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The influence of Cr and Y on the micro structural evolution of Mg—Cr—O and Mg—Y—O thin films

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1. Introduction

MgO based materials are of scientific and technological importance because of their applications in optical and electronic devices and as protective coatings, single tunnel barriers and gas sensors — to name a few [1–6]. Among the various thin film deposition techniques, magnetron sputtering is widely used especially for good adhesion, high density and also high upscale potential. Thin film deposition by such physical vapor techniques often produces a columnar structure with a fibrous alignment, usually oriented perpendicular to the substrate [2,7–11]. Many material properties are highly sensitive to such grain morphology and grain alignment. Grain growth in thin films is critical for their reliability, e.g. optical coatings with small grain sizes have a minimum light scattering [12].

Most of the new technologically interesting materials are multicomponent oxides and they are widely studied for their fascinating properties and applications. These multi-elemental materials allow us to tune many parameters, including crystal structure, electronic structure and magnetic properties. Subtle changes in the strength of the interaction between the valence electrons as a function of the type and position of the metal ions can change the electrical conductivity from insulator to superconductor, or can introduce for instance magnetoresistence, antiferromagnetism or piezoelectricity [13].

ABSTRACT

The compositional influence of Cr and Y on the microstructure of Mg—Cr—O, and Mg—Y—O films synthesized by reactive magnetron sputtering has been investigated by transmission electron microscopy, X-ray diffraction and molecular dynamics simulations. A decrease in crystallinity is observed in these films as the M (Cr or Y) content is increased. It is found that M forms a solid solution with MgO for metal ratios up to ~70% and ~50% for Cr and Y respectively. Above ~70% Cr metal ratio the Mg—Cr—O films are found to be completely amorphous. The Mg—Y—O films are composed of Mg(Y)O and Y₂O₃ nano crystallites, up to ~50% Y metal ratio. Above this ratio, only Y₂O₃ nano crystallites are found. The preferential <111> MgO grain alignment is strongly affected by the increase in M content. For M metal ratios up to ~50%, there is a selective promotion of the <100> MgO grain alignments and a decline in the <111> grain alignments.

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In the case of a ternary compound, the addition of an extra element can influence the crystal growth, chemical bonding, structure and morphology. Some additives can suppress the growth entirely, others may enhance the growth [14], and some may exert a highly selective effect, acting only on particular crystallographic planes [3,14–18]. The concentration required to introduce effective changes will of course depend on the crystal system. The microstructure has a direct impact on the properties of these systems [9,14,16,17]. Hence, it is of critical importance to understand the influence of the concentration of foreign elements on the overall microstructure of the compounds. A literature review indicates very little TEM investigations and MD simulations on Mg—Cr—O and Mg—Y—O films with no details on the influence of the metal composition on the micro structural evolution. In our study, transmission electron microscopy (TEM), high resolution TEM, electron diffraction (ED), energy filtered (EF) TEM, electron energy low spectroscopy (EELS), X-ray diffraction (XRD) and molecular dynamics (MD) calculations are used to investigate the influence of Cr and Y on the micro structural evolution of Mg—M—O films.

2. Experimental details

2.1. Thin film deposition

The Mg—M—O thin films were deposited by dual reactive magnetron sputtering, using two pure metal targets. RCA-cleaned silicon with a native oxide layer was used as substrate and was placed facing the two cathodes at 45°. The target-substrate distance was



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Table 1					
Short-range	potential	parameters1	used	in the	simulation

i-j	A [eV]	ρ [Å]	C [Å ⁶ eV]
$Cr^{3+}-O^{2-}$	1313.18	0.31650	-
$Y^{3+}-0^{2-}$	1766.40	0.33849	19.43
$0^{2}-0^{2-}$	9547.96	0.21916	32.0

¹ K.J.W. Atkinson, R.W. Grimes, M.R. Levy, Z.L. Coull, T. English, J. Eur. Ceram. Soc. 23 (2003) 3059.

adjusted to obtain the desired film composition. In each series the composition of Mg—M—O was changed from pure MgO to pure M_xO_y . The deposition time was varied in order to achieve a film thickness of ~1 µm. All thin films were deposited at a fixed argon pressure of 0.8 Pa. The discharge current for the Mg and Cr magnetrons was 0.5 A, while for Y it was 0.8 A. An oxygen flow was introduced near the substrate and its value depends on the obtained metal composition.



Fig. 1. Low magnification TEM images of the cross-sectional Mg—Cr—O films with (a) 81% Mg metal ratio; the selected area ED patterns from regions 1 and 2 are from the film only and film/substrate interface respectively; (b) 58% and (c) 30% Mg metal ratios; the corresponding ED patterns (insets in (b-c)) are from the films.

All depositions were performed in metallic mode [19]. The experimental procedure is described in more detail elsewhere [20].

2.2. Chemical composition, crystallinity and microstructure analysis

The chemical composition was obtained using an electron probe microanalyser (EPMA) JEOL JXA-8621MX, with a beam current of 30 nA and a voltage of 15 keV. Based on the chemical composition, the Mg metal ratio is defined as Mg/(M + Mg). The Mg metal ratios are denoted as %Mg within the context. Crystallinity and microstructure were evaluated by XRD $\theta/2\theta$ with a LynxEye Silicon Strip detector mounted into a D8discover apparatus (Bruker axs) and TEM. The crystallinity studied by XRD $\theta/2\theta$ using pole figures was discussed in [21].

Cross section and plan view samples for TEM were prepared by mechanical grinding to a thickness of about 20 µm followed by ion-beam milling. The cross section samples were cut parallel to a cubic plane of the substrate, perpendicular to the contact plane. TEM investigations were carried out using JEOL 4000EX, JEOL 3000F and FEI Technai G2 microscopes operated at 400 keV, 300 keV and 200 keV respectively.

2.3. Molecular dynamics methodology

The methodology used to simulate the deposition of thin films by the MD model is described in detail in [22]. The MD package DL_POLY [23] is used to simulate the deposition of atoms. A driving program is written, which automates the deposition and relaxation. The MD method is a technique for computing the equilibrium and transport



Fig. 2. (a) High magnification TEM image from the film region of the 81% Mg metal ratio Mg—Cr—O film; (b) HRTEM image from the region within the white box in (a). The inset in (b) shows the FT of the viewing region.

properties of a classical many-body system. Giving an initial set of positions and velocities of a system of N atoms, Newton's equations of motion are solved for this system [24]. Therefore, the reliability of the MD results is largely determined by the interatomic potential used in the simulation [25]. In the present study a classical pairwise ionic potential [26] describes the interactions between atoms:

$$U_{ij} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + A \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^{\ell}}$$

where q_i, q_i are the charges of atoms i and j, r_{ii} is the distance between the atoms, and A, ρ and C are parameters fitted for each pair of ions. The first term is the Coulomb interaction, the exponential term represents the short range repulsion and the term $(-r_{ij}^{-6})$ accounts for van der Waals attraction. It has been demonstrated that this potential yielded good agreement with experiments for the structure of deposited Mg(M)O thin films (M = Al, Cr, and Y) [21,22]. The potential parameters used in the present simulations are summarized in Table 1. For all investigated systems a rigid-ion model has been used, i.e. the ionic polarization is not considered. The ionic polarization can have a considerable contribution in static simulations if the dielectric properties or long-range polarization energy for defects are calculated [25]. However, the present work is concentrated on the MD simulation of the thin film growth. Similar to the observations reported by other researchers [25,27,28], it is found that adding a shell model to describe the polarization effects increases the computational time substantially and it does not influence the structural properties of the film.

 Mg^{2+} , M^{3+} and O^{2-} ions in different ratios are deposited one by one on an amorphous (Al_2O_3) substrate surface. An amorphous substrate was chosen in order to avoid a possible influence of the crystalline



Fig. 3. (a) High magnification TEM image from the film region of the 58% Mg metal ratio Mg—Cr—O film; (b) HRTEM image from a region within the white box in (a); the amorphous regions are marked with arrows.



Fig. 4. (a) Intensity of XRD (111) and (200) peaks as a function of Mg metal ratio; and (b) MgO crystallite sizes calculated from the XRD peaks, using Scherrer's formula (P. Scherrer Göttinger Nachrichten Gesell. 2 (1918) 98), for Mg—Cr—O film series.

substrate on the structure or orientation of the growing films in the simulations, as it was observed in our previous work when a MgO (100) substrate was used [22]. The cut-off radius is set to 0.8 nm, i.e. the film does not interact with the substrate at z-coordinates higher than 0.8 nm and therefore no difference is expected in the structure of the films deposited on different amorphous substrates. Al₂O₃ was chosen because good potential data are available [21,22].

The simulated operating conditions, i.e. initial position and velocity of the deposited ions, time-step and ensembles used in the model, can be found in [22]. The simulation cell was increased in comparison with the simulation cell described in [21,22], so that the x- and y- dimensions were set to 3.4 nm (compared to 1.7 nm used in our previous studies). The substrate temperature was set to 700 K in order to account for substrate heating during plasma exposure. It was found that the small system presented in [21,22] can be used for the fundamental prediction of the structure, while a larger system can be used to study details of the polycrystalline structure. However, the crystallinity predicted by the study of the small system was also found back in the larger system. The advantage of studying a smaller system is the comparatively short CPU time needed to complete the simulations. Indeed, the depositions on the small substrates as described in [21,25] took ~2 weeks. With the same computational facilities, increasing the substrate surface by a factor of 4, results in an increase in the simulation time of the thin film deposition of the same thickness to ~4-5 months.

The films have been grown up to 5–6 nm thickness. This is considerably lower than the experimental film thickness, but necessary to keep the calculation time reasonable. Films with stoichiometry close to the experimentally deposited thin films were investigated, i.e. films with Mg metal ratios of 80, 70, 60, 50, and 33% (i.e. stoichiometry

of the spinel structure). The structure of the deposited thin films by the MD simulations has been defined by calculating the radial and angular (O—M—O and O—Mg—O) distribution functions (RDF and ADF, respectively), and coordination numbers (CN) of the cations in the films. In order to calculate the RDF, the central part of the film is cut, so that the layers close to the substrate and the free surface are excluded. The position of the first peak in the M—O RDF defines the range in which the corresponding O—M—O ADF is calculated and the coordination number of M is counted.

3. Results and discussion

3.1. Mg—Cr—O films

Fig. 1(a) shows the cross section TEM image of a Mg—Cr—O film with 81% Mg grown on a Si substrate $(a = 0.542 \text{ nm}, \text{Fd}\overline{3}\text{m}(227))$ [29]. The selected area ED patterns are from the film region (1) and the film/substrate interface region (2) respectively. The corresponding images for the 58% and 30% Mg films are shown in Fig. 1(b) and (c) respectively. The ED patterns here are from the film only. The 81% Mg film shows a clear columnar granular structure whereas the films with a lower Mg metal ratio of 58% have a rather dense fibrous structure. The Mg—Cr—O film with 30% Mg shows no morphological features. The elongated reflections on the ED pattern in Fig. 1(a) suggest a preferential grain alignment. On the other hand, the ED of the 58% Mg film (Fig. 1(b)) is a continuous, sharp ring pattern, which implies random grain orientations. The ring pattern of the 30% Mg film (Fig. 1(c)) is very diffuse and broad, implicating a decreased crystallinity of the films. The ED patterns can be indexed as cubic MgO (a = 0.42 nm, space group $Fm\overline{3}m$ (225)) [30].

High magnification TEM images show the rather dominant columnar texture observed for the 81% as compared to the 58% Mg films (Figs. 2 and 3). The inclination (angle) of the columnar grains appears to be slightly misoriented away (<15°) from the perpendicular direction to the substrate (100) plane (Figs. 1 and 2). Fig. 2(b) is a HRTEM image from the area marked with the white box in (a). The Fourier transform (FT) (inset in Fig. 2(b)) of the grains is from the viewing region in (b). They can be matched to [011]* MgO. The ED pattern in Fig. 1(a) shows that Si [100] is parallel to MgO [111] (with a slight misalignment). This means that there is an out of plane preferential growth of the MgO grains along <111> parallel to Si substrate <100>.

Texture development has been observed during grain growth of fcc thin films and at certain deposition conditions they are found to exhibit a tendency to develop a <111> columnar texture which is associated with these closed packed planes [7,8,31]. Pure MgO (100% Mg metal ratio) films grown under the given deposition conditions are found to grow with a preferential out of plane <111>

alignment. The pure Cr_2O_3 (100% Cr metal ratio) films are found to be amorphous in structure. XRD study on the Mg—Cr—O films (Fig. 4(a)), suggests that the preferred <111> alignment of the MgO grains decreases as the Mg metal ratio decreases (100%>Mg>30%). However, MgO <100> grains are found to increase for the metal ratios between 80%>Mg>50%.

The level of crystallinity on the micro structural level is evident from the HRTEM images shown in Figs. 2 and 3. There appear to be small amorphous regions and randomly oriented grains in the 58% Mg films as compared to the 81% Mg films. It is also evident that the grains in the lower Mg metal ratio are smaller than those from the higher Mg metal ratio films. This is in agreement with the XRD study (Fig. 4(b)), which indicates that the MgO grain size decreases from ~23 nm to ~4 nm, as the Mg metal ratio decreases from about 100% to 40%.

Fig. 5 shows the snapshots from the MD simulation of Mg—Cr—O thin films with 80, 60 and 33% Mg. The 80% Mg film clearly exhibits a high level of crystallinity. By rotating the 60% Mg film in 3D, it can be observed that there are small regions which are crystalline and have random orientations to each other. Amorphous regions are also observed. Similar to the TEM observations, the MD snapshot for the 60% Mg film also contains a polycrystalline grain structure mixed with amorphous regions. The 33% Mg film is amorphous in structure. In agreement with the experimental results, a decrease in crystallinity is also predicted by the MD simulation.

The XRD spectra (not shown here) of these films also show a shift in the Bragg reflections of MgO (111) and (200) towards higher 2θ indicating a decrease in the MgO lattice parameters as Mg cations are replaced by Cr. This is also confirmed by the MD calculation of the O—O distance [21]. Further, based on the calculated RDFs, ADFs, and CNs results (not shown here), the crystalline regions of these films (~50% to 80% Mg), are found to have Cr in solid solution with MgO. Fig. 6(a-b) shows the EFTEM colour maps for the Mg—Cr—O film with ~81% Mg. These colour maps are a combination of the individual jump ratio maps of Mg, Cr and O. From these maps it is evident that there is an inhomogeneous distribution of Cr and Mg within the Mg(Cr)O solid solution. A STEM (scanning TEM) EELS study of 50 measurements at the top of the film and 50 measurements at locations in the bottom of the film leads to an average Mg/Cr ratio of 3.1 for the top part and Mg/Cr = 5.4 at the bottom part. A standard deviation of 1.12 for top and 2.99 for bottom is found. This standard deviation is far higher than the estimated deviation due to instrumental noise (<0.1)and can be attributed to inhomogeneities in the Mg/Cr ratio, as is also visually obvious from Fig. 6. From this, it can be stated that the Mg/Cr ratio is higher at the bottom of the film as compared to the top making use of a right tailed Student T-test (p value $1.12E^{-6}$). The average Mg/Cr ratio of this film from the EELS study (4.3) is in agreement with that from the EPMA results (4.4 ± 0.1) .



Fig. 5. Snapshots of Mg—Cr—O thin films obtained by MD simulations on an amorphous Al₂O₃ substrate with 80%, 60% and 33% Mg metal ratio. The colour code is shown at the left.



Fig. 6. (a) EFTEM colour maps of the cross-sectional Mg—Cr—O film with 81% Mg metal ratio. Each map is a combination of the individual jump ratio maps of Cr, Mg and O; the colour legend is shown in the lower left side of the image; and (b) high magnification colour map acquired from the top part of the film.

3.1.1. Discussion

3.1.1.1. *Microstructure*. Due to the non equilibrium nature of the vapor deposition methods, the microstructure of thin films is controlled fundamentally by their deposition conditions [7,8,31]. In physical vapor deposition (PVD) techniques, the governing factors are the temperature, aggregation/incorporation of depositing adatoms (geometry) and ion bombardment (reactive gas) [7,8,31].

Under thermodynamic conditions one would expect a structural transition from MgO (rock salt) to $MgCr_2O_4$ (spinel) to Cr_2O_3 (corundum) as the Cr metal ratio increases [21]. However a transition from a crystalline (pure MgO) to an amorphous (pure Cr_2O_3) structure obtained in the current films suggests that the growth process is kinetically driven. Numerous authors [7,9,10,32,33] have classified the microstructure of polycrystalline thin films based on the so called 'structure zone model'. According to these classifications the Mg—Cr—O



Fig. 7. Low magnification TEM images of (a-b) cross sectional 82% and 71% Mg and (c-d) plan view 82% and 53% Mg metal ratio Mg—Y—O films. The corresponding ED patterns (inset) are from the film.

films undergo a micro structural transition from zone T to zone 1 as the Cr content increases. These zone (1, T) morphologies are known to occur in the low thermally-induced mobility regimes [7,9,10,32,34]. Here the grain growth is primarily controlled by surface diffusion [7,9,11].

The structure evolution in thin films can also be strongly influenced by the amount of impurity (additive) concentration [35,36]. In the current study, with the decrease in crystallinity in the Mg-Cr-O films (smaller grain size, random grain orientation-weakening texture), it is apparent that the incorporation of Cr hinders the columnar structure formation. During the growth process, the impinging Cr can be adsorbed and segregated on the growing crystal faces and dissolved in the MgO crystal lattice. In the low temperature growth regime where volume diffusion is effectively frozen, solute (Cr) atoms can be trapped along the boundaries or surfaces. The surface chemical interaction of the Cr species and segregation conditions may depend on the type of crystallographic plane. Each (hkl) plane may display unique diffusion phenomena; e.g. for the MgO rocksalt structure the lowest surface mobility occurs at the (111) planes, whereas for the body centered cubic structure of Cr this takes place at the (100) planes [8]. According to Stubican [37] a divalent ion diffuses more rapidly than a trivalent ion at the surface layer of MgO. Moreover, trivalent Cr substituting divalent Mg in the MgO matrix has larger bond strength. The bond strengths of Cr-O and Mg-0 are 461 \pm 9 kJ/mol and 363.2 \pm 12 kJ/mol [38] respectively.

Besides, in the formation of Mg(Cr)O, the incorporation of Cr (up to ~70%), inevitably leads to volume changes and distorts the MgO crystal lattice. There will be a lattice distortion when a different valence and a smaller cation (Cr) substitutes for Mg. The cation radii of Cr^{3+} and Mg^{2+} are 0.62 Å and 0.72 Å respectively (~14% difference) [38]. The volume change and the lattice distortion would be expected to increase as the Cr content increases. So at contents exceeding 70%, this may lead to an unstable lattice and induce a completely amorphous structure. A detailed reasoning regarding the lattice distortion and the possibilities of this unstable structure is described elsewhere [21].

Thus, the micro structural evolution from a textured grain alignment to a more random orientation and finally to a completely amorphous structure can be envisaged by the retardation of the surface mobility of the adparticles and the unstable MgO lattice [21] as the Cr content is increased.

3.1.1.2. Crystallographic orientation (texture). From a thermodynamic point of view, the presence of large intrinsic stresses (and strain) is also known to play a role in understanding the texture evolution in thin films [14,16,31,39]. However, Gall et al. [40] and Greene et al. [31] have reported that a variety of kinetic effects associated with the growth process itself is also equally or even more important in determining the film growth orientation. As discussed earlier the low temperature (<673 K) growth process of these Mg—M—O films is associated to kinetics. So the texture evolution will to a greater extent be controlled by the kinetic effects of the reactive magnetron sputter deposition technique rather than by thermodynamics [7,31,40].

In the present study there is a transformation of the preferred [111] orientation of pure MgO to random orientations as the Cr metal ratio is increased (up to ~70%). In the case of zone T conditions, a preferential out of plane orientation is caused by an evolutionary overgrowth in which the grains oriented with the geometrically fastest growing direction perpendicular to the substrate overgrow other grains. Details of this mechanism are described elsewhere [7,8]. In the Mg—Cr—O films with a metal ratio 100%>Mg>50% (as the Cr concentration increases), there is a dramatic change in the texture of the MgO grains. There is an increase of the [100] aligned grains during the competing texture evolution between mixed [100] and [111] textures. However, this selective promotion of the [100] aligned grains is only up to a certain Cr concentration (~50%), above which a decrease in both [111] and [100] alignment is observed. Therefore it can be concluded that only up to ~50% Cr, [100] oriented grains are favored.



Fig. 8. HRTEM image of the Mg—Y—O film with 71% Mg metal ratio. The inset shows the FT of the nano crystallites. The arrows depict the amorphous regions.



Fig. 9. (a) MgO crystallite sizes calculated from the XRD peaks, using Scherrer's formula; and (b) XRD $\theta/2\theta$ spectra for the Mg—Y—O film series.

One of the possible mechanisms for the evolution in the crystallographic orientations of these grains may be influenced by the inhomogeneity in the Mg(Cr)O solid solution. Different concentrations of Cr distribution on different MgO grain boundaries and surfaces could result in a growth competition related to orientation selection among neighboring crystals. The selection mechanism could be based on the different growth rates along the crystallographic directions and the respective crystal face dependent segregation.

3.2. Mg—Y—O films

A prominent fibrous columnar structure is observed in the cross sectional Mg—Y—O films (Fig. 7(a)) with 82% Mg as compared to the weaker features observed in the 71% Mg films (Fig. 7(b)). The TEM plan view images (Fig. 7(c-d)) of the films with 82% and 53% Mg respectively also show a decrease in the level of texture and crystallinity.

The ED patterns (insets in Fig. 7) can be indexed as cubic MgO together with Y_2O_3 (a = 1.06 nm, space group Ia $\overline{3}$ (206)) [41]. The ring patterns reflect the polycrystalline nature of these films. It has been reported [42] that depending on the deposition conditions, Y_2O_3 thin films grown on Si substrates are often polycrystalline and display different crystallographic orientations.

Compared to the higher Mg metal ratio films, the ring diffraction pattern of the 53% Mg films (Fig. 7(d)) are more diffuse. The rather dense and sharp ring diffraction patterns of the higher Mg metal ratio films implies the presence of small crystallites as compared to the short range ordering in the latter. HRTEM images of the Mg—Y—O films with 82% (not shown here) and 71% Mg (Fig. 8) show the presence of nano crystallites. The FT from the nano crystallites can be indexed to match either the cubic structure of MgO or Y_2O_3 (Fig. 8).

In addition to the dominant $[011]^*$ zone axis of MgO and Y_2O_3 crystals, there are some $[001]^*$ oriented nano crystallites as well. Their size ranges between 4 and 10 nm. This is in agreement with the XRD analysis (Fig. 9(a)). Some small regions within both films (shown by black arrows) appear to be amorphous (Fig. 8). Because of the smaller size of the crystallites and the presence of amorphous regions in these Mg—Y—O films they lack a prominent texture as compared to the Mg—Cr—O films of the same metal ratio.

The XRD spectra (Fig. 9(b)) of the Mg—Y—O series show a shift of the (111) and (200) MgO Bragg reflections towards lower 2θ with decreasing Mg metal ratio. The XRD peak shift indicates an increase in the MgO lattice parameter with the incorporation of Y (cation radius of 0.90 Å [38]) or increasing O-O distance as calculated by the MD simulation [21]. The <100> MgO grain alignment is more prominent at higher Mg metal ratios (~85%) as compared to the Mg-Cr-O films (~70%). A decrease in the preferred <111> MgO grain alignment is also observed in the Mg—Y—O films as the Y content increases. Films with a Mg metal ratio less than 82% exhibit broad peaks associated to Y_2O_3 (region between $2\theta \sim 25$ and $\sim 33^\circ$, see Fig. 9(b)). The broad peaks in XRD suggest the presence of domains in the nano range. However, no Y₂O₃ was detected in the 82% Mg films. TEM analysis detected Y₂O₃ nano crystallites in the 82% Mg film but less compared to the 71% Mg film. This probably explains why it was not detected by XRD. The Y₂O₃ (100% Y metal ratio) films are polycrystalline.

Fig. 10 shows EFTEM images of the Mg—Y—O film with 71% Mg. The elemental maps of Mg, Y and O suggest that all elements are homogeneously distributed within the film with no apparent segregation. However, at the magnification of these elemental maps the presence of Mg(Y)O and Y_2O_3 nano crystallites (~4–10 nm) is difficult to distinguish. Besides, there are much lesser Y_2O_3 nano crystallites as



Fig. 10. EFTEM images of the cross-sectional Mg-Y-O film with 71% Mg metal ratio. The elemental maps are for Y, O and Mg.

compared to Mg(Y)O. Higher spatial resolutions lead to a decrease of the signal to noise ratio of Y, thus leading to very noisy elemental maps.

Fig. 11(a) presents snapshots of Mg—Y—O thin films obtained by MD simulation with 80%, 70% and 50% Mg metal ratio. In agreement with the experimental results, they also show a decrease in crystallinity as the Y content is increased. A lower level of crystallinity is observed at 80% Mg as compared to the Mg—Cr—O film at the same metal ratio (Fig. 5). The Mg—O and Y—O RDFs of the film at 80% Mg (Fig. 11(b)) are compared with the Mg—O RDF profile in the MgO crystal. The O—Mg—O and O—Y—O ADFs are shown in Fig. 11(c). The bold vertical lines present the bond angles in the MgO perfect crystal (cubic, space group $Fm\overline{3}m$). The calculated CN of Mg and Y are 5.4 and

5.8 respectively. Based on these distribution functions and CNs, it is also found that the crystalline region in this film has a structure of MgO with Y in solid solution. The transition region to an amorphous structure for the Mg—Y—O simulated films is found at a higher Mg metal ratio (between 60 and 80% Mg) as compared to the Mg—Cr—O films. Similar to the TEM observations (Fig. 8), the structure of the film with 70% Mg (Fig. 11(a)) consists of small randomly oriented crystals embedded in amorphous regions. However due to their small size and random orientations, the structure of these observed crystals from the MD simulations cannot be identified.

The Mg—O and Y—O RDFs and the O—Mg—O and O—Y—O ADFs of the films with 50% Mg are shown in Fig. 11(d) and (e) respectively.



Fig. 11. (a) Snapshots of Mg—Y—O thin films obtained by MD simulations on an amorphous Al₂O₃ substrate with 80%, 70% and 50% Mg metal ratio. The colour code is shown at the left; (b) Mg—O and Y—O RDFs, (c) O—Mg—O and O—Y—O ADFs in the Mg—Y—O film with 80% Mg metal ratio. The Mg—O RDF and bond angles (vertical bold lines) in a MgO crystal are shown for comparison in (b) and (c) respectively; (d) Mg—O and Y—O RDFs, (e) O—Mg—O and O—Y—O ADFs, (e) O—Mg—O and O—Y—O ADFs, and (f) Y—Y RDF in the Mg—Y—O film with 50% Mg metal ratio. The Y—O RDF, bond angles (vertical bold lines), and Y—Y RDF in a Y₂O₃ crystal are shown for comparison in (d), (e) and (f) respectively.

They are also compared with the data for a perfect Y_2O_3 crystal (cubic, space group *la*3). The Mg—O RDF and O—Mg—O ADF profiles represent an amorphous structure. The calculated CN of Mg decreases to 4.5, which means that the Mg position changes towards a tetrahedral site (CN=4) [21]. Although the Y–O RDF profile also represents an amorphous structure, the O-Y-O ADF profile (Fig. 11(e)) describes the bond angles of a perfect Y_2O_3 crystal. Further, the calculated CN of Y is 5.7, close to the CN of Y (CN = 6) in the perfect crystal. The comparison between the Y—Y RDF of the 50% Mg film and that of a perfect Y_2O_3 crystal (Fig. 11(f)) also represents some order in Y-Y. Analyzing these distribution functions and the CN of Y, it is found that there is some ordering of Y and O in the film similar to that found in a Y₂O₃ crystal.

3.2.1. Discussion

The structural transition of the Mg(Y)O polycrystalline grains to amorphous may also be related to the low adatom mobility and the unstable Mg(Y)O lattice [21], induced by the presence of Y, which is much larger and has a different valence. Indeed, the Y³⁺ radius (0.90 Å) is significantly larger than that of Mg²⁺ (0.72 Å) (~25% difference) [38]. This effect is similar to the case of the Mg-Cr-O films. The presence of separate Y₂O₃ nano crystallites may be understood as follows. Up to a certain extent the MgO lattice can accommodate Mg being replaced by Y. Any exceeding Y can form an oxide. It is known that ionic bonds also have some covalent character. The degree of covalency of Mg–O is considerably lower compared with Y—O [43]. Thus, when Y atoms are coordinated by O atoms they tend to retain their coordination sphere unlike in the case of Mg atoms. This directional dependence of Y-O bonding may promote its tendency to remain as Y₂O₃. Indeed there is the possibility of a very low content of Mg substitution in the Y₂O₃ lattice. Hence as the Y content is increased (up to ~50% Y), the Mg-Y-O films consist of mixed nano crystallites of Mg(Y)O and Y_2O_3 . Above ~50% Y, the films only consist of Y2O3 nano crystallites.

4. Conclusions

By comparison of experimental and simulation results, the influence of Cr and Y on the microstructure of Mg-Cr-O and Mg-Y-O films synthesized by a reactive magnetron sputtering technique has been investigated. The crystalline nature of the Mg-Cr-O and Mg-Y-O films is found to decrease with the increasing M content. It is found that Cr and Y form a solid solution with MgO, for Mg metal ratios 100%> Mg>30% (for Cr) and 100%>Mg>50% (for Y). Below ~30% Mg the Mg—Cr—O films are found to be completely amorphous. The Mg—Y—O films are composed of Mg(Y)O and Y₂O₃ nano crystallites for Mg metal ratios between 100%>Mg>50%. The size range of these nano crystallites is ~4–10 nm. Below ~50% Mg the Mg—Y—O films exhibit only Y_2O_3 nano crystallites. The microstructural transition from crystalline to amorphous is linked to the low adatom surface mobility and to the unstable MgO lattice as the M content is increased. The columnar MgO grain growth is suppressed as the M content increases. As a result, a decline in the preferred <111> MgO grain alignment is observed. However, the grains with <100> alignment are favored up to about 50% M content.

This work also shows that the MD simulations could predict not only the general trends but also the details of the microstructure.

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