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Murtaza Bohra, T.M. Pavan, Vincent Fournée, R.K. Mandal. Growth, structure and thermal stability of quasicrystalline Al-Pd-Mn-Ga thin films.. Applied Surface Science, 2020, 505, pp.144494. 10.1016/j.apsusc.2019.144494 . hal-02360309

HAL Id: hal-02360309 https://hal.science/hal-02360309

Submitted on 29 Nov 2020

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Full Length Article

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PII: DOI: Reference:	S0169-4332(19)33310-0 https://doi.org/10.1016/j.apsusc.2019.144494 APSUSC 144494
To appear in:	Applied Surface Science
Received Date:	3 August 2019
Revised Date:	19 October 2019

Accepted Date: 22 October 2019



Please cite this article as: M. Bohra, T.M. Pavan, V. Fournée, R.K. Mandal, Growth, structure and thermal stability of quasicrystalline Al-Pd-Mn-Ga thin films, *Applied Surface Science* (2019), doi: https://doi.org/10.1016/j.apsusc.2019.144494

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Growth, structure and thermal stability of quasicrystalline Al–Pd–Mn–Ga thin films

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Abstract

Growth of Al-Ga-Pd-Mn quasicrystalline thin film is hindered by the low melting temperature of Ga (30 °C) and the formation of residual binary phases. In this study, a stable icosahedral film with a composition near $Al_{67.5}Pd_{19}Mn_{7.5}Ga_{5.7}$ has been achieved using the co-sputtering of $Al_{64.9}Pd_{20.7}Mn_{8.4}Ga_6$ and Al materials followed by ex-situ annealing. The increase in the 6d lattice parameter from 6.45 to 6.48 Å of icosahedral phases suggested that Ga (+1) successfully replaced Al(+3) in the composition. The temperature-dependent XRD study (from RT to 700 °C) reveals that the icosahedral phase found only in a narrow temperature window of 350 – 450 °C. Interestingly, $Al_{63}Pd_{18}Mn_{7.5}Ga_6$ quasicrystalline thin film exhibits cluster spin glass behaviour due to spin-spin interaction of localized Mn ions. These stable icosahedral thin films with crack-free well-defined surfaces can be useful for potential surface-related applications.

Introduction

Intriguing properties of quasi-crystals (QC) such as significant negative thermoelectric power coefficients (up to several tens of $\mu V/K$), low thermal conductivity and high corrosion resistance (especially useful at high temperatures) have opened up multiple avenues for their applications [1-3]. The unique ability of Al-Pd-Mn QC to exist in two stable phases (I-icosahedral and D- decagonal) [4] and realization of a 2D ultrathin I-phase Al-Pd-Mn QC layer using liquid exfoliation has generated a lot of scientific interest [1]. When Fisher et al. [5] attempted to grow the Al-Pd-Mn icosahedral (I) single crystals; it was found that the flux (Ga) was incorporated into the QC structure. Owing to its comparable size and lower surface energy (600 mJ/m²), Ga can substitute Al atoms in Al (Ga)-Pd-Mn quaternary compositions [4-6]. In the Ga doped Al-Pd-Mn compound, the thermal conductivity effectively decreased to the low value of 0.91 W/m K with increasing Ga concentration (0 to 3%), thereby increasing the dimensionless figure of merit ZT by a factor of 1.4 [7–10] and giving rise to better thermoelectric materials. Low-temperature spin-glass behaviours have been reported in bulk Al-Pd-Mn system [11–12], however magnetic studies on Al (Ga)–Pd–Mn bulk and/or thin films are scarce. The IQCs of Al (Ga)-Pd-Mn having similar structure and sizes, exhibit different physical properties [4-10] depending on the synthesis methods. Hence the growth mechanisms of these IQCs must be understood in relation to chemical ordering and growth morphologies.

It can be noted that the formation of icosahedral phase is limited only to the composition near $Al_{70}Pd_{20}Mn_{10}$ in the ternary Al-Pd-Mn phase diagram [4–10]. The preparation of a pure quaternary Al_{70-x}Ga_xPd₁₇Mn₁₃ compound proves to be even more challenging owing to the formation of different phases after Ga substitutions. Figure 1 gives a summary of phase formations with respect to Ga substitution based on reports in the literature [5-7, 13-18]. Yadav et al. [13-14] have grown Al₇₀₋ $_xGa_xPd_{17}Mn_{13}$ (x = 2.5 to 20 %) by two different approaches, however, they succeeded in finding pure IQC phase in x = 2.5% (as-cast alloy) and at x=5% (melt-spun ribbon). For x > 2.5 at.% Ga content, the cast alloy exhibits multiphase materials, while melt-spun ribbons with 5 < x < 15 at.% Ga show a minority AlPd-type B2 phase which eventually transformed into a hexagonal Al_3Pd_2 phase at x = 20%. Interestingly, Yadav et al. [15] also utilized the rapid solidification by melt spinning technique to obtain the decagonal QC for x = 0 to 5 at.% Ga. These authors also grew Al₇₅Ga₅Pd₁₇Mn₁₃ QC thin film using flash evaporation technique [17], however rough surfaces of films limited their scope in non-stick coating appliances where properties like low adhesion and low-friction coefficients are required. We reported [18] formation of icosahedral phase in bulk $Al_{70-x}Ga_xPd_{17}Mn_{13}$ (x = 0 to 10 %) samples with x = 6 at.% Ga by induction skull melting followed by annealing; however Al-Pd phase was present as minority phase for x < 6% and majority phase for x > 6% respectively. This motivated us to grow a thin film of the same composition (x = 6 at.% Ga), but the impurity Al-Pd phases were still a major hurdle. In this study, we report a novel way for the growth of single-phase IQC $Al_{67,5}Pd_{19}Mn_{7,5}Ga_{5,7}$ thin films using the co-sputtering technique and explore their thermal stability and magnetic properties.



Figure 1. Summary of regions of phase stabilities of AlPdMnGa alloys/thin films prepared by different methods based on the reports in the literature with respect to Ga.

Experimental

Creating a thin film of composition Al_{64.9}Pd_{20.7}Mn_{8.4}Ga₆ was initially attempted using a single IQC Al_{64.9}Pd_{20.7}Mn_{8.4}Ga₆ target in a magnetron sputtering. However, Al-based (Al₃Pd₂ phase) binary alloys were formed in the process, reducing the overall Al% (typically \leq 60%) available for the icosahedral (Al_{59.8}Pd_{22.2}Mn_{8.4}Ga_{9.6}) compound. This Al deficiency was retained even after different *in-situ/ex-situ* growth and annealing protocols. Anton et al. [19] reported that in the ternary system Al–Pd–Mn, icosahedral order could be obtained for Al contents above 75 at.%, while crystalline Al–Pd phases segregated at lower Al contents. Having improved Al content in our films, it was decided to deposit thin films by co-sputtering of Al and Al_{64.9}Pd_{20.7}Mn_{8.4}Ga₆ targets at DC power of 100 W for 15 and 60 min, respectively. Al target was sputtered periodically with an interval of 11.25 min for 5 min each time, as illustrated within magnetron sputtering set up shown in Figure 2. These films were sputtered on various substrates (Si (100), glass and polished (up to ¹/₄ micron) 3041-stainless steel) under working gas Ar/H₂ pressure of 2×10⁻² mbar at room temperature (RT). Before deposition, substrates were RF sputtered for 5 min to remove any oxides layers from the substrate surfaces. The bulk Al_{64.9}Pd_{20.7}Mn_{8.4}Ga₆ alloy target was prepared by induction skull melting [18]. Films were *ex-situ* annealed in quartz ampoule under the vacuum of 5×10⁻⁵ mbar at 400 – 600 °C.



Figure 2. Schematic of co-sputtering and deposition scheme of Al_{64.9}Pd_{20.7}Mn_{8.4}Ga₆ and Al targets.

Structural characterization of the generated films was performed using Glancing angle X-ray diffraction (XRD)(SIE-MENS D500 diffractometer) with an incident angle of 1.5° . The scanning electron microscopy (SEM) (FEI QUANTA 600F) attached with energy dispersive analysis of X-rays (EDAX) (Bruker Quantax XFlash 4010) was used for chemical analysis. The magnetic properties were measured with in-plane film configuration in a Quantum Design physical property measurement system (PPMSTM) using vibrating sample magnetometer (VSM, 5–300 K). The susceptibility (χ) over the entire temperature range was measured in an applied field of 500 and 150 Oe following a zero-field-cooling (ZFC) and field-cooling (FC) protocol.

Results and Discussion



Figure 3. *XRD patterns of Al-Pd-Mn-Ga thin films fabricated by in-situ growth and ex-situ annealing process. Bulk Al_{72}Pd_{19.5}Mn_{8.5} reference data is included for comparison [18].*

Figure 3 shows room temperature XRD patterns of as-grown film at RT and *ex-situ* annealed films at 400 and 550 °C. The XRD pattern of $Al_{72}Pd_{19.5}Mn_{8.5}$ reference is also given for comparison. The asgrown film shows a broad hump in the vicinity of the positions of maximum intensity I'(111112) and I''(012102) icosahedral peaks, indicating some sort of short-range ordering in the amorphous state of the films. After annealing of these films in vacuum-sealed quartz tube at 400 °C for 1 h, one can notice that two strong icosahedral peaks appeared at the place of the hump along with other

icosahedral peaks. Slight shifts in peak positions compared to reference $Al_{72}Pd_{19.5}Mn_{8.5}$ data are expected because Ga is replacing Al, and this has also been observed in bulk $Al_{64.9}Pd_{20.7}Mn_{8.4}Ga_6$ samples [17–18]. The hypercube 6D lattice parameter (a_{6D}) can be estimated from inter-planar spacing (*d*) of the icosahedral symmetry, using below expression;

$$d(h/h',k/k',l/l') = \frac{a_{6D}\sqrt{2(2+\tau)}}{\sqrt{N+\tau M}}$$

where τ is the irrational golden mean (~1.618), and N/M are Cahn indices for I'(18/29) and I''(20/32) peaks [20–22], respectively. The a_{6D} is found to be 6.482 ± 0.021 Å, which is higher than the bulk Al₇₂Pd_{19.5}Mn_{8.5} value of 6.451 Å [18], inferring replacement of Al with Ga ions of possibly 1⁺ state. No any significant change in XRD patterns has been observed with an annealing time of 12 and 24 hrs (not included here). However, films annealed at a higher temperature of 550 °C show minute Al₃Pd₂ peaks along with icosahedral phase. Because 400 °C is the best *ex-situ* annealing temperature to produce single icosahedral phase, we also decided to *in-situ* grow thin films by keeping substrate temperature at 400 °C, however secondary Al₃Pd₂ phase present similar to the ex-situ annealed films at 550 °C.



Figure 4. SEM images of Al-Pd-Mn-Ga thin films grown on Si substrate at annealing temperature at 400 °C (a) and 550 °C (b). SEM images of films grown on glass(c) and stainless steel (d) substrates at annealing temperature at 400 °C. Insets of Fig. (c) and (d) are respective XRD patterns.

SEM micrographs for the annealed films at 400 and 550 °C are shown in Fig.4 (a) and (b). Micrograph of 400 °C annealed films seems to have uniform morphologies with sharp cracks. EDAX analysis for global semi quantification for film annealed at 400 °C has nominal elemental compositions around Al_{67.5}Pd₁₉Mn_{7.5}Ga_{5.7} compared to the as-grown state of Al_{63.7}Pd₁₉Mn_{7.8}Ga_{9.39}.

However, film annealed at 550 °C shows still cracks and appearance of minority phases. EDAX gives matrix composition around Al_{67.4}Pd_{22.8}Mn_{6.2}Ga_{3.5} and secondary analysis phase Al_{68.9}Pd₁₅Mn_{9.9}Ga_{6.1}, respectively. Observation of the cracks in our thin films could be due to several reasons. First, the thermal expansion coefficients mismatch between the depositing thin film material and the Si(100) substrate may play a role in straining the AlPdMnGa lattices [22]. The second reason could be that the lattice mismatch between the substrate and icosahedral structure, leading to enhancement of the stresses. Because our heating and cooling rates of annealing are prolonged so ruling out the possibility of quenching related stresses. To remove the cracks, we also deposited films on glass and steel substrates following same annealing protocol (at 400 °C) and their surface morphology is given in Fig. 4(c) and (d), respectively. The films deposited on glass still retain minor cracks and show two different phases with light (Al40.1Pd45.2Mn8.5Ga9.1) and dark grey (Al_{67.7}Pd_{19.3}Mn₇Ga_{5.9}) contrast, corresponding to two different compositions. This result is in agreement with the XRD pattern (Inset Fig. (c)) showing both rhombohedral AlPd and IQC phases. Interestingly, SEM micrographs (Fig. 4(d).) of films deposited on stainless steel substrate show crack free and uniform Al_{66.9}Pd₁₉Mn_{6.6}Ga_{7.5} composition throughout the samples. The single icosahedral phase $(a_{6D} = 6.481 \pm 0.011 \text{ Å})$ in these films is further confirmed from the XRD pattern given in the Inset of Fig. 4(d).



Figure 5 Temperature-dependent XRD pattern at various temperatures (RT - 700 °C). SEM image and EDAX analysis of 700 °C heated film.

To investigate icosahedral phase formation and its thermal stability below the melting point of the icosahedral phase, we plotted in-situ temperature-dependent XRD patterns in Figure 5(a). XRD measurement was performed at various temperatures in between RT - 700 °C under the vacuum of 10⁻⁶ mbar. Film heated from RT to 300 °C show only steel substrate peak located around $2\theta = 43.60^{\circ}$. As the temperature increased to 400 °C, prominent icosahedral peaks start appearing along with substrate peak. The two prominent icosahedral peaks, I'(111112) and I''(012102) are shown to be well separated at 450 °C. When film heated at 500 °C, dominant hexagonal Al₃Pd₂ phase suppressed I' and I" and substrate peaks. At higher temperatures (550 - 700 °C), the prominent I' and I" icosahedral peak again seems to appear, but their intensity ratio of I' and I'' are interchanged compared to the 450 °C case. However, at this juncture, it is difficult to say whether they are genuinely icosahedral peaks or they are overlapped with Al₃Pd₂ and substrate peaks. To further identify the phases, SEM and EDAX data of 700 °C heated sample are given in Fig. 5 (b) and (c), which shows three different types of regions (white, black and grey) dominated by Al and Pd based binary phases. This result infers us that the XRD data of higher temperatures sample contain majority Al₃Pd₂ phase along with minute icosahedra phase, and I' is 100% intensity peak of Al₃Pd₂ phase because I'' is 100% intensity peak of icosahedral phase. Both XRD/EDAX results, thus, clearly indicate that annealing at higher temperatures (> 500 °C) favours the formation of Al-Pd binary phases with increased lattice parameters (shown by the yellow ellipse).



Figure 6. Temperature dependence of susceptibility $(\chi-T)$ (at 150 and 500 Oe) and (b) field dependence of magnetization (M–H) at 5 and 300 K, of $Al_{67.5}Pd_{19}Mn_{7.5}Ga_{5.7}$ quasicrystalline films.

The magnetic state of quasicrystalline films (Al_{67.5}Pd₁₉Mn_{7.5}Ga_{5.7}) grown on Si substrate was measured in order to avoid magnetic contribution from steel substrate (if any). As shown in Figure 6, the susceptibility, χ vs T curves were measured at two different fixed fields under ZFC and FC conditions. While in case of lower field (150 Oe), ZFC and FC magnetization show clear bifurcation, but with the application of higher fields (500 Oe), these curves almost overlap, which is a typical signature of cluster spin glass behaviour [23–24]. A similar type of spin glassy nature was also observed in bulk Al₇₀Pd_{20+x}Mn_{10-x} (x = 0, 1) samples [11–12]. The χ -T variation (at low field of 150 Oe) shows broad maxima in magnetization, giving spins freezing temperature around, $T_g = ~100$ K. Below T_g , M-H loops (see in Inset) are expected to show coercivity, however non zero coercivity ~130 Oe around room temperature indicates that there might be presence of localized clustering of Mn ions in our samples. This clustering gives rise to spin-spin interactions, as against Curie-Weiss behaviour of paramagnetic Al-Mn alloys [25]. Moreover, Fisher *et al.* [5] also observed magnetic interaction in bulk Al₇₁Pd₂₁Mn₈ compound below 60 K. Thus, the observed magnetic properties in our quasicrystalline films can be attributed to thin film growth condition that causes clustering of Mn ions and smaller grain sizes of Al_{67.5}Pd₁₉Mn_{7.5}Ga_{5.7} which are responsible for spin-glass behaviour.

Conclusions

The need for producing stable icosahedral Al-Ga-Pd-Mn quasicrystalline thin films is important to comprehend their surface, structural and magnetic properties for various applications. In this study, we have shown how the optimization of the growth condition and post-annealing treatment is crucial in achieving icosahedral Al-Ga-Pd-Mn thin films. The following conclusions can be drawn from the present study:

- 1. The icosahedral Al-Ga-Pd-Mn phase can be stabilized by co-sputtering of Al_{64.9}Pd_{20.7}Mn_{8.4}Ga₆ and Al targets to compensate Al deficiencies.
- 2. Ex-situ annealing favours stable icosahedral phase rather in-situ annealing and in-situ growth while keeping substrate heated.
- 3. Control of binary Al-Pd alloy is significant challenge to get single-phase icosahedral films only in the critical temperature range (350 450 °C).
- 4. Selection of substrate material seems to key in getting uniform crack-free surfaces of the icosahedral phase.
- 5. Our Al_{67.5}Pd₁₉Mn_{7.5}Ga_{5.}7 IQC film exhibits typical spin glassy behaviour, hinting spinclustering of Mn ions.

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