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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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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 Y_2O_3 nano crystallites up to ~50% Y metal ratio. Above this ratio, only Y_2O_3 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.

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 multi-component 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].

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 parameters[1] used in the simulation.

i–j	A [eV]	ρ [Å]	C [Å^6 eV]
Cr^{3+}–O^{2-}	1313.18	0.31650	–
Y^{3+}–O^{2-}	1766.40	0.33849	19.43
O^{2-}–O^{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.

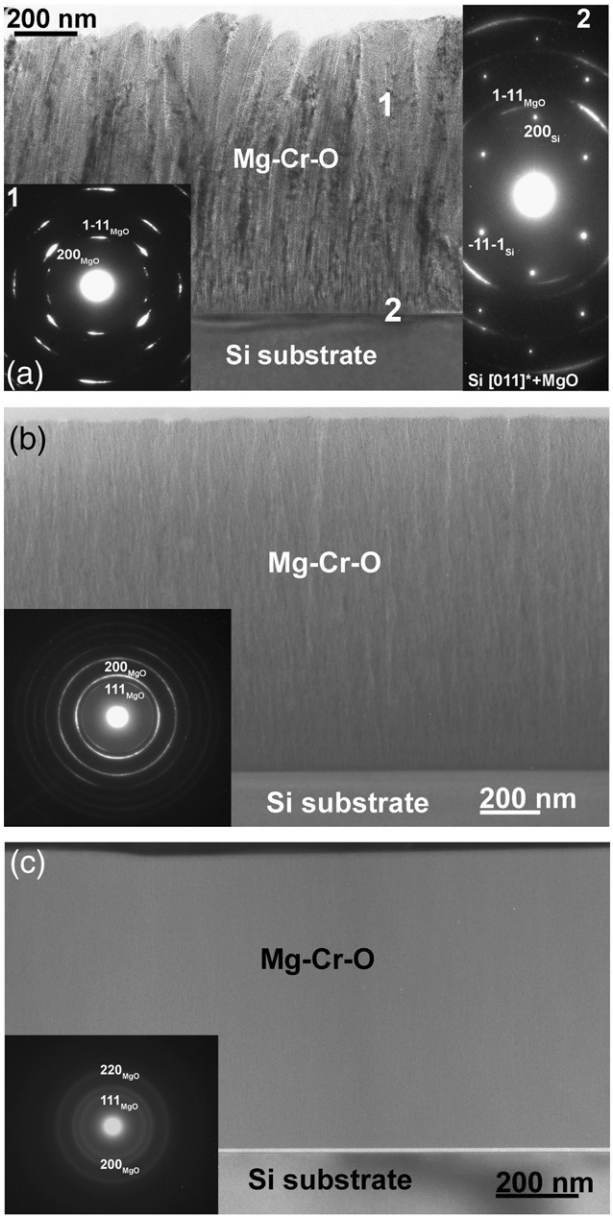

Fig. 1. Low magnification TEM images of the cross-sectional Mg—Cr—O films with (a) 81% Mg metal ratio; the selected area ED patterns from regions 1 and 2 are from the film only and film/substrate interface respectively; (b) 58% and (c) 30% Mg metal ratios; the corresponding ED patterns (insets in (b-c)) 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 θ/2θ with a LynxEye Silicon Strip detector mounted into a D8discover apparatus (Bruker axs) and TEM. The crystallinity studied by XRD θ/2θ 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

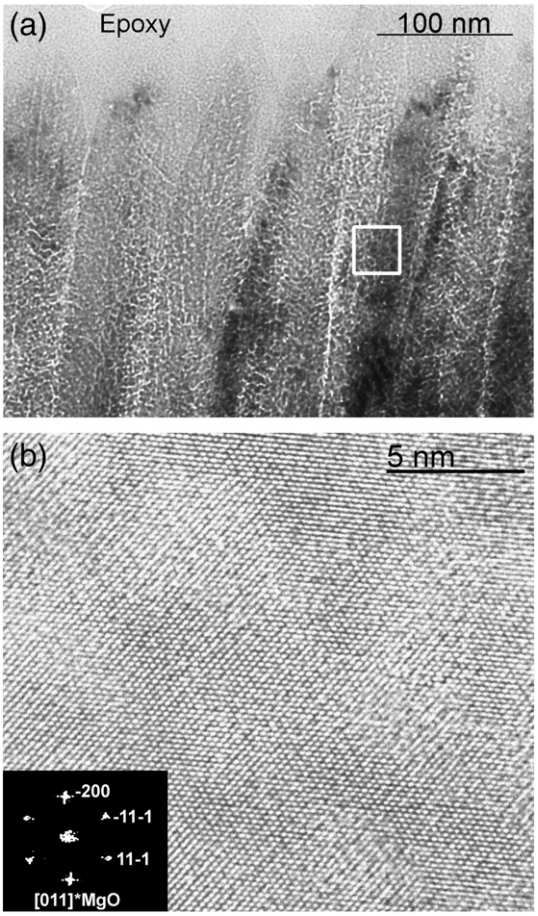

Fig. 2. (a) High magnification TEM image from the film region of the 81% Mg metal ratio Mg—Cr—O film; (b) HRTEM image from the region within the white box in (a). The inset in (b) shows the FT of the viewing region.