlN_{10nm} multilayers with a focus on the atomic-scale structure of the interfaces between the alloy and the AlN sublayers. Ag-Cu_{8nm}/AlN_{10nm} multilayers, comprising of 20 alternations of a 8 nm-thick Ag-40 at. % Cu sublayer and a 10 nm-thick AlN sublayer, were deposited on α -Al₂O₃(0001) substrates using reactive DC sputtering in a high vacuum chamber (base pressure <10⁻⁶ Pa) from two confocally arranged unbalanced magnetrons (without applying a substrate bias) equipped with 2 in. targets of pure Al (99.99%) and of Ag-40 at. % Cu alloy. During the AlN deposition steps, the argon and nitrogen flows were set at 15 sccm and 7 sccm, respectively, resulting in an Ar/N₂ reactive atmosphere and a total pressure of about 0.3 Pa. The sample temperature was kept below 343 K during deposition.

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The phase constitution and crystallographic structure of the as-deposited multilayers were investigated by a combinatorial approach using energy dispersive x-ray (EDX), x-ray diffraction (XRD), and high resolution transmission electron microscopy (HR-TEM). HR-TEM cross-sections were prepared by mechanical polishing (Tripod method) and subsequent ion milling (Bal-Tec RES101). The HR-TEM analysis was performed using a JEOL JEM 2200FS TEM, operating at 200 kV equipped with a field emission source, an Omega[®] energy filter, EDX, and HAADF detectors.

A bright-field TEM micrograph of a cross-sectional lamella of the Ag-Cu_{8nm}/AlN_{10nm} multilayer stack is shown in Fig. 1(a). The lighter and darker sublayers correspond to the AlN and the Ag-Cu alloy sublayers, respectively (the Al₂O₃ substrate is visible as the uniformly gray zone at the bottom of the image). Clearly, the thicknesses of the individual Ag-Cu_{8nm} and AlN_{10nm} sublayers are laterally uniform and constant throughout the stack. The resulting periodicity of alternating sublayers is also evidenced by the satellite spots (Laue fringes) around the spot of the primary transmitted beam in the selected area diffraction pattern in Figure 1(c) (inset). Elemental mapping of the cross-sectional Ag-Cu_{8nm}/AlN_{10nm} lamella by EDX (see Fig. 1(b)) reveals that the alloy sublayers, as deposited from an eutectic Ag-Cu alloy target, actually consist of separated domains of Ag (blue) and Cu (red). This suggests that a phase separation into nano-sized grains of pure Ag and Cu has occurred during the successive

alloy deposition steps, as driven by the large positive enthalpy of mixing between Ag and Cu.¹⁷ However, at the onset of each alloy deposition, the formation of a Ag-Cu solid solution phase or intermetallic compound could still have been favored by the surface and interface energy contributions of the evolving substrate/film system. A similar observation was made by Chen and Zuo,¹⁸ who reported the formation of an Ag-Cu single-phase solid solution on a carbon substrate for Ag-Cu film thicknesses below 5 nm. Only for film thicknesses larger than 5 nm, discontinuous films developed due to the phase separation of Ag and Cu. Hence, for the present samples, we cannot exclude the initial formation of an eutectic alloy and subsequent phase separation of the Ag-Cu sublayers at a sublayer thickness exceeding 5 nm. However, in contrast to the Ag-Cu films growth on carbon substrates,¹⁸ the phase-separated 8 nm-thick Ag-Cu sublayers on AlN form continuous films (Fig. 1).

A selected area electron diffraction (SAED) pattern of the cross-sectional TEM lamella (see Fig. 1(c)) shows two arrays of diffraction spots, one originating from the AlN sublayers (corresponding to AlN[2 $\bar{1}$ 10] zone axis; yellow) and one from the Ag grains in the Ag-Cu sublayers (corresponding to Ag[1 $\bar{1}$ 2] zone axis; blue). The overlap of the Ag[111] with the AlN[0002] spots indicates that the Ag grains in the alloy sublayers and the AlN_{10nm} sublayers maintain a constant crystallographic orientation relationship according to Ag{111}<110>||AlN{0001}<0 $\bar{1}$ 10> throughout the multilayer stack. Hence, the preferred growth directions of the Ag grains and the AlN sublayers are 111 and 0001, respectively. The pronounced Ag(111) and AlN(0001) textures were also evidenced in corresponding XRD phi-scans for AlN(101) and Ag(200), as shown in Fig. 1(d). On the contrary, the corresponding phi scans for Cu(200) indicate a random texture of the Cu grains in the Ag-Cu sublayers (see Fig. 1(d)). Consequently, the reflections from the Cu phase in the electron diffraction pattern of Fig. 1(c) cannot be easily identified (i.e., only a few randomly-in-plane-oriented Cu grains were in diffraction condition for this zone axis). The random in-plane orientation (fiber texture) of the Cu grains was also evidenced by Fourier analysis of a selected Cu area in the recorded HR-TEM image of the cross-sectional lamella (see Fig. 2(d)).

Since the structures of the interfaces between the individual Ag and Cu grains and the AlN sublayers can be decisive for the MPD of the Ag-Cu sublayers (see above), the interface structures were investigated in more detail by HR-TEM (Fig. 2(a)). It followed that the Ag/AlN interface is very regular (Figs. 2(c) and 2(e)). The initial lattice mismatch of about 7% at the Ag/AlN interfaces is accommodated by isolated misfit dislocations with a density lower than 0.2 nm⁻¹. The semi-coherency of Ag/AlN interface, as observed by HR-TEM, complies with the aforementioned orientation relationship between the Ag grains and the AlN sublayer, as evidenced from the SAED pattern in Fig. 1(c) and from the phi scans in Fig. 1(d). On the contrary, the atom arrangement in the close vicinity of the Cu/AlN interface appears rather distorted (compare Figs. 2(b) and 2(c)), which is in accordance with the random in-plane texture of the Cu grains from XRD (Fig. 1(d)). The first Cu planes parallel to the interface boundary have in-plane disorder (Figure 2(b)). However, a few atomic

FIG. 1. (a) Scanning transmission bright field electron image of a cross-sectional lamella of the Ag-Cu/AlN multilayer stack (light: AlN, dark: Ag-Cu, bottom layer: Al₂O₃ substrate); (b) EDX map of Ag, Cu, and Al, as taken from the marked region in (a) showing phase separation of the deposited eutectic Ag-Cu alloy into Ag and Cu grains; (c) selected area diffraction pattern from the marked region in (a), indicating the growth of Ag [111] along AlN [0001] (zone axis: Ag[1 $\bar{1}$ 2] / AlN[2 $\bar{1}$ 10]) (blue: Ag, yellow: AlN); (inset of (c)) enlargement of the Laue fringes around the transmitted primary electron beam, as originating from the periodicity of the multilayer sequence; (d) XRD phi-scans for AlN(101), Cu(200), and Ag(200) indicating an epitaxial relationship between the AlN and the Ag sublayers (and a strong Ag(111) texture). The Cu sublayers are randomly in-plane textured.

FIG. 2. (a) HRTEM image of a selected region of the cross-sectional TEM lamella in Fig. 1(a). The upper panels of (b) and (c) are enlargements of the marked regions in (a) illustrating the atomic-scale structure of the Cu/AlN and Ag/AlN interfaces. The lower panels in (b) and (c) correspond to the inverse Fourier transformations of the selected regions, as obtained after application of a mask around the AlN[0110] diffraction spot. The corresponding (unfiltered) Fourier transformations of the selected regions are shown (d) and (e). The red, yellow, and blue arrows in (b)-(e) indicate the position of the interface.

planes away from the interface, a rather perfect Cu bulk structure is observed. Unfortunately, the HR-TEM analysis did not allow resolving the atomic structures of the semi-coherent Ag/AlN and the incoherent Cu/AlN interfaces in greater detail. Therefore, the experimental investigations were complemented by modelling the interface structures by atomistic simulations using density functional theory (DFT).^{19,20}

For the DFT calculations, the Perdew-Burke-Ernzerhof functional²¹ with ultra-soft pseudopotentials for N, Cu, and Ag and norm-conserving ones for Al was used. All structural models considered (see below) were fully optimized (relaxed) until the largest residual force was smaller than 0.0015 a.u., while adopting periodic boundary conditions in all directions. The vacuum region, separating periodic images in z-direction, was 17 Å. The k-space was sampled in the gamma point. The energy cutoff for the charge density was set to 320 Ry.

The Ag-Cu/AlN multilayers were deposited in a N-rich atmosphere, which should result in a N-polar AlN(000 $\bar{1}$) surface.²² Hence, in the DFT calculations, the substrate was modeled by a relaxed $5 \times 5 \times 3$ AlN(000 $\bar{1}$) slab (i.e., a stacking of three 5×5 AlN(000 $\bar{1}$) unit cells). According to the literature,^{23,24} the N-polar AlN(000 $\bar{1}$) surface is reconstructed with an Al(H3) surface termination. However, *ab initio* calculations of an Ag(111) slab on top of an Al-terminated $2 \times 2 \times 3$ AlN(000 $\bar{1}$) slab show that the replacement of Al adatoms by Ag atoms is energetically favorable. The case of Cu/AlN is more complex; due to the high lattice mismatch, larger superstructures (i.e., larger than 2×2) should be considered. For the sake of comparison with the Ag/AlN system, interfacial Al was also not considered for the Cu/AlN configurations. Here, it is emphasized that, due to the high solubility of Al in Ag (up to 15 at. %), any Al adatoms on the AlN surface will probably dilute in the bulk of the Ag overlayer during deposition. The same applies to Cu.

Preliminary calculations for one monolayer (ML) of a 5×5 unit cell of Ag on the relaxed $5 \times 5 \times 3$ AlN slab revealed that Ag atoms always relaxed to on-top nitrogen sites, creating a coherent interface, in accordance with the HR-TEM observations (Fig. 2(c)). One ML of a 5×5 unit cell of Cu on $5 \times 5 \times 3$ AlN, on the other hand, relaxed to an in-plane disordered structure, also in agreement with HR-TEM (Fig. 2(b)). The different behaviors are caused by the much larger lateral misfit of about 20% for the 5×5 Cu(111) ML on $5 \times 5 \times 3$ AlN(000 $\bar{1}$), as compared to the lateral misfit of 7% for the 5×5 Ag ML on $5 \times 5 \times 3$ AlN(000 $\bar{1}$). Therefore, as a next step, one ML of a 6×6 unit cell of Cu on $5 \times 5 \times 3$ AlN(000 $\bar{1}$) was considered, since it reduces the lateral misfit to about 1% (Fig. 3(a)). It followed that, in the region where the Cu atoms are approximately aligned with N atoms, they tend to relax to create strong bonds with on-top N atoms, whereas the Cu atoms are significantly weaker bonded in the vicinity of the Al-hollow-sites. Consequently, for the relaxed AlN/Cu $6 \times 6 \times 1$ slab, the adsorbed 6×6 Cu layer is corrugated (Figs. 3(b) and 3(g)).

Finally, on the basis of the above described DFT calculations, the preferred structural model for the Cu{111}||AlN(000 $\bar{1}$) boundary plane was evaluated by generating the following slab configurations:

- Three MLs of a 5×5 Cu(111) unit cell elastically strained on the $5 \times 5 \times 3$ AlN(000 $\bar{1}$), further denoted by AlN/Cu $5 \times 5 \times 3$. After slab relaxation, the structure of the Cu layers is strongly disordered, both along lateral and perpendicular directions with respect to the boundary plane of the interface (Figs. 3(c) and 3(g)). However, the HR-TEM analysis of the Cu/AlN interface only shows a significant disorder parallel to the interface boundary plane (see above and Fig. 2(b)). The AlN/Cu $5 \times 5 \times 3$ structural model therefore seems to be unrealistic.
- Four MLs of a 6×6 unit cell of Cu(111) on $5 \times 5 \times 3$ AlN(000 $\bar{1}$) (with a reduced lattice mismatch of 1%), further denoted as AlN/Cu $6 \times 6 \times 4$. Evidently, the Cu layer adjacent to the interface boundary plane is much less corrugated for the relaxed AlN/Cu $6 \times 6 \times 4$ slab than for the relaxed AlN/Cu $5 \times 5 \times 3$ slab (Figs. 3(b), 3(d), and 3(g)).

FIG. 3. DFT model calculation of the atomic structure of different (relaxed) Ag and Cu slabs on the nitrogen-terminated $5 \times 5 \times 3$ AlN(000 $\bar{1}$) slab. (a) Top view of a relaxed 6×6 Cu(111) monolayer; (b) cross-sectional view showing a corrugation of the 6×6 Cu(111) monolayer; (c) relaxed AlN/Cu $5 \times 5 \times 3$ slab; (d) relaxed AlN/Cu $6 \times 6 \times 4$ slab; (e) relaxed AlN/Cu $5 \times 5 \times 1$, Cu $6 \times 6 \times 3$ slab; (f) top view of the interface-adjacent Cu layer, as indicated by the arrow in the AlN/Cu $5 \times 5 \times 1$, Cu $6 \times 6 \times 3$ slab of panel (e); (g) z coordinates of the atoms in the relaxed model structures showing possible corrugations of the first Cu layer nearest to the Cu/AlN interface boundary plane.

(c) A stacking sequence of one single 5×5 Cu(111) and three additional 6×6 Cu(111) MLs on top of the $5 \times 5 \times 3$ AlN(000 $\bar{1}$) substrate, further denoted as AlN/Cu $5 \times 5 \times 1$, Cu $6 \times 6 \times 3$ (Fig. 3(e)). The relaxed AlN/Cu $5 \times 5 \times 1$, Cu $6 \times 6 \times 3$ slab is energetically more favorable than the AlN/Cu $6 \times 6 \times 4$ slab by 3.1 eV (i.e., 0.12 J/m^2 ; calculated using the Cu chemical potential²⁵). Noteworthy, for the relaxed AlN/Cu $5 \times 5 \times 1$, Cu $6 \times 6 \times 3$ slab, the first Cu layer adjacent to the interface boundary plane shows a higher degree of order than for the relaxed AlN/Cu $6 \times 6 \times 4$ slab (Figures 3(b), 3(e), and 3(g)).

Hence, we propose the relaxed AlN/Cu $5 \times 5 \times 1$, Cu $6 \times 6 \times 3$ slab as the preferred structural model of the incoherent Cu/AlN interface. Although energetically concurrent interface structures are possible, such more complex configurations were not calculated, as their description would include much larger periodicities and misfit dislocations. For the Ag/AlN interface, a 5×5 supercell with epitaxial overlayer was chosen (due to favorable mismatch), thus allowing a similar strain relief as for Cu/AlN. The calculations confirm that the formation of a coherent Ag/AlN interface is structurally possible, although the 7% strain connected with this interface has to be relaxed by the formation of misfit dislocations resulting in a semi-coherent interface, in accordance with the HR-TEM analysis (Fig. 2(c)). On the contrary, the formation of a (semi-)coherent Cu/AlN interface is unfavorable; the energetically favorable situation shows the presence of at least one incoherent Cu layer between AlN and bulk-spaced Cu. This DFT prediction complies well with the HR-TEM analysis of the Cu/AlN interface.

In conclusion, the confinement of 8 nm thick Ag-Cu sublayers by intercalation with AlN sublayers results in continuous, phase-separated metallic sublayers, which consist of

individual nano-sized grains Ag and Cu. The Ag phase grows on (0001) AlN along the $[111]_{\text{Ag}}/[0001]_{\text{AlN}}$ direction, thereby forming a semi-coherent interface with a low density of misfit dislocations. Conversely, the Cu phase forms an incoherent interface with the (0001) AlN sublayers, resulting in a random texture of the Cu grains. The experimental characterization of the multilayer stack and its interfaces by HR-TEM and XRD is consistent with DFT model predictions of the corresponding interface structures.

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