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Formation of α -approximant and quasicrystalline Al-Cu-Fe thin films

Simon Olsson,* Fredrik Eriksson, Jens Birch, and Lars Hultman

Thin Film Physics Division, Department of Physics (IFM), Linköping University, SE-581 83 Linköping, Sweden

*E-mail: simol@ifm.liu.se

Abstract. Multilayered Al/Cu/Fe thin films have been deposited by magnetron sputtering onto Si and Al₂O₃ substrates with a nominal global composition corresponding to the quasicrystalline phase, 5:2:1. Subsequent annealing was performed on samples up to 710 °C. It is found that when using Si as substrate a film-substrate reaction occurs already below 390 °C, where Si diffuses into the film. This changes the composition, promoting the formation of the α -approximant Al₅₅Si₇Cu_{25.5}Fe_{12.5} in the temperature range 400 to 650 °C over the quasicrystalline ψ -phase. When annealing the same Al-Cu-Fe thin film grown on Al₂O₃ substrates the Al_{62.5}Cu₂₅Fe_{12.5} icosahedral quasicrystalline phase is formed.

Keywords: Quasicrystal, Approximant, Al-Cu-Fe, Al-Cu-Fe-Si, X-ray diffraction, Annealing, Phase evolution, Multilayer

1. Introduction

Quasicrystals are well ordered intermetallic structures without periodicity that exhibit rotational symmetries not present in regular crystals [1]. Due to this aperiodicity, these materials, despite

being metallic alloys, exhibit high hardness, wear resistance, and low electrical and thermal conductivity. In addition, attractive surface properties like low coefficient of friction have been reported [2]. This combination of properties may be utilized in a variety of tribological applications. Because quasicrystals are brittle in bulk, most proposed applications employ thin films [2,3].

Quasicrystalline thin films are often formed using high temperatures either during or after deposition of the film which often, initially, have either an amorphous or multilayered structure. Annealing temperatures above 600 °C is not uncommon. Such high temperatures limit the useable substrate materials to be deposited due to undesired effects, e.g., film cracking, caused by differences in thermal expansion or chemical reactions between the film and substrate. One major difficulty for application of quasicrystals is the limited thermodynamical stability. Few elemental systems containing a quasicrystalline state have a thermodynamically stable quasicrystal, seldom yet stable at room temperature. They also form in a very narrow compositional range, requiring accurate control of the chemical composition to prepare a single-phase material.

Related to the quasicrystals are phases called approximants [2], which are periodic, but locally structurally similar to the quasicrystals. This is reflected in their properties, which resemble those of quasicrystals, although less pronounced due to the deviation from the aperiodic state [4]. The approximants are, however, more commonly found as stable phases and also often found over larger compositional ranges, thus facilitating their use in applications [2].

The first stable quasicrystal was found in the Al-Cu-Fe system at a composition close to $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ [5]. From studies of multilayered Al/Cu/Fe thin films [6,7] it was shown that binary Al-Cu phases, such as $\theta\text{-Al}_2\text{Cu}$, $\eta\text{-AlCu}$, and $\gamma\text{-Al}_4\text{Cu}_9$, form initially whereafter Fe is incorporated into the $\omega\text{-Al}_7\text{Cu}_2\text{Fe}$, $\lambda\text{-Al}_{13}\text{Fe}_4$, $\beta\text{-Al}_{50}(\text{CuFe})_{50}$, and the icosahedral

quasicrystalline ψ -Al_{62.5}Cu₂₅Fe_{12.5} phases. There are several related approximants to this quasicrystal, among them the cubic α -Al₅₅Si₇Cu_{25.5}Fe_{12.5}, where a low amount of Al has been substituted for Si [8]. It has been shown in bulk that the ψ -phase can not co-exist with the approximant α -phase, as the substitution destabilizes the ψ -phase [8]. The approximant α -phase in this system has previously not been synthesized as a thin film.

In this work, α -Al₅₅Si₇Cu_{25.5}Fe_{12.5} thin films have been fabricated by solid state diffusion of multilayered Al/Cu/Fe films on Si substrates. To determine the phase formation, isothermal annealing experiments were performed in a high-temperature X-ray diffraction furnace on multilayer structures of different layer thicknesses and periodicities. In addition it is shown, for an identical film, that the quasicrystalline phase is formed when a diffusion-resistant Al₂O₃ substrate is used.

2. Experimental Details

Multilayered Al/Cu/Fe thin films were sequentially deposited in a triple cathode, high vacuum, DC magnetron sputtering system onto both Si(001) and Al₂O₃(0001) substrates. The size of the chamber was 500 mm in diameter and 350 mm in height with a background pressure of approximately 4×10^{-5} Pa (3×10^{-7} Torr). Depositions were made at ambient temperatures (up to 50 °C due to plasma heating). The substrate table was rotating with 60 rpm and kept electrically isolated enabling an external bias voltage of -30 V to be applied in order to attract ions from the plasma. The three sputtering targets, Al (99.99% purity, 50 mm diameter), Cu (99.95%, ϕ 75 mm), and Fe (99.95%, ϕ 75 mm), were placed 125 mm above the substrate table, tilted with the substrate in direct line-of-sight. Ar (99.999%) at a pressure of 0.4 Pa (3 mTorr) was used as the sputtering gas. The magnetron discharges were established with current-regulated power

supplies giving currents (voltages) of 50 mA (440 V) for Al, 40 mA (270 V) for Cu, and 100 mA (320 V) for Fe. This yielded deposition rates of ~ 0.6 nm/s for all three elements, as determined by X-ray reflectivity thickness measurements of single-layer films. The magnetrons were running continuously during deposition and the material fluxes were controlled by manually-operated shutters placed in front of the magnetrons.

Elemental layers of Al, Cu, and Fe were sequentially deposited on top of each other to form a multilayered stack. The multilayered Al/Cu/Fe thin films were produced with multilayer period thicknesses ranging from $\Lambda=2$ nm to $\Lambda=400$ nm, and nominal layer thicknesses ratios of Al:Cu:Fe equal to 7:2:1 to maintain a global chemical composition ratio of 5:2:1 corresponding to the ideal quasicrystalline phase. The number of periods was varied from $N=1$ to $N=50$, with total film thicknesses between 100 and 400 nm. Al was deposited as a top layer in all samples to prevent oxidation other than the approximately 2 nm natural, passive surface oxide.

Isothermal heat treatments and in-situ X-ray diffraction (XRD) were performed on all samples using a Philips X'Pert MPD Bragg-Brentano, θ - θ diffractometer with Cu- K_α X-rays, equipped with a Bühler HDK 2.4 high-temperature high-vacuum chamber with a Be window. The temperature was increased in steps of 20 °C or 100 °C, and kept for a minimum of 3 h up to 72 h at each temperature from ambient up to 710 °C. The pressure of the annealing chamber was 3×10^{-3} Pa (2×10^{-5} Torr). XRD, θ -2 θ measurements, was continuously recorded in a 2θ -range of 6-49°. A collecting time of 5 s was used at each 2θ step increment of 0.02° for all measurements. Several scans were made at each temperature to ensure phase stability. Since the X-ray footprint was slightly larger than the samples, diffraction peaks corresponding to the Ta heating filament were also detected and appear in the measured scans.

Additional heat treatments of the films grown on Si substrates were performed in a Heraeus quartz tube furnace 4/25 using a constantly flowing Argon atmosphere. The temperature was

kept at 600 °C for 4 h. These samples were analyzed before and after annealing using a Philips PW1710 powder diffractometer using the same instrumental settings as above.

The relative metallic compositions were determined before and after the heat treatments using energy dispersive X-ray spectroscopy (EDX) analysis in a LEO Gemini 1550 FEG scanning electron microscope (SEM), equipped with an Oxford LINK ISIS system with a Ge detector. The instrument was operated at 20 kV accelerating voltage and a 60 s effective acquisition time was used. A Co standard was used for quantitative calibration using the INCA software. The sum of Al, Cu, and Fe was normalized to 1. By scanning the surface with the electron beam a compositional map of the surface could be obtained. For EDX mapping, an acceleration voltage of 20 kV and a 500 s acquisition time was used. Topographical plan-view images were obtained by secondary electron imaging in the same instrument operated at 5 kV.

To quantify the amount of Si in the films EDX composition analysis is not possible due to the signal from the underlying Si substrate. Instead, the Si content of selected samples was investigated using ToF-Elastic Recoil Detection Analysis (ToF-ERDA). A 34 MeV $^{127}\text{I}^{8+}$ primary beam having an incident angle of 67.5° relative to the surface normal was used, and the energy detector was placed at a recoil scattering angle of 45°. The measured recoil ToF-ERDA spectra were analyzed using the CONTES code, where the measured recoil energy spectrum of each element was converted to relative atomic concentration profiles.

3. Results and Discussion

The structure of the investigated as-deposited samples are summarized in Table 1, showing the layer sequence, total thickness, and measured normalized composition. The samples are categorized into two groups; Al-deficient (A) and Al-rich (B), based on their amount of Al as compared to the ideal icosahedral ψ -phase composition. The investigated samples, and the

regions of the quasicrystalline ψ -phase and the approximant α -phase [9,10], are shown in the ternary phase diagram in Figure 1.

Figure 1. Ternary compositional phase diagram of the Al-Cu-Fe system [9,10] showing regions of pure phases and global compositions of the as-deposited Al-Cu-Fe thin films as determined by EDX in groups A and B presented in Table 1.

3.1 Phase evolution of Al-Cu-Fe thin films on Al_2O_3

The evolution towards the quasicrystalline $\psi\text{-Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ phase is known in both bulk [11,12] and thin film samples [7]. However, in order to clearly illustrate the differences in using a Si substrate (section 3.3) compared to a Al_2O_3 substrate, sample A_1 was simultaneously deposited on both Si and Al_2O_3 substrates and annealed using the same procedure. A selection of diffractograms during annealing of sample A_1 on Al_2O_3 is shown in Figure 2, and measurements of the as-deposited sample showed diffraction peaks only corresponding to Al(111), Cu(111), and Fe(110), i.e. only from the elemental constituents, and the substrate in the measured range. Thus, no reactions between the layers had occurred during the deposition.

Figure 2. Selection of XRD measurements of sample A₁ on Al₂O₃ substrate at temperatures ranging from room temperature to 710 °C.

At temperatures up to 290 °C the Cu has reacted with the Al to form binary Al-Cu phases, first θ -Al₂Cu and γ -Al₄Cu₉, whereafter the γ -phase is replaced by η -AlCu. At 390 °C only the η -phase remain while some formation of the ternary ω -Al₇Cu₂Fe phase occurred by mixing with the Fe layer, which at 480 °C becomes dominant.

At 570 °C the icosahedral ψ -phase appears along with the ω -phase. All diffraction peaks corresponding to the ψ -phase can be indexed by a set of icosahedral indices according to Cahn [13]. These phases remain at 650 °C while at 710 °C the ω -phase disappears and the icosahedral diffraction peaks become larger and sharper, signifying an increased grain size and improved structural quality of the icosahedral phase. The quasilattice parameter determined from the positions of the diffraction peaks is 0.6395 nm, and the valence electron concentration is calculated using Pauling's phenomenological theory to be 1.73 e/a (electron-to-atom ratio).

Thus, both entities indicate that the present icosahedral phase is of the Mackay-type, like most of the Al-based transition metal icosahedral quasicrystals.

At this temperature, also a small amount of β -Al₅₀(CuFe)₅₀ phase is detected. This can be correlated to the composition of sample A₁ being just outside the triangle of pure icosahedral phase (Figure 1), in the region where the β - and ψ -phases coexist. The sample was left at 650 °C for 3 days after which the icosahedral phase entirely disappeared in favor of the β -phase. This is likely caused by Al evaporation, mentioned in other works [7,14], driving the composition towards the single β -phase. This is all in agreement with earlier works [7].

3.2 Isothermal annealing of Al/Cu/Fe multilayers on Si

All samples grown on Si were identically annealed in a tube furnace at 600 °C for 4 h, a temperature sufficient to form the quasicrystalline phase. X-ray diffraction after annealing is shown in Figure 3 (a) for Al-deficient and in (b) for Al-rich compositions. All peaks could be assigned to known phases [7,8,9,15].

It can be seen that the Si-containing quaternary approximant α -AlSiCuFe phase is the dominating phase in almost all samples, i.e. irrespective of the initial layer thicknesses, layer sequence or deviations in composition. It is clear that during the annealing Si diffuses from the substrate into the film where it reacts with the elemental layers. From investigations of bulk samples it is known that Si addition of up to 3 at.% gradually decreases the volume fraction of the quasicrystalline phase [16], and completely prevents formation above 3 at.% [17]. The region of stable approximant phase in bulk is 5-15 at.% Si, while the best quality single-phase approximant is reported for 9 at.% Si [17].

Figure 3. XRD measurements of (a) Al-deficient and (b) Al-rich samples annealed at 600 °C for 4 h.

Even though several diffraction peaks (≥ 7) belonging to the α -phase are visible in the measured angular range, theoretically, as many as 37 peaks should have been present (although many with low theoretical intensities). Based on the Miller indices it can not be concluded that a preferential orientation of the film has developed during annealing, and thus the α -phase can be considered to be polycrystalline. The missing diffraction peaks are rather the result of too small crystallites/diffracting volumes for total film thicknesses < 400 nm, giving diffracted intensities not discernible from the background intensity. It should be clarified that the truncated diffraction peaks labeled Si 002 at diffraction angles $2\theta \sim 33^\circ$ originate solely from multiple scattering from lattice planes in the 001-oriented Si substrate, and is a dynamic effect which is apparent only in perfect crystals, which would not be the case for Si in the film.

ToF-ERDA identified an average Si concentration of 9 at.% in the films annealed at 600 °C for 4 h, and that the ratio of Al, Cu, and Fe is preserved to the as-deposited state. The calculated magnitude and direction of the shift in composition after introduction of 9 at.% Si is shown by

the arrow in Figure 1. It can be seen that the Al-deficient samples move closer to the region of pure α -phase, while the Al-rich samples move away from this region.

Al-deficient samples

In the Al-deficient samples, Figure 2 (a), the α -phase is clearly the dominating phase, irrespective of the layer sequence. This is because the composition, after introduction of Si, is very close to that of the ideal α -phase. There are however traces of the Al-Fe-Si τ -phases; hexagonal τ_5 ($\text{Al}_{7.4}\text{Fe}_2\text{Si}$) and monoclinic τ_7 ($\text{Al}_3\text{Fe}_2\text{Si}_3$) [15].

The τ_5 -phase, as shown in Section 3.3, forms during the initial diffusion of Si into the film, and might have been preserved due to the limited time of annealing and relatively high formation enthalpy of -25 kJ/mol [18]. The amount of τ_7 -phase is seen to increase slowly during extended annealing at 600 °C.

In addition, a single diffraction peak, probably related to the FeSi_2 -phase, is observed only in the single period film (A_1), and may have been due to a strong reaction between the relatively thick Fe-layer towards the Si-substrate in this sample. This phase is not observed during the longer sequential annealing of sample A_1 (section 3.3).

Al-rich samples

When Si is diffusing into the Al-rich structures, the average composition of the samples is moving further away from the region where the pure α -phase can formed (Figure 1). In the measurements of the Al-rich samples in Figure 2 (b) diffraction peaks corresponding to the crystalline phase ω - $\text{Al}_7\text{Cu}_2\text{Fe}$ appears in addition to the α -phase peaks as a major phase. The

presence of the ω -phase can be correlated to the excess of Al, since all Al can not be included into the α -phase and thus the ω -phase, which contains more Al, has to remain to maintain the balance. According to the phase diagram [10] the Al-rich samples, after inclusion of Si, are in a region of α and ω -phase at 650 °C. Thus, these samples are expected to have the ω -phase present at 600 °C.

It is worth noting that samples B₂ and B₃ have diffraction peaks only belonging to the approximant α -phase, indicating a single-phase material. To reveal whether the films have any minority phases or amorphous content below the detection limit of X-ray diffraction, electron microscopy studies were performed. From these it was observed that traces of Al-Fe-Si phases are present in the same way as in Al-deficient samples presented below even if they could not be resolved by XRD.

Overall, the α -phase is the dominant phase in all samples, indicating a reaction between the film and the substrate where Si has diffused into the film irrespective of the layer thicknesses, layer sequence or deviations in compositions. Further, there is no indication of any icosahedral ψ -phase, meaning that the amount of Si in the films is sufficient to completely prevent the quasicrystal formation in favor of the approximant α -phase.

For all thicknesses, the peak intensity of the α -phase is strongest for the samples with 10 periods of stacking, signifying a higher quality. This indicates a more suitable condition for homogenization of the sample during the annealing as Si diffuses into the film. The lattice parameter of the α -phase at room temperature was found to be in the range 1.225 nm to 1.229 nm for all samples (lowest values for Al-deficient samples), as tabulated in Table 1. This is slightly shorter than the 1.231 nm to 1.240 nm reported for bulk samples, see e.g. [8,10,16,19]. Since the lattice parameter of the α -phase depends on the amount of substitutional Si diffusion into the film (more Si, smaller lattice parameter), this could indicate a higher Si content than the

investigated bulk samples. In addition, the ratio of Al:Cu:Fe is not the same as in the references, and the samples are not a single-phase material, which may explain the deviation.

3.3 Phase evolution of Al-Cu-Fe thin films on Si

To investigate the phase evolution of the multilayered films on Si, as a mean to understand the formation of the approximant phase instead of the expected icosahedral ψ -phase, sample A₁ was annealed in steps of increasing temperature and continuously monitored using *in-situ* X-ray diffraction. Selected diffractograms are shown in Figure 4, and in Table 2 the phase evolution sequences for Al-Cu-Fe on Al₂O₃ and Si are summarized. The as-deposited film show broad diffraction peaks from each element, Al, Cu, and Fe. Up to 290 °C, parts of the Al and Fe-peaks remain while all Cu has been consumed. The Cu has reacted with portions of Al and Fe into the binary Al-Cu phases γ -Al₄Cu₉, θ -Al₂Cu, η -AlCu, and the ternary ω -Al₇Cu₂Fe phase, similar to when the Al₂O₃-substrate was used. At 390 °C the first diffraction peaks belonging to a Si containing phase, τ_5 -Al_{7.4}Fe₂Si, appeared. It coexists with the η and ω -phases at this temperature. Thus, Si diffuses into the film and forms phases at temperatures between 290 °C and 390 °C. At 480 °C the final binary Al-Cu phase, η , has transformed, and instead the α -phase (lattice parameter, $a=1.242$ nm) is present along with the ω - and τ_5 -phases. A piece of the A₁-sample was monitored with smaller temperature steps from 390 °C to more accurately determine the formation temperature of the α -phase. The α -phase first appeared after 1 h at 430 °C, which is a temperature lower than the formation temperature for the icosahedral ψ -phase mentioned in literature [12,20]. At 570 °C only the ω , with weaker intensities, and α -phases (lattice parameter, $a=1.247$ nm) are present. The presence of the ω -phase in this treatment compared to isothermal treatment at 600 °C is attributed to the temperature difference. Additional experiments (not

shown) showed that the ω -phase indeed does disappear with another temperature increment to 600 °C for all Al-deficient samples. The weaker intensities of the ω -phase at 570 °C are an indication that it is decreasing in amount.

Figure 4. Selection of XRD measurements of sample A₁ on Si substrate at temperatures ranging from 190 °C to 570 °C. The approximant α -phase is indexed in the top measurement.

3.4 Scanning Electron Microscopy and Energy Dispersive X-ray Analyses

SEM imaging and EDX mapping were performed on sample A₁ after the heat treatments at constant 600 °C and after forming the α -phase at 430 °C shown in figure 5 (a) and (b) respectively. The SEM images from the other samples after annealing at constant 600 °C shows a surface of some roughness with a few darker areas where the significant difference between the treatments are the slightly larger sizes and higher density of dark areas of 600 °C treatment. EDX mapping of a section covering one of the larger dark areas is shown in Figure 6. It was noted that the elements were regionally evenly distributed over the entire light area while at the

dark areas there was no Cu present and gradients of increasing Si and decreasing Al and Fe towards the darkest areas. This suggests that the light areas are the α -phase while the dark areas are Al-Fe-Si phases, in agreement to the phases detected by XRD. All samples, including B₂ and B₃, had these dark areas. Thus, no sample was truly single-phase even when only one phase was detected by XRD due to limited diffracting material. The dark areas, however, constituted less than 1% of the surface area, suggesting that the films are almost entirely α -phase.

Figure 5. SEM images of sample A₁ on Si-substrate annealed a) isothermally at 600 °C b) up to 430 °C where α -phase forms, in two magnifications.

4. Conclusions

The quaternary α -Al₅₅Si₇Cu_{25.5}Fe_{12.5} approximant phase forms during annealing of a ternary multilayered Al/Cu/Fe thin film on a Si substrate. The formation temperature of the α -phase is 430 °C and it remains up to at least 600 °C with increasing quality. The α -phase forms in all samples included in this article, irrespective for film composition, thickness and number of

periods, when Si was used as substrate. The quality of the α -phase in the film increases when the composition of the samples are on the Al-deficient side as compared to the composition of ideal icosahedral ψ -phase, and is further improved in the film with 10 periods. Diffusion of Si into the film occurs at temperatures below 390 °C, which prevents the formation of the icosahedral ψ -phase. If a Si-free stable substrate, like Al_2O_3 , is used with the same film, the icosahedral ψ -phase is formed at a temperature above 480 °C, which is much higher than the temperatures of Si diffusion and the α -phase formation.

Figure 6. SEM image of sample A₁ on Si with elemental maps of the different elements. Bright contrast corresponds to high concentration.

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Table 1. Layer sequence, film thickness, and global composition of the investigated multilayered Al/Cu/Fe samples. Al is kept as the top layer and the nominal layer thickness ratio of Al:Cu:Fe is 7:2:1. The approximant α -phase room temperature lattice parameter after 4 h, 600 °C annealing are also given.

Sample	Layer sequence	Substrate	Total film thickness (nm)	Normalized composition (at.%)	Lattice parameter (nm) of α -approximant
A ₁	(Al/Cu/Fe)×1	Si, Al ₂ O ₃	400	61.0 – 25.5 – 13.5	1.227
A ₂	(Al/Cu/Fe/Cu/Al)×1	Si	400	55.6 – 31.7 – 12.7	1.228
A ₃	(Al/Cu/Fe)×3	Si	400	58.6 – 29.4 – 12.0	1.225
A ₄	(Al/Cu/Fe)×10	Si	400	58.7 – 29.8 – 11.5	1.226
B ₁	(Al/Cu/Fe)×1	Si	100	68.1 – 20.6 – 11.2	1.229
B ₂	(Al/Cu/Fe)×10	Si	100	67.9 – 20.3 – 11.8	1.229
B ₃	(Al/Cu/Fe)×50	Si	100	66.4 – 22.4 – 11.2	1.229
B ₄	(Al/Cu/Fe)×1	Si	200	68.8 – 20.5 – 10.8	1.228
B ₅	(Al/Cu/Fe)×10	Si	200	68.8 – 20.7 – 10.4	1.228
B ₆	(Al/Cu/Fe)×50	Si	200	67.6 – 20.8 – 11.6	1.227

Table 2. Summary of phase evolution sequences for Al-Cu-Fe thin films on Si and Al₂O₃ during annealing at stepwise increasing temperatures.

	RT	190 °C	290 °C	390 °C	480 °C	570 °C	600 °C	
Si	Al	Al	Al	η	α	α	α	
	Cu	Fe	Fe	ω	ω	ω	(τ ₇)	
	Fe	γ	η	τ ₅	τ ₅			
		θ	θ					
			(ω)					
		Binary Al-Cu		Ternary Al-Cu-Fe Si-phases	Approximant α-phase forms		Approximant α-phase the major constituent	
	RT	190 °C	290 °C	390 °C	480 °C	570 °C	650 °C	710 °C
Al ₂ O ₃	Al	Al	Al	η	η	ψ	ψ	ψ
	Cu	Fe	Fe	ω	ω	ω	ω	(β)
	Fe	γ	η					
		θ	θ					
		Binary Al-Cu		Ternary Al-Cu-Fe	Quasicrystalline phase forms		Quasicrystalline phase the major constituent	