Texture and microstructure in co-sputtered Mg-M-O (M=Mg, Al, Cr, Ti, Zr, and Y) films

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Abstract Mg-M-O solid solution films (M=Mg, Al, Cr, Ti, Zr, and Y) with various M contents are grown employing reactive co-sputtering by varying the target-to-substrate distance. It is shown that all films are biaxially aligned. When the two cathodes are equipped with the same target material (Mg), the in-plane alignment is determined by the cathode closest to the substrate, i.e., by the largest material flux. In the case of nearly equal material fluxes from the two cathodes, double in-plane orientation is observed. This is also the case for the Mg-Al-O and Mg-Cr-O films, while the Mg-Ti-O, Mg-Zr-O and Mg-Y-O films exhibit single in-plane orientation. Pole figures indicate that the grains in Mg-M-O (M different than Mg) are titled; in the Mg-Al-O, Mg-Cr-O and Mg-Ti-O films the grains tilt towards the Al, Cr and Ti metal flux, respectively, while the grain tilt of the Mg-Zr-O and Mg-Y-O films is found to be towards the Mg metal flux. Furthermore, SEM cross-sectional images of the Mg-M-O films reveal columnar microstructure with columns tilted to the same direction as the grains. A mechanism which is

based on the cation radius change upon the incorporation of an M atom in the MgO lattice is proposed to explain the tilting.

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I. INTRODUCTION

Material properties are largely determined by their chemical composition, i.e., the nature and the relative fraction of the constituent atoms. Characteristic examples are materials in the form of films with the general composition Mg-M-O, where M is a metal different than Mg (e.g., Al, Cr, Ti, Zr, Zn). For a very well defined composition range and structure, Mg-Al-O has interesting catalytic properties,[1,2] Mg-Cr-O is a an important refractory material,[3] Mg-Ti-O is known to be a high T_c superconductor,[4] Mg-Zr-O films can be used as protective layers[5] and ionic conductors, and Mg-Zn-O has a wide band gap which is interesting for optical devices.[6]

One technique to synthesize the above mentioned materials in the form of films is magnetron sputtering, employing one or two ceramic and/or metallic targets (the latter implies sputtering in reactive atmosphere). While industrially this class of materials is often deposited from compound targets, for research purposes co-deposition using two metallic sources in an Ar-O_2 ambient is frequently chosen to increase the flexibility with respect to the chemical compositions that can be accessed.[7-9] This combinatorial approach has been extensively used to study the effect of multiple targets on the deposition process characteristics and to investigate the effect of the chemical composition on microstructure, phase formation and properties of various multicomponent films.[9-15] In such multi-source combinatorial approaches the substrate and target normal are not parallel with respect to each other, i.e., off-normal deposition is performed. Thus, the substrate encounters an asymmetric flux of film forming species, which can have implications for the film microstructure. A manifestation of the result of an asymmetric flux of material is the formation of biaxially aligned films, i.e., films that exhibit both in-plane and out-of-plane alignment orientation.[16-20] From a technological point of view these films are important as they are used as buffer layers between non-textured substrates and superconductive thin films to minimize the current losses at the

film-substrate interface.[21] In addition, biaxial alignment of films with magnetic[22] and piezoelectric[23] properties has been shown to allow for enhancement of the performance of the corresponding thin film devices. The correlation between off-normal deposition from one source and biaxial alignment is well documented and understood for several materials. [16,19,20,24-27] This is not the case when growing films from two material sources in a co-sputtering arrangement.

The goal of the current study is to contribute to the understanding of the atomistic mechanisms that determine out-of-plane and in-plane alignment and their effect on the microstructure of the films grown in a confocal (co-sputtering) arrangement. To this purpose, Mg-M-O films are deposited employing reactive magnetron sputtering (in an Ar-O_2 atmosphere) from two off-normal (Mg, M) sources. The coexistence of two different metals, i.e., Mg and M, with differences in atomic sizes, number of valence electrons and surface mobility is very likely to affect the kinetics and the thermodynamics of film growth and thus influence the out-of-plane and in-plane alignment. Therefore, the metals (M) Al, Cr, Ti, Y and Zr are chosen to systematically vary the cation valence electron number and the atomic size and to study in this way their, currently unexplored, effect on the film microstructure and crystallographic properties.

II. EXPERIMENTAL PROCEDURE

Mg-M-O thin films were deposited by dual reactive magnetron sputtering in an Ar-O_2 atmosphere. The depositions were performed using two home-made unbalanced planar circular magnetrons placed at an angle of 90° with respect to each other and each at an angle of 45° with respect to the substrate. Both magnetrons were fixed on a linear translator, allowing for in-vacuum modification of the target-to-substrate distance. One magnetron was permanently equipped with a Mg target while on the other one several metallic targets M (M=

Al, Cr, Ti, Y and Zr) were mounted. Experiments were also performed with both magnetrons equipped with Mg targets, for reference. All targets were 5 cm in diameter and 3 mm in thickness, with a purity of at least 99.95% (Kurt Lesker). The magnetrons were fed by a PFG 1500 DC Hüttinger power supplies. More details on the experimental setup can be found in a previous report[28]. Films were deposited on RCA-cleaned Si (100) substrates covered by a ~2nm native SiO_2 layer. The substrates were fixed on a grounded holder without intentional heating or cooling. A fixed argon pressure of 0.8 Pa was used for all depositions. Both magnetrons were operated at constant current mode. The current for the magnetron permanently equipped with the Mg target was 0.5 A. For the other magnetron, current (I_d) values $I_{d,Al}$ = 0.7 A, $I_{d,Cr}$ = 0.5 A, $I_{d,Ti}$ = 0.7 A, $I_{d,Zr}$ = 0.8 A and $I_{d,Y}$ =0.8 A were used. Mg-M-O films with metal sublattice compositions ranging from pure MgO to pure M_xO_y were grown by changing the target-to-substrate distance. The O_2 flow was regulated to simultaneously ensure deposition of fully oxidized films and avoid operation of the target in poison mode. The deposition time was varied in order to obtain films with a thickness of ~1 μm as determined by a Talystep (Taylor-Hobson) profilometer.

The effect of the deposition conditions on the chemical composition was studied using an electron probe microanalyzer (EPMA) JEOL JXA-8621MX, with beam current of 30nA and voltage of 15 keV. In the following the ratio $C_M = \frac{M}{Mg + M}$ is used as a quantity to describe the film composition, e.g., $C_{Cr} = 19\,\%$ refers to a sample with composition $Mg_{0.81}Cr_{0.19}O_{1.095}$. The crystallographic properties were investigated by X-ray diffractometry (XRD). XRD measurements were performed in Bragg-Brentano (θ/2θ) geometry with a LynxEye Silicon Strip detector mounted into a D8 discover apparatus (Bruker axs), also equipped with a quarter Eulerian cradle. This apparatus was also used to perform the pole figure measurements in combination with a Sol-X Energy dispersive X-ray detector. In the pole

figures measurements, χ (the polar angle) and φ (the azimuthal angle) were varied from 0-80° and 0-360°, respectively, in steps of 2°.

A field emission gun scanning electron microscope (FEG-SEM) was used to study the topographical and cross-sectional microstructure of the thin films. Cross-sectional microstructure was also studied by means of transmission electron microscopy (TEM). Since deposition from two sources results in highly anisotropic flux, TEM was also used to determine spatial variations of the chemical composition in the nm range. Details about sample preparation and operation conditions of TEM can be found elsewhere.[29]

III. RESULTS AND DISCUSSION

A. In-plane alignment

Figure 1 presents the (200) pole figures of the Mg-Mg-O films deposited at various distances of one magnetron from the substrate, while the other magnetron was at a fixed target-substrate distance of 14.5 cm. Figure 1(a) corresponds to the (200) pole figure for a Mg-Mg-O thin film deposited by two sources positioned at 18.5 and 14.5 cm. The arrows indicate the position of the sources with respect to the substrate. All other pole figures are oriented in the same way. For the largest distance (Fig. 1(a)) three poles can be seen at χ ~55° and φ ~60, 180 and 300°. When connecting the poles, a triangle pointing to the left source is formed. The decrease of the distance of one source from 18.5 to 16.5 cm results in a new set of three poles (along with the original ones) with position χ ~55° and φ ~0, 120 and 140°. By connecting these poles a triangle pointing to the right source is formed. Further decrease of the distance to 12.5 cm leads to a pole figure that consists of three poles, forming a triangle pointing to the right source (Fig. 1 (d)), i.e., to the opposite direction as compared to that in Fig. 1(a). The intensity of these poles increases progressively as the target to substrate distance decreases from 12.5 to

10.5 cm (Fig. 1 (d) – (e)). The plan view SEM image of the Mg-Mg-O thin film corresponding to the pole figure in Fig. 1 (a) can be seen in Fig. 1 (f). The image reveals a "roof-tile" structure and the existence of mainly one orientation of the columns facets, although not all perfectly aligned, as is indicated by the solid white lines.

Figure 2 shows the pole figures of three Mg-Al-O thin films with $C_{Al} = 15, 19, \text{and } 27\,\%$ (Fig. 2 (a), (b) and (c), respectively). The above mentioned C_{Al} values were achieved by using Al target-to-substrate distances of 18.5, 16.5 and 14.5 cm, respectively. Similarly to what has been observed in Fig. 1 (b) and (c), the use of two sources results in pole figures that exhibit two sets of three poles forming each set a triangle, pointing to opposite directions. A decrease of the Al source-substrate distance (or an increase in C_{Al}) results in a diminution of the poles intensity. The plan view SEM image of the Mg-Al-O thin film corresponding to the pole figure in Fig. 2 (a) can be seen in Fig. 3 (a). The image reveals a faceted type of film surface similar to what was observed for the Mg-Mg-O film, Fig. 1 (f). The existence of two column directions is indicated by the solid white lines.

Within the composition range that corresponds to crystalline films,[30] similar trends with respect to the effect of the composition on the intensity of the poles in the (200) pole figures were found for all Mg-M-O systems considered in this study. The (200) pole figures for representative Mg-M-O films at a certain C_M value for each system are plotted in Fig. 3 (b), (c), (d), (e), and (f) for M=Al, Cr, Ti, Zr, Y, respectively. Similarly to the Mg-Al-O case (Fig. 3 (b)) the existence of two sets of poles is also observed for the Mg-Cr-O system, as can be seen in Fig. 3 (c). On the contrary, the Mg-Ti-O, Mg-Zr-O and Mg-Y-O films exhibit only one set of poles pointing to the right (see Fig. 3 (d), (e), (f), respectively). Due to the defocussing effect only one pole is clearly visible in Fig. 3 (e) and (f).

The distinct poles indicate the presence of in-plane alignment in the Mg-Mg-O and Mg-M-O films. This is consistent with previous investigations where Mg-O films deposited from one

source forming an angle with the substrate normal also exhibited in-plane alignment.[19,25,31] This can be understood from a model previously presented by our group.[19] The tilting of the substrate results in a directional flux of the adatoms. Depending on their in-plane orientation the growing crystals have a different adatom capture probability. This probability can be calculated from the so-called capture length, which is the projection of the crystallite cross section on a plane perpendicular to the direction of the incoming flux.[19] For the particular case of [111] out-of-plane oriented films, the in-plane alignment is caused by the angular dependence of the adatom capture length of the {100} crystal facets which form a triangle. The angles of largest capture length are 30° and 90° with respect to the flux direction.[19] However, the experimental results reported so far in the literature have shown that in plane alignment occurs only at 90°. The two sets of poles in Fig. 1 (b) and (c) for the Mg-Mg-O films indicate a double in-plane alignment. In light of that model, we suggest here that the double in-plane alignment is caused by the presence of two material fluxes originating from the two confocally arranged Mg sources each promoting in-plane alignment to one direction, as depicted schematically in Fig. 4. This suggestion is further supported by the fact that the two triangles formed by the distinct poles point towards the direction of the incoming fluxes. Along the same lines, variation of the relative flux of material from each source (by varying the relative target-to-substrate distance) promotes one growth direction at the expense of the other, enabling one to switch from in-plane (one set of poles) to double in-plane (two sets of poles) and again back to in-plane aligned films (Fig. 1 (b)-(f)). In the case of single in-plane alignment the orientation of the grains coincides with the position of the source placed closest to the substrate, i.e., it is determined by the largest material flux. In the case of Mg-Al-O and Mg-Cr-O, similar to what was observed for Mg-Mg-O, a double in-plane alignment is noticed. This is clear not only from the pole figures (Fig. 3 (b) and (c)) that show 6 poles, but also from the two sets of triangles pointing to two directions in SEM top view image (Fig.3

(a)). The other three systems, i.e. Mg-Ti-O, Mg-Zr-O and Mg-Y-O exhibit single biaxial alignment. An explanation for the differences in the in-plane alignment in the various Mg-M-O systems is provided in section III. C.

B. Out-of-plane alignment and microstructure

The three poles shown in Fig. 1 represent the stereographic projection of the {100} facets. Because the poles are positioned at $\chi = 55°$ it can be concluded that the films exhibit an [111] out-of-plane orientation perpendicularly to the substrate surface, which is the direction for $\chi = 0°$. For the Mg-Mg-O films the crystals have the same out-of-plane orientation independently of the target-to-substrate distance of the two sources. This is not the case when the Mg target of one source is replaced by a target of another element. The center of the triangle(s) which connects the three poles does not coincide with the center of the pole figure. This is an indication of a tilt of the [111] out-of-plane orientation. The same conclusion can be drawn from the pole in the (111) pole figure (not shown here) which is also shifted with respect to $\chi = 0°$. For Mg-Al-O, Mg-Cr-O and Mg-Ti-O, the tilt was found to be 22, 16 and 10° towards the Al, Cr and Ti source, respectively. For the Mg-Zr-O and Mg-Y-O thin films, the measured tilt was 9 and 22°, respectively, towards the Mg source. From these findings it is evident that the direction and the magnitude of the grain tilt are material dependent. Furthermore, cross-section SEM analysis revealed that all Mg-M-O films exhibit a columnar microstructure. This is shown for Mg-Al-O, Mg-Mg-O and Mg-Zr-O in Fig. 5 (a), (b) and (c), respectively. There, it is also seen that the columns of the Mg-Mg-O film are parallel to the substrate normal. This is not the case for Mg-Al-O and Mg-Zr-O where the columns are tilted towards the Al and the Mg source, respectively. In summary, in the case of Mg-Al-O, Mg-Cr-O and Mg-Ti-O the columns tilt towards the Al, Cr and Ti sources, 16, 12 and 6°, respectively while in the Mg-Zr-O and Mg-Y-O systems, the columns tilt towards the Mg cathode 9 and

22°, respectively. Similarly to the grain tilt, the direction and angle of column tilt presented in the SEM cross-section images in Fig. 5 is material dependent. This can be visualized in Fig. 6 where the column tilt is plotted as a function of the grain tilt. It can be seen that the tendency found for column tilt is consistent with the tendency for grain tilt.

C. Effect of composition and metal atom size

The use of two different material sources induces anisotropy in the flux encountered by the substrate during the film growth. The anisotropic deposition flux results in spatial variations in chemical composition along the columns width as observed in the energy filtered TEM (EFTEM) in Fig. 7. The left side of the columns has a higher Cr concentration than the right one. Moreover, Fig. 7 shows also column tilting in agreement with the SEM cross-sectional images presented in Fig. 5.

Radnóczi *et al.*[32] have demonstrated that composition gradient leads to grain tilt in single crystalline $Al_{1-x}In_xN$ whiskers grown epitaxially on ZrN. This was shown to be the consequence of stacking of the crystallographic planes that tilt towards Al due to the existence of a difference in chemical composition along the whisker and the fact that the ionic radius of Al is smaller than that of In. To explore the relevance of this mechanism for our results, the measured tilt on the (111) planes has been plotted in Fig. 8 as a function of the relative change of the cation (M) radii with respect to the Mg radius. In agreement with the work by Radnóczi *et al.*[32], the (111) planes tilt towards the source equipped with that target for which the cation radius is the smallest. The magnitude of tilt is proportional to the cation size difference between the host (Mg) and the substituting element (M). When both are the same, i.e., Mg-Mg-O, no tilt is observed. As shown in sections III.A and III.B our Mg-M-O films are polycrystalline with collumnar microstructure. Since crystallites (grains) are the building

blocks of collumns, the correlation between column and grain tilt observed in Fig. 6 can be understood.

In the case of [111] out-of plane oriented grains, the densest packed planes of the oxygen anions are parallel to the substrate with metal atoms positioned between the oxygen planes. In the presence of a composition gradient, the average size of the metal cation will change from one side to the other side of the growing grain, as shown schematically in Fig. 9. Consequently the next plane of oxygen anions will be tilted by an angle α defined by the composition gradient $\frac{\partial C_M}{\partial x}$ and the difference in the cation radius $\left(r_{Mg} - r_M\right)$, i.e.,

$$\alpha = arctg\left(\frac{\partial C_M}{\partial x}\left(r_{Mg} - r_M\right)\right). \quad (1)$$

As this angle is small, the following simplification is allowed

$$\alpha = \frac{\partial C_M}{\partial x}\left(r_{Mg} - r_M\right). \quad (2)$$

As the crystal grows by alternating metal and oxygen layers, the tilt will increase with crystal size. The latter can be expressed by

$$\beta = \frac{k\alpha}{\mathrm{a}/\sqrt{3}}, \quad (3)$$

with k the crystal size, and $\mathrm{a}/\sqrt{3}$ accounting for the d-spacing in the (111) orientation.

Combining Eqs. (2) and (3) the following formula for the tilt is obtained:

$$\beta = \frac{\sqrt{3}k}{\mathrm{a}}\frac{\partial C_M}{\partial x}\left(r_{Mg} - r_M\right), \quad (4)$$

Equation (4) predicts that the tilt increases with the composition gradient. The latter, in turn, can be expected to be proportional to C_M. However, the experimental results (see e.g. Fig. 2 for the Mg-Al-O system) do not show any correlation between C_M and grain tilt. At the same time, the crystallite size, k, calculated for all Mg-M-O systems using the Scherrer's formula[33]

was found to be inversely proportional to C_M (Fig. 10). This, according to Eq. (4) counteracts the effect of an increased $\frac{\partial C_M}{\partial x}$ and may explain the constant values of grain tilt at different chemical compositions. Moreover, the competing effect between composition gradient and crystallite size can explain the linear dependence of the grain tilt on the cation radius change (Fig. 8).

As stated before, it can be expected that the magnitude of the composition gradient depends on C_M. For a given C_M value a maximum composition gradient can be estimated assuming that all M atoms reside at one side of the growing crystal. In that case, the gradient is given by twice the average composition divided by the smallest distance between two metal atoms in the MgO lattice, i.e., the distance between two oxygen anions ($d_{O\text{-}O}$);

$$\left(\frac{\partial C_M}{\partial x}\right)_{\max} = \frac{2C_M}{d_{O-O}}. \qquad (5)$$

At the same time, since the crystallite size can be determined independently (see Fig. 10), it is possible to calculate the composition gradient $\frac{\partial C_M}{\partial x}$ by combining Eqs. (3) and (4) for known values of tilt and atomic radii. Subsequently, the ratio of the calculated $\frac{\partial C_M}{\partial x}$ to the maximum composition gradient $\left(\frac{\partial C_M}{\partial x}\right)_{\max}$ can be used to calculate the relative gradient according to the expression:

$$\left(\frac{\partial C_M}{\partial x}\right)_{relative} = \frac{\mathrm{a}\beta d_{O-O}}{k 2C_M \sqrt{3}\left(r_{Mg} - r_M\right)}. \qquad (6)$$

The relative concentration gradient for the various Mg-M-O systems is plotted in Fig. 11. The metals can be classified into two groups, i.e., Al and Cr with a relatively small and Ti, Zr, and Y with a relatively large $\left(\frac{\partial C_M}{\partial x}\right)_{relative}$ values. We suggest here that the small relative gradient

for Al and Cr indicates longer – as compared to the other metals –diffusion lengths that can even out compositional variations formed upon deposition. Moreover, enhancement of adatom surface diffusion is known to promote in-plane alignment.[19] Therefore, we argue that the larger diffusivity of Al and Cr leads to double in-plane preferential orientation in the Mg-Cr-O and Mg-Al-O systems, as opposed to the single in-plane orientation observed for Mg-Ti-O, Mg-Zr-O and Mg-Y-O.

IV. CONCLUSIONS

Biaxially aligned Mg-M-O thin films with columnar microstructure were deposited by means of reactive magnetron co-sputtering in a confocal configuration. It was found that when the two sputtering cathodes were equipped with the same target material (Mg), the in-plane alignment is defined by the source closest to the substrate, i.e., by the largest material flux. Thus, films exhibiting either single or double in-plane alignment could be deposited. Double in-plane alignment was also observed for the Mg-Al-O and Mg-Cr-O films, while Mg-Ti-O, Mg-Zr-O and Mg-Y-O exhibit single in-plane alignment. It is argued that the double in-plane alignment in the case of Mg-Al-O and Mg-Cr-O films is promoted by the larger diffusivity of Al and Cr compared to Ti, Zr, and Y. The grains and the columns of the Mg-Al-O, Mg-Cr-O and Mg-Ti-O films were found to be tilted towards the Al, Cr and Ti flux, respectively, while for the Mg-Zr-O and Mg-Y-O the tilt occurs towards the Mg material flux. The tilt of the grains can be understood from the difference of the two cation radius in the Mg-M-O cell, which triggers a distortion in the lattice. The stacking of the distorted cells in the grain results in a tilt of the columns. Both, grains and columns, tilt towards the direction of the material flux with the smallest cation radius.

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CAPTION OF FIGURES

FIG. 1. (a)-(e) (200) pole figures of Mg-Mg-O films deposited at various target-to-substrate distances. The arrows in (a) indicate the position of the two magnetron sources. (f) Plan view SEM image of the Mg-Mg-O film presented in (a). The white solid triangles indicate the direction of the crystal facets.

FIG. 2. (200) pole figures of Mg-Al-O thin films deposited at various target-to-substrate distances from the Al source, while the Mg source target-substrate distance was fixed at 10.5 cm. The dashed arrow indicates the direction of the Mg flux, while the solid arrow indicates that of the Al target. Variation of the Al target-to-substrate distance resulted in C_{Al} values of (a) 15, (b) 19, and (c) 27 %

FIG. 3. (a) Plan view SEM image of the Mg-Al-O film deposited at target-to-substrate distance of 10.5 and 18.5 cm for Mg and Al, respectively. The white solid triangles indicate the direction of the crystal facets. (b)-(f) (200) pole figures of Mg-M-O films deposited at different target-to-substrate distances. The dashed arrow indicates the direction of the Mg flux, while the solid arrow indicates the M flux direction. The C_M values are also provided for reference.

FIG. 4. Schematic representation of the 2D growth of triangular shaped [111] out-of-plane oriented grains with a {100} facets, for deposition using two cathodes, with M = Mg, Al, Cr, Ti, Y and Zr. The dashed lines indicate orientations with the largest capture length.

FIG. 5. Cross-section SEM images of (a) Mg-Al-O, (b) Mg-Mg-O, and (c) Mg-Zr-O thin films. The arrows indicate the material flux direction.

FIG. 6. Column tilt of the Mg-M-O thin films as a function of the grain tilt (as measured from the (111) pole figures). The red dashed line is fit of the data points to a linear function.

FIG. 7. High magnification EFTEM color map of the cross-sectional Mg-Cr-O with $C_{Cr} = 19\%$.

FIG. 8. Grain tilt angle in Mg-M-O films (as measured from the (111) pole figures) as a function of the corresponding change in cation radii. The red dashed line is fit of the data points to a linear function.

FIG. 9. (Online color) Schematic representation of alternating layers of the (111) densest packed planes of oxygen anions (blue) and metal cations (red).

FIG. 10. Crystallite size of the Mg-M-O films (calculated from the Scherrer's formula) as a function of $1/C_M$.

FIG. 11. Effective concentration gradient in the Mg-M-O films calculated from the experimental column tilting.