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Bonding at copper–alumina interfaces established by different surface treatments: a critical review

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Abstract The present study summarizes the effects of processing conditions and substrate cleaning procedures on the structure, chemistry and bonding of Cu/(0001)Al_2O_3 interfaces as determined by advanced transmission electron microscopy techniques. The Cu/(0001)Al_2O_3 samples were prepared by molecular beam epitaxy (MBE) and solid-state diffusion bonding. Investigations of the MBE samples showed that the Al_2O_3 cleaning procedure alters the interfacial bonding. Metallic bonds occurred for an Ar^+ ion sputtering and subsequent ultra-high vacuum (UHV) annealing treatment. Strongly ionic–covalent bonds were found for a wet chemical cleaning process followed by UHV annealing. The interfacial electronic structure did not reveal any significant changes compared to the bulk electronic structure for samples where the substrate surface was annealed in an oxygen-containing atmosphere after Ar^+ ion pre-sputtering and UHV annealing. The results obtained at the solid-state diffusion-bonded Cu/Al_2O_3 samples indicated that the processing parameters such as temperature and load do not change the bonding behavior. Post-annealing of the solid-state diffusion-bonded Cu/Al_2O_3 samples in a well-defined oxygen partial pressure led to the formation of $CuAlO_2$ at the interface between Cu and Al_2O_3, which improved the adhesion.

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Introduction

For more than two decades the Cu/Al_2O_3 system has been extensively studied experimentally [1–11] and theoretically [2, 10–16] as a model system to fundamentally understand interfacial adhesion between dissimilar materials. A practical reason to investigate Cu/Al_2O_3 is that it is used in microelectronic devices, where interfacial delamination is a severe reliability problem [17, 18]. A strong adhesion is required which in turn is affected e.g. by the substrate termination, the presences of interfacial reaction phases, and impurities. Thus, a fundamental knowledge of these key factors is a pre-requisite for designing and optimizing the electrical and mechanical properties of the Cu/Al_2O_3 system.

One powerful method to determine the interfacial structure between different materials is transmission electron microscopy (TEM) (see [19]). Compared to surface science investigations which are conducted on ultra-thin films deposited on substrates, TEM permits the study of buried interfaces. The atomistic structure of interfaces and possible reaction phases can be investigated by high-resolution TEM (HRTEM) or Z-contrast imaging [20, 21]. Energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS) in the TEM can be used to determine the chemical composition down to the sub-monolayer level [20, 21]. Electronic structure and bonding characteristics can be revealed by analyzing electron energy-loss near-edge structures (ELNES) in the EELS spectra [22, 23].

The present paper summarizes our ongoing research studies on Cu/Al_2O_3 interfaces [8, 9, 24–27] which were prepared by different processing techniques and investigated by various advanced TEM methods. It will be shown that the surface treatment procedure of the (0001) α-Al_2O_3 substrate prior to the deposition of Cu by molecular beam epitaxy (MBE) modifies the electronic and atomic structure of the Cu/Al_2O_3 interface. In addition, our analysis of the solid-state diffusion-bonded samples revealed changes of the interfacial microstructure due to annealing treatments.

Experimental details

Materials

Thin Cu films were deposited on (0001) oriented, single-crystalline α-Al_2O_3 substrates by MBE (base pressure $p \leq 10^{-8}$ Pa) at a substrate temperature of 200 °C and 600 °C, respectively. Prior to the deposition, the substrates were subjected to three different surface treatments in order to manipulate the (0001) α-Al_2O_3 surface structure.

In the applied substrate cleaning procedure I [24, 25, 28], the α-Al_2O_3 substrate surfaces were chemically cleaned in acetone and ethanol, and subsequently annealed for 1 h at nominally 900–1000 °C in the ultra-high vacuum (UHV) chamber to remove surface distortions caused by the polishing procedure. The surface was then sputtered for 10 min using 1 keV Ar^+ ions to remove remaining contaminants, followed by a second annealing for 2 h at nominally 900–1000 °C in UHV. The second annealing was performed to recrystallize the surface layer [29] damaged during the sputter cleaning procedure.

For procedure II all steps were identical to those of procedure I, but the sputter cleaning was performed with 200 eV Ar^+ ions and, in addition to the UHV annealing, a further annealing at nominally 800°C in an oxygen containing atmosphere with an oxygen partial pressure $P_{O_2} = 10^{-3}$ Pa was performed for 5 min [24]. On those substrates, films were only deposited at 200 °C.

Another substrate treatment (procedure III) involved the chemical cleaning of the α-Al_2O_3 substrates using tetrachlorethylene, acetone and methanol [8, 9]. After this procedure, the substrates were directly annealed for 2 h at nominally 1200 °C in the UHV chamber, without using an additional Ar^+ pre-sputtering process [8, 9].

In addition, Cu/Al_2O_3 samples were also prepared by UHV solid-state diffusion bonding of single crystalline (111) Cu to (0001) oriented α-Al_2O_3 single-crystals using two different orientation relationships (OR I and OR II, see below) [24, 30, 31]. The α-Al_2O_3 single-crystals were subjected to cleaning procedure I prior to the joining procedure. The Cu/Al_2O_3 sample possessing OR I was bonded at a nominal temperature of 950 °C for 60 hours. Only during the first 20 hours a load of 1.8 MPa was applied [24, 31]. For the Cu/Al_2O_3 joint having OR II, the bonding was performed at nominally 1000 °C using a load of 4.8 MPa and a diffusion bonding time of 8 h [30]. Some of these latter samples were then annealed at 1000°C for 96 hours in an oxygen partial pressure $P_{O_2} = 0.02$ Pa [30].

Characterisation

The microstructure of the different Cu/Al_2O_3 samples was studied in detail by conventional TEM and by HRTEM. Conventional TEM was performed on a JEOL 2000 FX operated at 200 kV, while for HRTEM investigations a JEOL JEM ARM1250 microscope (1250 kV, point resolution 0.12 nm) was used. Analytical TEM was conducted on a dedicated scanning TEM (STEM) (VG HB 501 UX) operated at 100 kV. The STEM is equipped with an ultra-thin window Si(Li) energy-dispersive X-ray spectrometer (EDS) capable of light element detection and with a parallel EELS system (first a Gatan DigiPEELS 766, and later a Gatan UHV Enfina system). The experimental ELNES data shown were taken with one or the other of these spectrometers. The VG HB 501 UX STEM has a beam diameter of less than 1 nm, enabling analytical measurements with high spatial resolution. For the TEM investigations, cross-sectional TEM samples were prepared following the technique described in [32].

The crystallographic structure of the reaction phase, which formed in the solid-state diffusion bonded samples after annealing in an oxygen partial pressure of 0.02 Pa, was additionally investigated by X-ray diffraction (XRD). The measurements were conducted on fractured samples in a conventional Siemens D5000 powder diffractometer. In addition, the morphology of the reaction phase was studied by scanning electron microscopy (SEM) using a Zeiss DSM 982 Gemini.

Results and discussion

Influence of the Al_2O_3 surface treatment on the interfacial structure

In general, different surface terminations of the (0001) α-Al_2O_3 substrate can occur depending on the cleaning routine and conditions, and thus affect the atomic structure and bonding behavior at the interface. The three possible bulk surface terminations are: the stoichiometric, aluminium termination (one aluminium layer), the aluminium-rich termination (two layers of aluminium) and the oxygen termination [38]. In the following, the influence of the Al_2O_3 surface treatment on the interfacial structure of as-deposited epitaxial Cu films will be described in detail. The paragraph will also include observations on the atomic and electronic structure of solid-state diffusion bonded samples.

The as-deposited MBE films possessed a hetero-epitaxial orientation relationship (OR I) to the Al_2O_3 substrates with the close-packed planes and directions parallel to each other: $(111)_{Cu}\langle 110\rangle_{CU} \parallel (0001)_{Al_2O_3}\langle 10\bar{1}0\rangle_{Al_2O_3}$ [7, 9, 24, 28]. The degree of epitaxy, i.e. the regions/islands of the film having OR I, was higher for a growth temperature of 600 °C than for 200 °C if the substrate surface was pre-sputter cleaned using 1 keV Ar^+ ions (procedure I) [28], while the opposite is true for the samples where the substrate was only subjected to a wet chemical cleaning (procedure III) [7, 9].

The Cu films grown at 200° C on α-Al_2O_3 substrates, pre-sputter cleaned with 1 keV Ar^+ ions (procedure I) or with 200 eV Ar^+ ions and oxygen annealed (procedure II) revealed in addition to OR I a second orientation relationship which is rotated by 30°: $(111)_{Cu}\langle 110\rangle_{CU} \parallel (0001)_{Al_2O_3}\langle 2\bar{1}\bar{1}0\rangle_{Al_2O_3}$ (OR II) [24]. However, only a few grains ($<5\%$) showed this second orientation relationship.

For orientation relationship I the lattice mismatch $\delta_{ORI} = (d_{30\bar{3}0} - d_{220})/d_{30\bar{3}0} = +0.070$ assuming rigid lattices with lattice plane spacing of $d_{30\bar{3}0} = 0.137$ nm for α-Al_2O_3 and d_{220} = 0.128 nm for Cu. No localized misfit dislocations, which could accommodate this large lattice misfit, were detected by the HRTEM investigations [7, 9, 24–26]. All of the MBE samples showed atomically abrupt, incoherent interfaces and no distinct interfacial phase was observed in the lattice images [7, 9, 24–26]. In Fig. 1 an HRTEM micrograph of the Cu film deposited at 200 °C on an α-Al_2O_3 substrate, which had been subjected to procedure III, is displayed as an example [7, 9]. Lattice images taken at solid-state diffusion-bonded samples possessing OR I, with the α-Al_2O_3 substrates cleaned according to procedure I, showed similar characteristics at the interface region as the as-deposited MBE samples [24].

A HRTEM image of the solid-state diffusion bonded joint where the crystals (cleaning procedure I) were aligned to OR II in respect to each other is given in Fig. 2. For this orientation relationship the lattice mismatch $\delta_{ORII} = (d_{2\bar{1}\bar{1}0} - d_{110})/d_{2\bar{1}\bar{1}0} = -0.074$, with $d_{2\bar{1}\bar{1}0} = 0.238$ nm for α-Al_2O_3 and d_{110} = 0.256 nm for Cu. There are some indications that the interface is semicoherent [33], but further analyses of the lattice images are necessary to clarify this point. Nevertheless, no reaction layer was found and the interface is abrupt (Fig. 2).

The interfacial bonding of the different samples was studied experimentally by ELNES investigations [8, 9, 24–26]. Thereby, the spatial difference method [34, 35] was applied to determine the interface-specific ELNES components. The Cu-$L_{2,3}$-ELNES was found to change significantly when differences in the interfacial bonding occur [8, 9, 24–26] and this will be described and discussed in the following. A detailed description of the

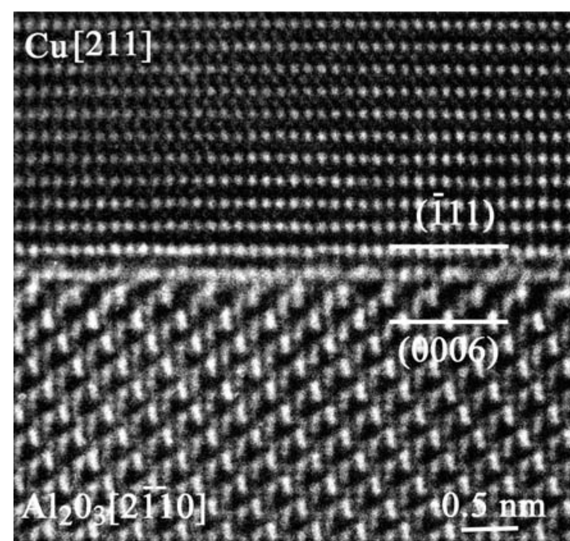

Fig. 1 HRTEM micrograph of the Cu film deposited on a wet chemically cleaned Al_2O_3 substrate [9]. The interface is devoid of any reaction phase due to the applied growth conditions

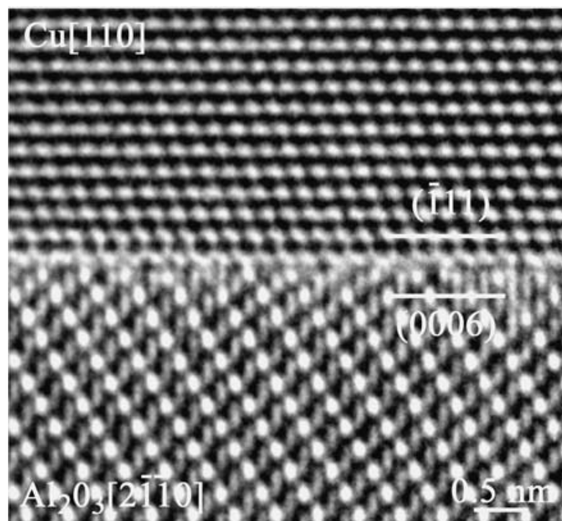

Fig. 2 Lattice image of the Cu/Al_2O_3 sample possessing OR II which was prepared by solid-state diffusion-bonding. The image is taken in $\langle 2\bar{1}\bar{1}0\rangle_{Al_2O_3}$ zone axis

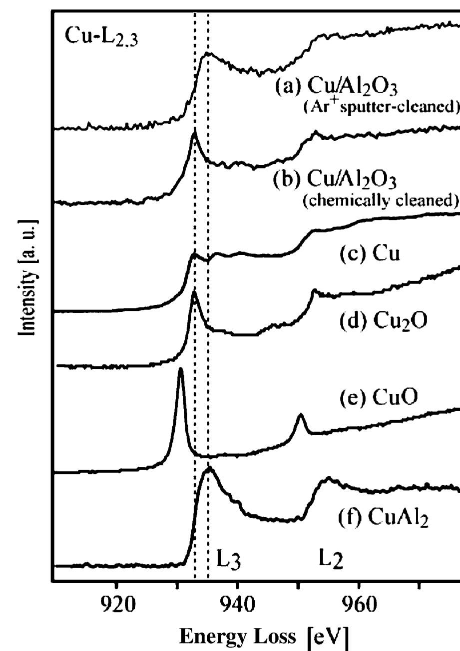

Fig. 3 Cu-$L_{2,3}$-ELNES of epitaxial Cu films grown by MBE on (**a**) 1 keV Ar^+ pre-sputter cleaned Al_2O_3 (procedure I) and (**b**) wet chemically cleaned Al_2O_3 (procedure III). For comparison the Cu-$L_{2,3}$-ELNES of bulk (**c**) Cu, (**d**) Cu_2O, (**e**) CuO, and (**f**) $CuAl_2$ are included. Taken from [26]

changes occurring at the other relevant ionization edges, i.e. Al-$L_{2,3}$ and O-K-edge, can be found in [8, 25, 26].

As examples, the Cu-$L_{2,3}$-edges of the MBE films possessing a high epitaxial quality i.e. deposited at 600 °C on 1 keV Ar^+ pre-sputter cleaned substrates (procedure I) [25, 26] and grown at 200 °C on substrates treated by a wet chemical cleaning (procedure III) [8, 9, 26] are displayed in Fig. 3. In addition, the Cu-$L_{2,3}$-edges of bulk Cu, Cu_2O, CuO and $CuAl_2$ are also shown in the figure. As can be seen, the Cu-$L_{2,3}$-ELNES features of the MBE sample, where the substrate was subjected to 1 keV Ar^+ pre-sputter cleaning, are similar to those observed in an intermetallic $CuAl_2$ compound (Fig. 3a and f). The edge onset of both spectra is shifted by 1.8 ± 0.3 eV to higher energy losses compared to bulk Cu (Fig. 3c). Different Cu-$L_{2,3}$-ELNES features were found for the specimen, where a wet chemical substrate cleaning was used (Fig. 3b). The shape and edge onset of the white-line is similar to the one measured in bulk Cu_2O (Fig. 3d) [8, 9, 26]. It should be noted that the similarity between the interfacial ELNES to the bulk $CuAl_2$ and Cu_2O, respectively, does not imply the formation of a reaction phase but indicates that a similar electronic structure exists at the interface.

For the MBE sample where the substrates were cleaned according to procedure II, no interface specific Cu-$L_{2,3}$-ELNES was detected indicating that the Cu atoms at the interface are in the metallic state [24]. For Cu films grown at 200 °C on substrates subjected to procedure I, we observed in a few areas also a vanishing Cu-$L_{2,3}$-ELNES most likely related to surface inhomogenities caused by the sputtering process [24].

The investigations of the solid-state diffusion-bonded samples (all substrates were treated using 1 keV Ar^+ ions and annealed in UHV) revealed, independent on the orientation, a similar Cu-$L_{2,3}$-ELNES as shown in Fig. 3a [24, 33]. I.e. a metallic Cu–Al bonding characteristic was established at the interface similar to the one found for the MBE samples where an Ar^+ pre-sputtering process had been used to clean the α-Al_2O_3 substrates.

In summary, the ELNES studies of the different Cu/(0001)Al_2O_3 samples indicated that the Al_2O_3 surface treatment plays an important role for the interfacial bonding. In the presented data, the differences of the processing routes, i.e. MBE and solid-state diffusion bonding, were not found to affect the interfacial bonding. In the following, the results will be explained and discussed with respect to the literature.

At the interface between Cu films and Al_2O_3 substrates, which had been subjected to 1 keV Ar^+ sputtering (procedure I), metallic Cu–Al bonds occurred [24–26]. More than 30 years ago several research groups had discovered that Ar^+ sputtering can lead to an oxygen loss and thus to the formation of an Al rich Al_2O_3 surface [36, 37]. A theoretical study performed by Batyrev et al. [38] revealed that an Al rich surface might be stable at very low oxygen partial pressures and that it possesses a metallic character. Considering these results, it can be assumed that procedure I leads

to an Al rich surface with Al atoms in the metallic state, which explains the metallic Cu–Al bonds found by the ELNES experiments [24–26]. This idea is also supported by calculations from Zhang and co-workers [16]. They predicted that a double Al termination at the Cu/(0001)Al_2O_3 interface can be energetically stable at very low oxygen partial pressures and that this interface configuration can result in metallic bonding contributions [16]. The results obtained at the solid-state diffusion-bonded samples possessing OR I and OR II [24, 33] can be explained following the same arguments as for the MBE samples since the Ar^+ pre-sputter cleaning and subsequent substrate annealing (procedure I) was also applied. It should be mentioned, that the interfacial O-K edge observed in the samples, where the Al_2O_3 had been treated using 1 keV Ar^+ sputtering, were explained in an earlier paper [26] by multiple scattering calculations using a single Al terminated model. It is most likely, that the agreement between the experimental and calculated O-K edge would be improved for a double Al terminated Cu/Al_2O_3 interface configuration. However, these calculations have not yet been performed.

The Cu-$L_{2,3}$-ELNES investigations performed at Cu/Al_2O_3 interfaces, where the substrates had been pre-sputter cleaned with 200 eV Ar^+ ions and annealed in an oxygen containing atmosphere (procedure II), revealed no pronounced modifications of the interfacial electronic structure compared to the bulk and the Cu atoms were staying in the metallic state [24]. Recent experiments and calculations have shown that the adhesion between Cu and stoichiometric, single Al-terminated Al_2O_3 is weak and that the Cu atoms remain metallic [10, 11, 14]. Thus, we can explain our experimental finding if we assume that the Al rich surface caused by the sputtering process is transformed into a stoichiometric surface configuration (single Al termination) by the subsequent substrate annealing in the oxygen containing atmosphere. This assumption seems reasonable if we consider calculations of Batyrev et al. [38] who predicted this scenario.

The ELNES results obtained at Cu/Al_2O_3 samples, where the Al_2O_3 substrates were treated only by a wet chemical cleaning (procedure III) and then annealed at 1200° C, indicated the formation of ionic-covalent Cu–O bonds with Cu in a nominal Cu^{+1} state and the non-participation of the Al atoms in the interfacial bonding [8, 9, 26]. This implies an oxygen terminated or hydroxylated Al_2O_3 surface prior to the Cu deposition. The latter surface is energetically favored in the presences of water compared to a single Al termination [39]. The OH-groups, which in our case might stem from the wet chemical cleaning procedure, can be stable even at high temperatures applied during subsequent annealing treatments [39–42]. As has been shown in recent research studies, the OH-groups dissolve during the growth of copper facilitating the formation of Cu–O bonds at the Cu/(0001)Al_2O_3 interface with Cu in a nominal Cu^{+1} state [10, 11, 15]. Taking into account these experimental and theoretical findings, it is most likely that the wet chemical cleaning procedure used in our experiments resulted in a stable hydroxylated Al_2O_3 surface causing the formation of Cu–O bonds [8, 9, 26].

Recently, we succeeded to prepare a hydrogen free O termination by using a high temperature (750 °C) oxygen plasma treatment (all other procedures are the same as for procedure II) and a post annealing at 500 °C [43]. It is important to note, that these films were polycrystalline after room temperature deposition and that they rearranged to OR II after the post annealing treatment [43]. The samples did not show a uniform interface configuration, but instead atomically abrupt areas as well as region possessing an interfacial γ-Al_2O_3 phase [43]. Pronounced Cu–O bonds were found at these Cu/Al_2O_3 interfaces [43]. An ab-initio study initiated by our experimental findings was performed by Hashibon and co-workers [44] to explain the formation of OR II. They found that although OR I and OR II possess different interface structures, the work of separation and the local atomistic structures are similar [44]. Recently, Dehm et al. managed to prepare epitaxial Cu films on α-Al_2O_3 substrates possessing OR II by magnetron sputtering [45]. They pointed out that the mobility of the Cu ad-atoms and the growth/annealing temperature might be important for the formation of OR II [45]. Additionally it is interesting to note that Cu (111) pole figure measurements reveal a full width of half-maximum of up to 11° for the in-plane alignment between Cu and Al_2O_3 for OR II, while only 1° is observed for OR I [43, 45].

For the post-annealing experiments in $P_{O_2} = 0.02$ Pa described below, solid-state diffusion bonded samples possessing OR II were used. This is caused by the experimental observation, that solid-state diffusion bonded samples having OR I are more difficult to prepare and easily broke in comparison to those with OR II [46]. It seems that OR I is extremely sensitive to an exact alignment of the two crystals involved and only after improving the accuracy of the crystal alignment in the UHV bonding apparatus [31], we succeeded to prepare solid-state diffusion bonded samples having OR I [24, 31].

Taking these findings into account, we suggest that the interfacial energy function versus in-plane orientation possesses a minimum at OR I and OR II, however, the minimum is narrow for OR I, while it is broad for OR II.

Influence of a reaction layer on the interfacial structure

The formation of a reaction layer was studied at solid-state diffusion bonded Cu/Al_2O_3 samples (OR II, the initial interface structure is shown in Fig. 2) post-annealed at 1000 °C in various oxygen partial pressures [27, 30]. In the following only the results obtained at samples which were annealed in a low oxygen partial pressure of $P_{O_2} = 0.02$ Pa will be described. The effect on the evolving microstructure by using a higher oxygen partial pressure can be found in [27, 30].

After the post-annealing, some of the samples were fractured and the corresponding surfaces were analyzed by X-ray diffraction and in a SEM [27, 30]. The investigations revealed the formation of a $CuAlO_2$ layer possessing a rhombohedral structure. It was found that the layer is not continuous but interrupted by many pores which are most likely caused by an agglomeration of vacancies within the Cu and a result of the non-wetting behavior of Cu on Al_2O_3. The vacancy flux is supported by diffusion of H_2 and O_2 (which are present in the reaction atmosphere) through the Cu at 1000 °C [27, 30].

TEM investigations confirmed the presence of a $CuAlO_2$ reaction layer at the interface between Cu and Al_2O_3 [27, 30]. Fig. 4 shows a conventional TEM micrograph and a selected area diffraction pattern of the $CuAlO_2/Al_2O_3$ interface region. The reaction layer has a thickness of about 20 nm and possesses a $(0001)_{CuAlO_2}\langle 10\bar{1}0\rangle_{CuAlO_2} \parallel (0001)_{Al_2O_3}\langle 2\bar{1}\bar{1}0\rangle_{Al_2O_3}$ orientation relationship to the Al_2O_3 crystal [27, 30]. HRTEM studies revealed that the in-plane orientation was slightly off. A lattice image taken in $\langle 2\bar{1}\bar{1}0\rangle_{Al_2O_3}$ zone axis is presented in Fig. 5. No grain boundaries or other planar defects were found by conventional TEM and HRTEM within the reaction layer [27, 30].

TEM images of interfacial pores, which were found in the annealed and also in the as-bonded samples, were used to measure the solid state contact angle in order to estimate the effect of the interfacial $CuAlO_2$ layer on the adhesion [27, 30]. Although the absolute values are affected by the projection of the pores in the TEM micrographs, we were able to estimate that the work of adhesion is increased by a factor of two for the annealed sample in comparison to the as-bonded sample ignoring possible contributions from torque terms [27, 30]. This is in accordance with results reported in literature, where the work of adhesion of liquid copper in contact with Al_2O_3 was determined from sessile drop experiments [47–49].

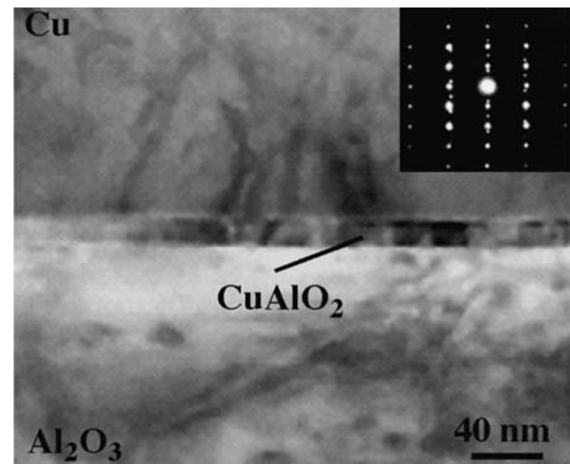

Fig. 4 Conventional TEM bright-field image of a solid-state diffusion-bonded $Cu/(0001)Al_2O_3$ sample annealed at 1000 °C in an oxygen partial pressure of 0.02 Pa revealing a thin $CuAlO_2$ layer between Cu and Al_2O_3 [27]. The inset shows the SAD pattern of the $Al_2O_3/CuAlO_2$ interface in $\langle 10\bar{1}0\rangle_{Al_2O_3}$ and $\langle 2\bar{1}\bar{1}0\rangle_{CuAlO_2}$, respectively

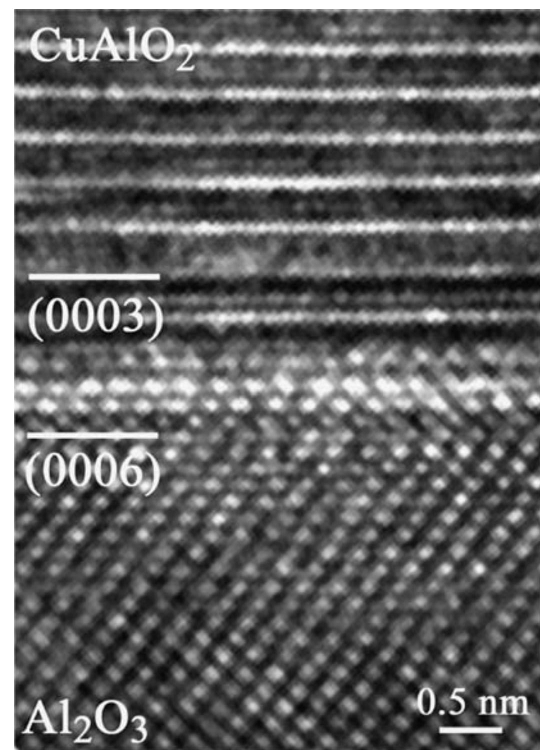

Fig. 5 Lattice image of the $CuAlO_2/Al_2O_3$ interface occurring after annealing at 1000 °C in an oxygen partial pressure of 0.02 Pa [27]. The HRTEM micrograph was taken in $\langle 2\bar{1}\bar{1}0\rangle_{Al_2O_3}$ zone axis

It should be noted, that the formation of the $CuAlO_2$ reaction phase is in accordance to the equilibrium phase diagram for the Cu–Al–O system at 1000 °C [50, 51] and agrees well to other experimental studies reported in literature [3, 4, 52, 53]. Most of these earlier investigations were conducted on eutectic-bonded samples where a liquid Cu_2O layer on a pre-oxidised Cu surface was bonded to an Al_2O_3 crystal. Since the molten layer contained a high amount of oxygen, reaction phases could easily form. Depending on the experimental conditions, the ternary aluminates $CuAlO_2$ and $CuAl_2O_4$ or the binary oxides Cu_2O and CuO were found [3, 4, 52, 53], all of them being possible phases in the Cu–Al–O system [50, 51].

Summary and Conclusions

The interface structure between Cu and α-Al_2O_3 can be modified by surface treatments of the α-Al_2O_3 substrate and by the formation of an interfacial reaction phase. For specimen prepared by MBE a difference in the interfacial atomistic arrangement and in the bonding mechanism was found depending on the cleaning procedure of the Al_2O_3. For Cu films deposited on Ar^+ ion pre-sputter cleaned and UHV annealed substrates the presence of metallic Cu–Al bonds at the Cu/Al_2O_3 interface were observed. In contrast, the interfacial electronic structure did not show any pronounced modifications compared to the bulk electronic structure in the sample where the substrate was additionally annealed in oxygen after the pre-sputtering and UHV annealing. Cu films grown on α-Al_2O_3 substrates, subjected only to a wet chemical cleaning procedure and subsequent UHV annealing, revealed Cu–O bonds at the interface. The modification of the $Cu/(0001)Al_2O_3$ interface configuration was further studied by post-annealing solid-state diffusion-bonded samples. It was shown that the microstructure of $Cu/(0001)Al_2O_3$ interfaces is changed during the post-heating treatment due to the formation of a thin $CuAlO_2$ layer between Cu and Al_2O_3.

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