In situ studies of magnetron sputtered Al–Cu–Fe–Cr quasicrystalline thin films

E.J. Widjaja*, L.D. Marks

Department of Materials Science and Engineering, Northwestern University, Cook Hall, 2225 North Campus Drive #2036, Evanston, IL 60208-3108, USA

Abstract

In situ studies have been performed on thin films in the Al rich region of the Al–Cu–Fe–Cr quasicrystalline phase field. Thin films were grown by magnetron sputtering on atomically flat MgO (0 0 1) and Al_2O_3 (0 0 0 1) and subsequently studied by transmission electron microscopy and X-ray photoelectron spectroscopy. High resolution electron microscopy shows that thin films (<30 nm) grown at room temperature are essentially amorphous. At higher temperatures (>573 K), the film growth is identified to be island mode. Upon subsequent ultra high vacuum annealing at 583 K, the films transform into a mixture of quasicrystalline and crystalline grains. Further annealing results in grain growth. A hexagonal crystalline phase in the films with $a=2.23$ nm and $c=1.25$ nm was identified as an approximant of the decagonal phase. For annealing temperatures above 848 K, the films phase separate into thick quasicrystalline and thin crystalline regions.
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1. Introduction

Quasicrystals are orientation-ordered structures with classically forbidden rotation symmetries (e.g. five and tenfold rotation axes) which are incompatible with periodic translational ordering. Quasicrystalline materials, which include quasicrystals as well as their approximants, exhibit properties that are very different from conventional metallic materials. They are mostly metallic alloys, and show high hardness and stiffness but low electrical and thermal conductivity. The coefficient of friction and surface energy of the quasicrystalline materials are also very low; for reviews of their properties see Refs. [1–5].

Limited by their exceptionally low fracture toughness, pure quasicrystalline materials can be difficult to work with and may not be viable for most applications. However, employing them in the form of coatings has immense technological potential [1,6]. Plasma spraying has been used widely to synthesize quasicrystalline films, but it has problems (e.g. porosity, unmelted particles, cracks, oxides) [1,6,7]. More suitable techniques rely upon physical vapor deposition and are now routinely used for the production of a large variety of thin films [1]. A standard industrial method to produce high quality thin films is magnetron sputtering. This method yields dense materials, is relatively cheap and can be adapted to coat complicated shapes.

Understanding the initial stages of quasicrystalline film growth is critical to reproducible film fabrication. Research in this area involves ion sputtering and annealing in ultra high vacuum (UHV) systems to remove surface contamination prior to study which may alter the surface chemistry/structure [8]. Since the elements involved are very prone to oxidation, scientific studies require both growth and characterization under UHV conditions for definitive answers. Several in situ studies are available, but are mostly limited to X-ray diffraction (XRD) [9].

In this paper we present preliminary in situ transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) studies in UHV of magnetron sputtered Al–Cu–Fe–Cr quasicrystalline thin films. We also confirm the existence of the new hexagonal approx-

*Corresponding author. Tel.: +1-847-491-7809; fax: +1-847-491-7820.

E-mail address: e-widjaja@northwestern.edu (E.J. Widjaja).

imant for decagonal quasicrystals published previously [10].

2. Experimental

2.1. Experimental systems

In situ studies were carried out in sample preparation, evaluation, analysis and reaction (SPEAR), a system which allows sample manipulation, thin film growth, surface characterization and electron microscopic analysis all with the sample in UHV conditions. The system includes a magnetron sputtering chamber for thin film growth, Hitachi UHV H-9000 TEM and a Phi X-ray Source and Analyzer for XPS. Details of the system have been published elsewhere [11].

2.2. Substrate preparation

Magnesium oxide (MgO) (0 0 1) substrates were prepared using standard TEM sample preparation techniques: thinning; mechanical dimpling; chemical etching (50% phosphoric acid at 358 K) to perforation followed by Ar$^+$ ion milling to remove the residual contaminants from etching. Subsequently the substrates were annealed in oxygen at 1273 K for 2–3 h to allow recovery and recrystallization from defects introduced during preparation [12]. After insertion into the UHV chamber, samples were evaluated using XPS and TEM to ensure surface cleanliness and to document substrate surface morphology prior to deposition. XPS studies show a clean MgO surface and TEM studies reveal the presence of step bunches separated by 100–150 nm wide terraces. Aluminum oxide (Al$_2$O$_3$—sapphire) (0 0 0 1) substrates were also prepared by thinning, dimpling and ion milling to perforation; annealing at 1673 K in air yielded atomically flat samples [13].

2.3. Thin film deposition

Depositions were done in a magnetron sputtering chamber with a base pressure of 6.7×10^{-9} Pa. All depositions were carried out at 3.7×10^{-1} Pa Argon (99.998% purity), 150 W and no substrate bias. The target was a metal alloy made through vacuum arc melting. The deposition rate at room temperature was determined to be approximately 13 nm/min. The sample manipulation stage was used to heat the substrate and thus anneal the thin film. The substrate temperature was measured with a close-focus infrared pyrometer calibrated to sample emissivity.

2.4. Composition measurement

XPS was used to measure the composition of as-deposited thin films using peak area values estimated with FitXPS Version 2.0 [14]. Peaks chosen for integration and their atomic sensitivity factors are based upon empirical peak area value corrected for the transmission function for our XPS system [15]. The relative metallic composition of the as-deposited films was also measured by ex situ energy dispersive X-ray spectroscopy (EDX) in a Hitachi S-3500 scanning electron microscope. The compositions of decagonal and hexagonal grains were determined from EDX in Hitachi HF-2000 TEM. All EDX measurements were calibrated using standard samples whose compositions were determined by atomic emission spectroscopy.

2.5. Ex situ work

A small portion of this work was done outside SPEAR. Thin films were deposited on sodium chloride crystals at room temperature and annealed in a tube furnace under flowing Argon at different temperatures (573–848 K) and times (30 min–5 h). The substrates were removed by dissolving in water to acquire free standing thin films (~130–260 nm). These were then suspended on holey-carbon films in Ni or Cu grids and studied using Hitachi H-8100 and HF-2000 TEMs.

3. Results and discussion

3.1. Room temperature growth and annealing treatment

Thin films of approximately 25 nm thickness were grown on MgO (0 0 1) at room temperature and an even coverage of film on the substrate was observed. In addition to MgO diffraction spots, selected area diffraction (SAD) shows diffuse patterns characteristic of an amorphous structure (Fig. 1a). In situ High resolution electron microscopy (HREM) of film extending out of the edge of MgO (Fig. 1b) shows a featureless image. The power spectrum of the HREM image (Fig. 1c) confirms the absence of crystalline order in the film. Therefore, it can be concluded that growth at room temperature results in thin film with an amorphous structure.

This amorphous phase in the initial sample is metastable; after a short UHV annealing (~4 min) at 583 K, the film transforms into a mixture of quasicrystalline and crystalline grains. Diffraction patterns from the decagonal phase (tenfold axis) and its hexagonal approximant ([1 1 0] zone axis) on the MgO substrate are shown in Fig. 2a and b. Further annealing experiments showed coarsening behavior (Fig. 3a). Moiré fringes that were sparse and hard to discern in the annealed sample become clearly visible after further annealing for 4 min at 633 K (Fig. 3b). The fringes in the annealed image show large overlapping grains.

For thicker film (130–390 nm), room temperature growth shows some level of crystallinity (Fig. 4a) which
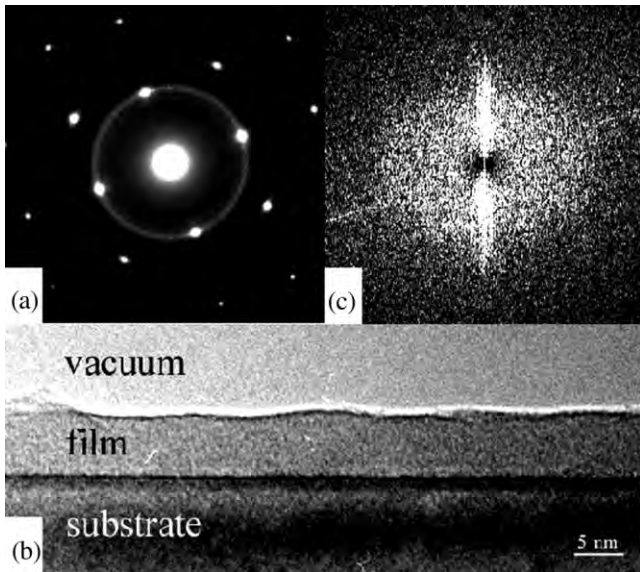
Fig. 1. Room temperature growth on MgO (0 0 1) (a) Diffraction pattern; (b) HREM image; (c) Power spectrum of (b). In (a) there is some 'ring-like' character, indicating partial order (e.g. first and second nearest neighbours) in the initial material.

can be attributed to substrate heating during deposition. Upon atom bombardments, the substrate temperature increases resulting in higher adatom mobility leading to the formation of crystalline phases. The diffraction patterns from these thicker films grown at room temperature are similar to those from films grown on heated substrates (Fig. 4b), albeit with a difference in the grain sizes. These nanocrystalline phases may be similar to those observed in other studies of as-deposited films using XRD [16].

3.2. High temperature growth and annealing treatment

Growth at higher temperature ($\sim$623 K) on rough MgO (0 0 1) substrate exhibits a turtle shell-like pattern with large plateaus surrounded by channels (Fig. 5a and
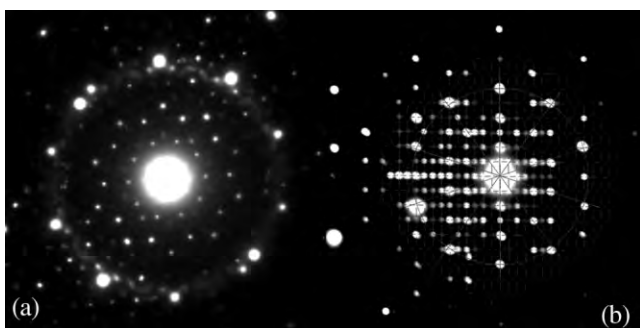

Fig. 2. Diffraction pattern of quasicrystalline phases in annealed film (a) SAD pattern of decagonal phase along tenfold axis; (b) Microprobe diffraction pattern of hexagonal approximant along [1 1 0] zone axis, marked are unit cell and pseudo tenfold rotation.
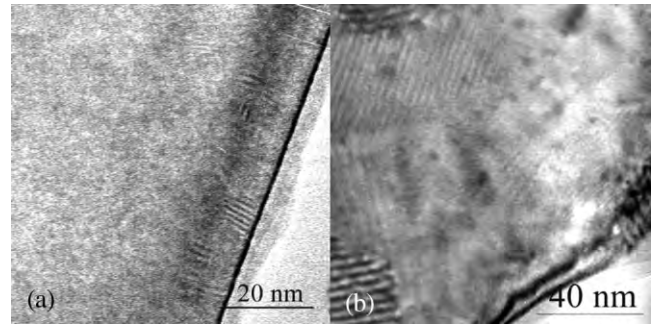

Fig. 3. Bright field (BF) images of annealed film showing grain growth (a) annealed at 583 K for 4 min; (b) further annealing at 633 K for 4 min.

b), characteristic of island growth. XPS studies (Fig. 6) of this film show a very noticeable Mg peak which can be attributed to the spaces between the plateaus formed by the islands—the Mg peak would otherwise be undetectable by XPS for this film thickness as evident from room temperature growth with similar coverage. Growth at this temperature results in a crystalline film (Fig. 4b) which transforms into a mixture of quasicrystalline and crystalline phases upon subsequent annealing. High temperature growth on atomically flat Al_2O_3 and MgO substrates also follows similar trends and the films preserve the step features of the substrate.
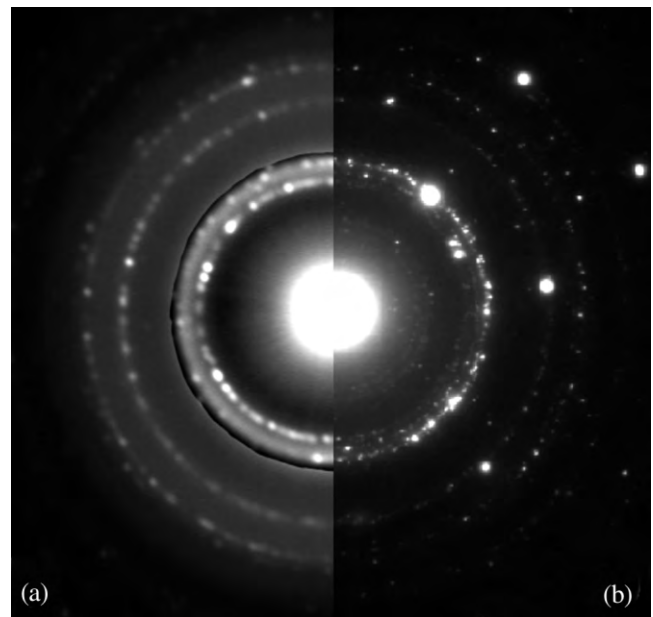

Fig. 4. Comparison of diffraction patterns. (a) Composite diffraction pattern with different exposure times from as-deposited film on salt, grown at room temperature, film thickness $\sim$390 nm. (b) Diffraction pattern from film deposited at 583 K on MgO, film thickness $\sim$60 nm.
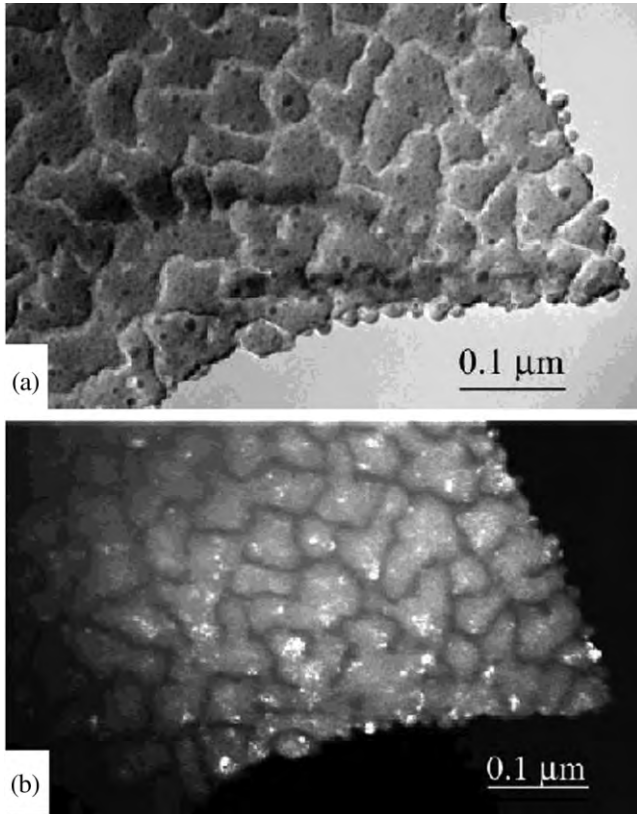
Fig. 5. (a) Bright field (BF) and (b) dark field (DF) images of deposition on MgO at 583 K showing island growth, film thickness ~25 nm.

3.3. Chemical composition

In situ XPS measurements reveal the composition of the as-deposited films to be $Al_{86.3\pm4.4}Cu_{3.9\pm0.7}Fe_{5.4\pm0.4}Cr_{4.4\pm0.5}$. The oxygen content at the surface is less than 5% and that of the film (determined by depth profiling) is approximately 1%. Keeping the sample at 1.3×10^{-4} Pa for one day results in increase of both the oxygen (~40%) and aluminum content of the surface. Ex situ EDX measurements show the composition of as-deposited samples to be $Al_{82.5\pm4.3}Cu_{4.0\pm0.5}Fe_{7.9\pm0.7}Cr_{5.5\pm0.3}$. Chemical composition analysis in TEM shows the average decagonal and hexagonal grains composition to be $Al_{78.3\pm4.5}Cu_{7.6\pm1.4}Fe_{7.5\pm1.9}Cr_{6.6\pm1.0}$ and $Al_{76.1\pm4.3}Cu_{10.8\pm1.3}Fe_{7.3\pm0.4}Cr_{5.8\pm0.3}$, respectively.

3.4. Quasicrystalline phases

We analyzed the films after heat treatments and found they consisted of a decagonal phase and its approximants (mainly hexagonal), an icosahedral phase and its approximants, and other crystalline phases. We observed the existence of a hexagonal approximant with $a=2.23$ nm and $c=1.25$ nm; [1 1 0] is the pseudo tenfold axis,

where the lattice parameters were calculated using the MgO substrate as a calibrant (Fig. 2b). This confirms the previous report of the hexagonal phase as a new crystalline approximant of the Al–Cu–Fe–Cr decagonal phase [8] in addition to the known orthorhombic and monoclinic approximant phases [17].

3.5. Film structure

For samples with annealing temperatures ranging from 573 to 823 K, we observed transformation from amorphous phases to a mixture of quasicrystalline and crystalline phases and grain growth. Higher annealing temperatures and longer annealing times resulted in larger grains. However at temperatures above 848 K, diffusion is highly enhanced. This results in thick quasicrystalline grains (Fig. 7) and also leads to massive surface roughening. The regions surrounding these phases are crystalline and are very thin compared to the quasicrystalline grains.

EDX shows the average composition of the thin regions to be $Al_{38.9\pm3.6}Cu_{4.7\pm0.6}O_{56.4\pm4.1}$. The Cu signal observed is from the supporting grid and hence the composition of the crystalline regions is $Al_{41}O_{59}$—fully oxidized aluminum film. This can be explained as follows: enhanced diffusion leads to the rapid growth of quasicrystalline phases resulting in the expulsion of excess elements (mainly aluminum) to the surrounding matrix. These get oxidized upon subsequent exposure to air.

4. Conclusions

Room temperature growth results in thin films with an amorphous structure; this amorphous phase is metastable and transforms to a mixture of quasicrystalline and crystalline phases upon short annealing. Further annealing results in grain growth. Growth at high temperature (>573 K) results in islands. The films contain a hexagonal approximant to the decagonal phase, as well as other phases and Al_2O_3. At temperatures above
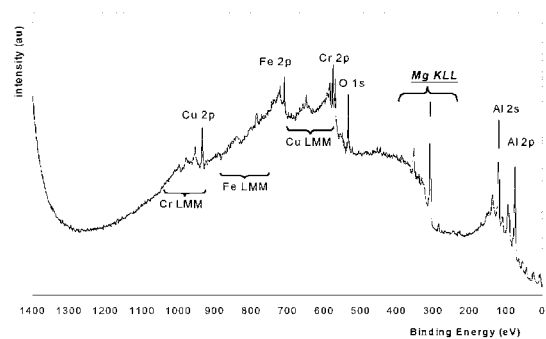

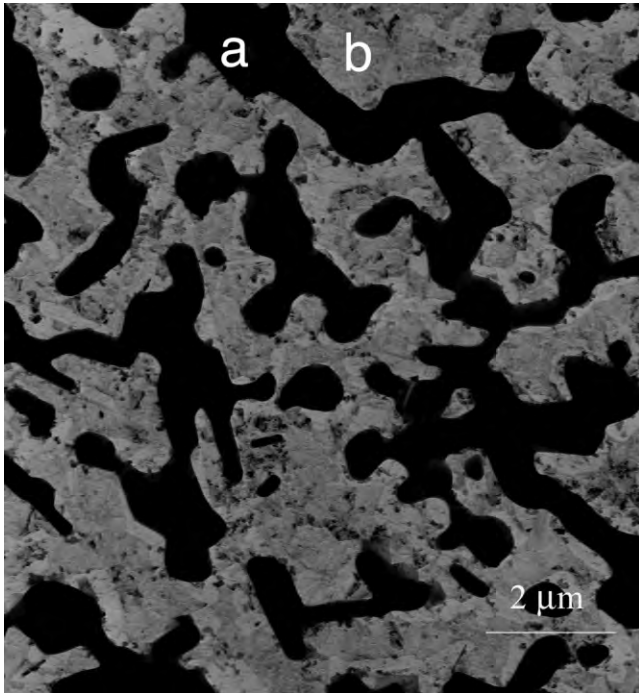Fig. 6. XPS spectrum from deposition on MgO at 583 K, film thickness ~25 nm.

Fig. 7. BF image showing thick quasicrystalline grains (a) after annealing at 848 K for 3 h. Crystalline regions (b) surrounding these grains are very thin compared to the quasicrystalline regions.

848 K, diffusion is highly enhanced and results in the roughening of films.

Acknowledgments

References

[1] J.M. Dubois, Mater. Sci. Eng. A 294–296 (2000) 4.
[2] P. Archambault, C. Janot, MRS Bull. November (1997) 48.
[3] C.J. Jenks, P.A. Thiel, MRS Bull. November (1997) 55.
[4] K. Urban, M. Feuerbacher, M. Wollgarten, MRS Bull. November (1997) 65.
[5] C.J. Jenks, P.A. Thiel, Langmuir 14 (1998) 1392.
[6] M.F. Besser, T. Eisenhammer, MRS Bull. November (1997) 59.
[7] D.J. Sordelet, S.D. Widener, Y. Tang, M.F. Besser, Mater. Sci. Eng. A 294–296 (2000) 834.
[8] B. Bolliger, M. Erbudak, A. Hensch, D.D. Vvedensky, Mater. Sci. Eng. A 294–296 (2000) 859.
[9] J.Z. Jiang, C.H. Jensen, A.R. Rasmussen, L. Gerward, Appl. Phys. Lett. 78 (2001) 1856.
[10] X.Z. Li, L.D. Marks, J. Maciejewski, L. Fehrenbacher, J. Zabinski, J. O'Neil, Metal. Mater. Trans. A 33A (2002) 675.
[11] C. Collazo-Davila, E. Landree, D. Grozea, G. Jayaram, R. Plass, P.C. Stair, L.D. Marks, J. Microsc. Soc. Am. 1 (1995) 267.
[12] S.S. Perry, P.B. Merrill, Surf. Sci. 383 (1997) 268.
[13] Y. Kim, T. Hsu, Surf. Sci. 258 (1991) 131.
[14] D.L. Adams, J.N. Andersen, Surf Interface Anal, submitted for publication.
[15] C.D. Wagner, L.E. Davis, M.V. Zeller, J.A. Taylor, R.H. Raymond, L.H. Gale, Surf. Interface Anal. 3 (1981) 211.
[16] M.J. Daniels, J. Maciejewski, J.S. Zabinski, Z.U. Rek, S.M. Yalisove, J.C. Bilello, in: E. Belin-Ferre, P.A. Thiel, A.-P. Tsai, K. Urban (Eds.), Quasicrystals—Preparation, Properties and Applications, Mat. Res. Soc. Proc., 643 (2000) K.8.4.
[17] X.Z. Li, C. Dong, J.M. Dubois, J. Appl. Crystals 28 (1995) 96.