

Formation of AlCuFe quasicrystalline thin films by solid state diffusion

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We show that thin films 3000 Å in thickness of the icosahedral AlCuFe phase can be formed by solid state diffusion of sputtered Al, Cu, and Fe layers. As for bulk materials, we propose that the icosahedral phase grows by diffusion of the Cu in the Al₃Fe layer previously formed by interdiffusion of the Al and Fe layers. These films present high resistivity values comparable to those obtained in bulk samples of high structural quality.

Since the discovery of the first icosahedral phase in a rapidly quenched AlMn alloy in 1984,¹ many experiments have been carried out in order to clarify the structure and properties of this new state of condensed matter. Most of the quasicrystalline phases discovered up to now are metastable, however a few of them are thermodynamically stable and among them the AlCuFe alloy provided for the first time pure icosahedral phases of high structural quality.^{2,3} Very peculiar electronic and magnetic properties such as very high electrical resistivity values increasing as the structural quality of the sample is improved,^{4,5} a low density of states at the Fermi levels,^{4,5} a strong composition dependence of the resistivity and the Hall coefficient,⁴ and a diamagnetic susceptibility⁴ were then observed.

These samples were prepared either by melt spinning or long term annealing of bulk ingots; monograins of millimeter size could even be produced. Recently, films about 10 μm in thickness have been obtained by cosputtering of three elements onto liquid nitrogen cooled substrates and subsequent annealing of the films.⁶ Binary metastable quasicrystals have also been produced by solid state diffusion of either sputtered^{7,8} or evaporated layers.⁹ Decagonal Al₃Pd phase have even been obtained by lateral diffusion of Al islands on a Pd thin film.¹⁰ We report here on the first elaboration of very thin films (3000 Å) of the ternary stable AlCuFe quasicrystals by solid state diffusion of Al, Cu, and Fe layers.

Al, Fe, and Cu layers were sputtered consecutively at room temperature on SrTiO₃ substrates using a rf magnetron sputtering system with a base pressure of about 1×10⁻⁷ Torr. High purity argon (2–3 mTorr) was used as a sputtering gas. The rf power was 200 W; the distance between the targets of each element and the sample holder was about 2 in., leading to sputtering rates of about ~10, 15, and 5 Å/s for Al, Cu, and Fe, respectively. To ensure a good thickness homogeneity, the sample holder was oscillating at 0.5 Hz below the target. These oscillations were essential to get a good control of the sample composition since, as we will see later, the quasicrystalline phase can only be obtained in a very narrow composition range. The SrTiO₃ substrates were stuck to the sample holder with a small amount of grease and hence its temperature did not get above 100 °C during sputtering. The thickness of the different layers was controlled very carefully using a vibrating quartz thickness monitor calibrated with pure elements. The films were then subsequently annealed in a quartz tube under high vacuum (10⁻⁶ Torr) first at 350 °C overnight and then at 600 °C for 2 h.

Previous studies on bulk samples showed that the electrical resistivity depends strongly on the nominal composition and the structural quality of the sample, being maximal for Al_{62.5}Cu₂₅Fe_{12.5}.⁴ This peculiar composition corresponds to a 7.0/2.0/1.0 thickness ratio for the Al, Cu, and Fe layers, respectively. We thus sputtered first a 2100-Å-thick Al layer on our substrate, followed by a 300 Å Fe layer and a 600 Å Cu top layer. To compensate for small calibration errors of the thickness monitor we investigated different samples where the thickness of the Cu and Fe layers changed by 10 Å.

Measurements performed on bulk samples have shown there is a close relationship between the electrical resistivity of the samples and their purity and structural quality.⁴ We thus made, as a first characterization, resistivity measurements of the films using a four-probe Van der Pauw technique. The structural quality of the films of highest resistivity was then checked using a low angle x-ray diffraction technique. Scanning electron microscope images were also performed in order to check the quality of the films.

An intensive study of the Al-rich part of the AlCuFe phase diagram¹¹ showed that pure icosahedral samples can only be obtained in the very narrow composition range, typically Al_{100-x-y}Cu_xFe_y with 24.4<x<26.0 and 12.0<y<13.0. This phase diagram is shown in Fig. 1; the icosahedral phase is surrounded by many binary and ternary crystalline phases, especially the β-AlFe(Cu) cubic phase which is usually present as a contaminating phase in the as-quenched ribbons.

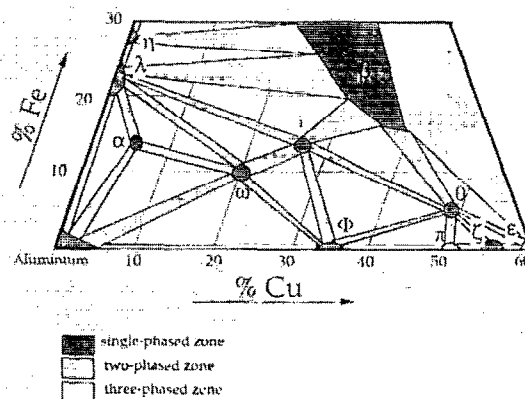


FIG. 1. The Al-rich part of the AlCuFe phase diagram.

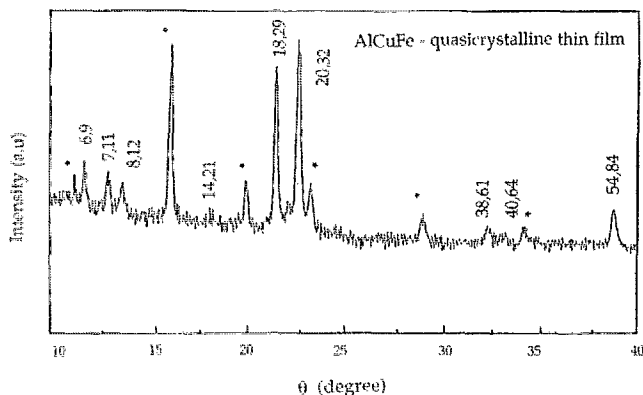


FIG. 2. Low angle x-ray diffraction pattern of AlCuFe quasicrystalline thin film 3000 Å in thickness. All the peaks could be attributed either to the SrTiO₃ substrate (*) or the quasicrystalline structure.

After the first annealing treatment (350 °C overnight) the copper color of the top layer completely disappeared showing that the different elements had mixed together. However the resistivity values of these films were only a few tens of $\mu\Omega$ cm, suggesting that they were highly contaminated by crystalline phases. A further annealing at 600 °C provided several samples with resistivity values ranging from 2000 to 3000 $\mu\Omega$ cm for 600 Å < Cu layer < 640 Å and 280 Å < Fe layer < 300 Å. Outside this range the resistivity rapidly dropped by an order of magnitude, emphasizing the strong dependence of the electrical properties on the purity of the sample. It is important to note that the resistivity also decreased for annealing above 700 °C whereas in bulk samples an annealing at 800 °C was necessary to get pure quasicrystalline phase of high structural quality.

Figure 2 presents the x-ray diffraction pattern of one of the quasicrystalline films. Except for a very small peak present in this case between the two main icosahedral peaks all the peaks could be attributed to either the icosahedral phase or the SrTiO₃ substrate. From this x-ray diffraction pattern we estimate the direct lattice parameter to be about 6.31 Å, in good agreement with results previously found in bulk materials.³ A scanning electron microscope picture of this film is presented in Fig. 3. This picture shows the poly-

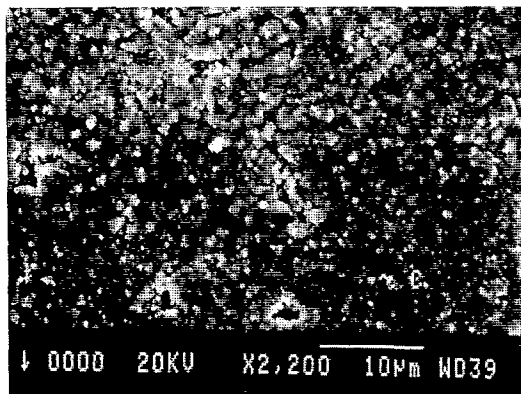


FIG. 3. Scanning electron micrograph of the AlCuFe thin film showing the polycrystalline structure of the film.

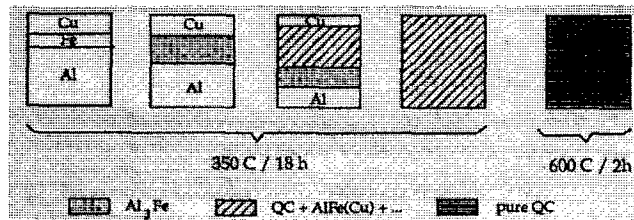


FIG. 4. Schematic representation of the different steps involved in the formation of the pure quasicrystalline thin film after sputtering the elements.

crystalline structure of the film consisted of small quasicrystalline grains about 1 μm in diameter. All the film seems, however, to be quite homogeneous.

Since there is almost no interdiffusion between Cu and Fe, especially at 350 °C, we assumed that Al will first diffuse into the Fe layer up to forming the alloy with the highest aluminum content: Al₃Fe. This alloy is of particular interest since it presents icosahedral local order and is considered as the first approximant of the decagonal AlFe alloy.¹² Moreover in bulk systems the quasicrystal forms through a peritectic reaction involving Al₃Fe, liquid, and other crystalline phases depending on the composition.^{11,13} The growth of the *i* phase was then attributed to an enhanced solubility of Cu into Al₃Fe at high temperature.¹⁴ We thus assumed that in our thin films the quasicrystal will also grow by diffusion of the Cu (and the remaining Al) into the Al₃Fe layer but through a solid state diffusion process with no liquid present. However, after the first heat treatment all the films presented very low resistivity values, indicating that the quasicrystalline phase was highly contaminated by the surrounding crystalline phase and especially the cubic-type AlFe(Cu) (see Fig. 1). Note that Chien *et al.*⁶ did also first get a cubic crystalline phase when annealing their amorphous films below 515 °C, however in their case this crystalline phase presented a surprisingly high resistivity value. Another annealing at a higher temperature caused the elimination of these contaminating phases leading to pure quasicrystalline films. Figure 4 gives a schematic representation of the different steps involved in the formation of the quasicrystalline film. It is interesting to note that we were able to get pure icosahedral films using only three layers, which is in striking contrast to the result obtained by Levi and Schechtman⁷ in the metastable AlCr compound. Indeed, these authors could only form pure icosahedral phases by annealing a very thin alternating layer (Al+Cr layer < 50 Å) with heat treatments of thicker layers always leaving residual aluminum. Note that the sequence in which the different layers were sputtered was important since we could not get pure quasicrystalline film using an Al-Cu-Fe sequence. This result emphasizes the important role played by the Al₃Fe intermediate compound which could not be produced by sputtering the Cu on the Al.

Our highly resistive films present a strong negative temperature dependence of the resistivity as for bulk samples. Indeed, the resistivities increased by a factor of 1.5–2 when the films were cooled down to liquid nitrogen temperatures in good agreement with results previously obtained in bulk samples.^{4,5}

A very fine tuning of the composition allowed us to form

pure AlCuFe quasicrystalline thin films about 3000 Å thick. As in bulk samples these films presented high resistivity values of about 3000 μΩ cm at room temperature. These films are important for accurate electrical and optical measurements and maybe even for applications of this unusual class of materials.

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