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Short communication

The influence of the pressure on the microstructure of yttria-stabilized zirconia thin films deposited by dual magnetron sputtering

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ABSTRACT

Mixed oxide thin films, such as yttria-stabilized zirconia, deposited by dual reactive magnetron sputtering on a non-rotating substrate show a typical microstructure of bended, or tilted columns. Two effects define the tilt. The first effect is the compositional gradient over each column which results in a different lattice spacing. To accommodate this difference, the column bends. As such, the chemical composition has a major influence on the final columnar tilt. The second effect is ballistic shadowing which is controlled by the pressure-distance product. At higher pressure-distances, this second effect plays a more prominent role, and a different behaviour of the columnar tilt as a function of the film composition is noticed. The experimental trends can be understood by the use of a particle trajectory code which provides the angular and energy distribution of the atoms to a ballistic aggregation Monte Carlo code simulating the resulting microstructure.

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During the last decade there is an increasing interest for multi-component films. This is not surprising given their wide range of properties and hence different applications. Indeed, most of the new technological materials have a complex chemical (and crystalline) structure. These multi-elemental materials allow to tune many parameters, including lattice constants, electronic band structures, and magnetic properties. Materials research is however not only tailoring deposition conditions to obtain the desired properties, but more and more changing the composition and microstructure to adjust the intrinsic material properties. The role of combinatorial research becomes therefore more prominent. The interpretation of the obtained results for some studies must be handled with some care because when the substrate is not rotated a link between the microstructure, texture and composition can exist. Without substrate rotation, the deposition of mixed oxide thin films by dual reactive magnetron sputtering results indeed not only in a compositional gradient over the deposition area. The compositional gradient will depend on the inclination angle of the two magnetrons (A and B), and can be quite strong when the inclination angle is large. At low processing pressure, the gradient affects the thin film microstructure. The constituent columns are bent or shows a clear tilt. As shown in previous studies for Mg(M = Al, Cr, Mg, Ti, Y, Zr)O [1] and YSZ (yttria-stabilized zirconia) thin films [2–4], the tilt is defined by a difference in composition over the column width. The column side exposed to target A (Mg or Zr) has a higher concentration for element A as compared to the opposite column side which is more abundant for element B (Al, Cr, Mg, Ti, Y, Zr in the case of Mg(M)O thin films, or Y in the case of YSZ). As element B substitutes element A in the oxide lattice of A_nO_m (MgO or ZrO_2), a different lattice parameter is obtained at the two opposing sides of the columns. Analogous to a bimetal, where two metal strips with different thermal expansion coefficients are joined together, the difference in lattice expansion results in the bending of the column. A straightforward model to predict the tilt angle was previously proposed [4]. Fig. 1 illustrates the above discussion at a glance. It shows for a low pressure experiment (0.5 Pa) the columnar tilt as a function of the position on the substrate which defines the average chemical composition of the sample. There is a clear link between the composition and the columnar tilt. The experiments presented in this paper have been discussed in depth in Refs. [2–4], and we refer to these references for more details on the experimental conditions. In short, the thin films were deposited by dual reactive magnetron sputtering using a Y target and a Zr target. By local reactive gas addition at the substrate position, fully oxidized thin films could be deposited in metallic mode, i.e. at high deposition rate. The change in Y content was ensured by

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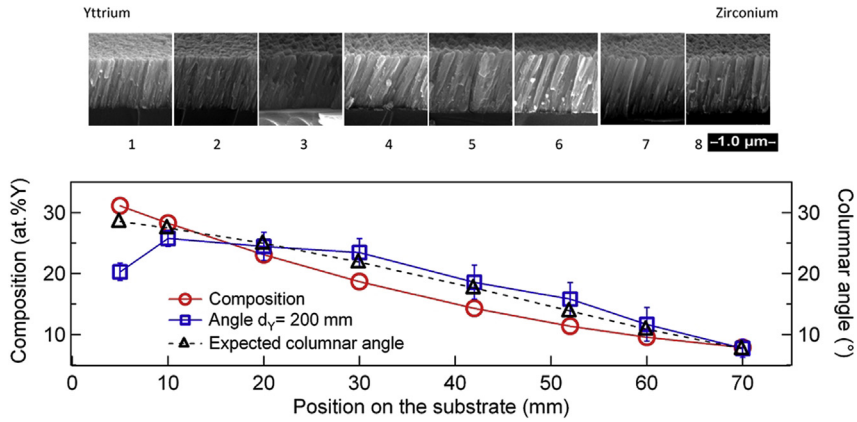

Fig. 1. The top figure shows a compilation of SEM cross sectional images taken at different positions along a 76 mm long glass substrate. The inclination angle of both magnetrons was 45°. The target centres were focused to the same point on the glass substrate. The centre of the glass plate was 90 mm from the Zr target, while 200 mm from the Y target. The pressure was fixed at 0.5 Pa. Other details of the deposition conditions can be found in Refs. [2–4], and in the text. The bottom figure shows the composition (expressed in at.%Y, left axis, circles) of the film shown in the top figure, together with the measured columnar angle (right axis, squares) as evaluated from the shown film cross sections. The result of the model discussed in Ref. [4] is also shown (right axis, triangles).

altering the Y target–substrate distance. Other parameters, such as target currents ($I_Y = 0.2$ A, $I_{Zr} = 0.5$ A) and the Zr target–substrate distance ($d_{Zr} = 90$ mm) remained constant. Two series of experiments were performed at low (0.5 Pa) and high (0.95 Pa) argon pressure. The influence of the oxygen addition on the total pressure was negligible as the deposition was performed in metallic mode. Fig. 2 summarizes the main experimental results. At low argon pressure (0.5 Pa, left figure) the columns and the grains of the thin film tilt when the yttrium is increased, i.e. when the Y target is brought closer to the substrate. This can be understood from the (200) pole orientation. At low yttrium content no tilt is observed and the (200) pole coincides with the normal on the substrate. As the yttrium content increases, the (200) pole orientation follows to a first approximation the striped line which indicates the substrate position. The right hand side of the pole figures corresponds with the position of the zirconium target. This allows to conclude that at high yttrium content, the (200) pole points, just as the columns, towards the zirconium target. The strong tilt observed at high yttrium content almost coincides with the [111] direction. At high argon pressure (0.95 Pa, see right figure), the tilt of the columns or grains hardly changes with the yttrium content. At low yttrium content a strong tilt towards the Zr target is observed, but approximately the same tilt is observed at high yttrium content. The main difference as a function of the yttrium content is a larger spread of the columnar (or grain) tilt. In summary, the experiments show a clear dependence on the Y content of the columnar tilt at low pressure, while at high pressure no influence of the Y content was noticed. In this short communication the reason for this difference will be addressed by the assistance of Monte Carlo simulations. The choice for this approach is inspired by the importance of ballistic effects at higher pressure. An increase of the pressure results in more scattering of the sputtered atoms by the sputter gas atoms. As a result, the energy of the sputtered atoms is strongly decreased, the deposition profile is modified, and the deposition rate decreases. All these effects strongly influence the final thin film microstructure. It is well known that at higher pressure more porous thin films are obtained. At constant pressure an equivalent mechanism occurs by increasing the target to substrate distance. The microstructure of these films grown can be modelled using so called ballistic aggregation Monte Carlo simulations (e.g. Refs. [5–7]). This kind of models is applicable under zone I conditions [8] where the mobility of the arriving atoms at the substrate is low, i.e. at high pressure-distance products, and their importance in elucidating the processes during sputter deposition have

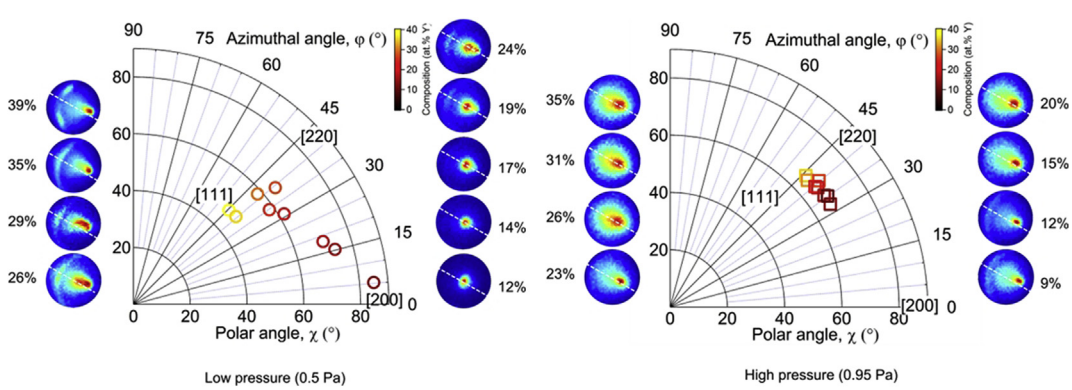

Fig. 2. The tilt angle of the columns based on the (200) pole figures measured at different Y concentrations. The composition was varied by a change of the Y target-substrate distance. The Y concentration expressed in atomic percentage is mentioned next to the respective pole figure. The striped line on the pole figure indicates the position of the substrate. The Y target is located on the left hand side of the striped line, while the Zr target is positioned on the right side. The left figure shows the change of the tilt angle at low pressure while the high pressure experiment is shown on the right hand side.

demonstrated by many authors [9–13].

The code used here, Simul3D [5], treats each atom as a cubic pixel. These pixels form the basic unit of the simulator and the final microstructure is built on the cubic lattice. The final position of the particles is not only defined by their incoming angle, and energy, but Simul3D also allows atom mobility depending on the number of neighbouring particles. The incoming direction of the atoms arriving at the substrate is modelled by the SIMTRA code [14,15]. The latter is a particle trajectory code which follows sputtered atoms from the target towards their final position, accounting for gas scattering. A crucial point in the input file of SIMTRA is the nascent angular distribution, i.e. the angular distribution of the Y and Zr atoms which leave the target. This distribution does not only depend on the target/gas combination but it is also affected by the target roughness and usage. To obtain the angular distributions for both target materials, the following strategy was used. The composition of 9 samples deposited at different Y target–substrate distances (80 up to 240 mm in steps of 20 mm) was measured by EDX along the sample at 6 different positions, which results in 54 data points. SIMTRA simulations were performed using the angular distribution of both targets as a fitting parameter. More specific, the angular distribution was described by

$$s_i(\theta) = \cos\theta\left(1 + \beta_i \cos^2\theta\right) \quad (1)$$

with i = Zr, Y. Hence, the simulations were repeated for different values of β until the error between the experimental and the calculated composition was minimal. As Fig. 3 (left) shows the value of β for Y is clearly defined at −0.5 which results in an under-cosine distribution. For Zr the value of β is less well defined but the best fit is obtained for $\beta_{Zr} = 0$, i.e. for a cosine distribution. With the optimized angular distributions at hand it is possible to calculate the impact angle of the arriving atoms at the substrate. The results for the Y atoms at different target–substrate distances and for the two experimental pressures are shown in Fig. 4. At low pressure, most atoms arrive at an angle of 45° with the substrate, i.e. the angle between the target normal and the substrate normal. At higher target–substrate distance, a stronger deviation is noticed, and the contribution of atoms scattered by the sputter gas becomes more important. As the scattering process is defined by the distance-pressure product, it is not surprising that at higher pressure, atoms have almost the same probability to arrive from both sides (see Fig. 4, right). Only at short distances (90 mm) a preferential direction is noticed. As the Zr target is always located at 90 mm, the pressure effect is indeed less strong for the Zr impact angle distribution.

The SIMTRA output files have been used as input for the Simul3D simulations of the microstructure. Only the angular distribution of the arriving atoms was used in the simulations. As the arriving energy of the Zr atoms is always somewhat higher than for yttrium, the atom mobility of zirconium and yttrium was respectively set at 3 and 2 displacements during the simulation. It is however important to realize that this small difference will have a minor impact on the simulation results because Simul3D mainly highlights the ballistic contribution. For both pressures and at the different Y target–substrate distance simulations of zirconium and yttrium thin films were performed with the composition given by the experiments (see Fig. 5, central images highlighted by a stripped box). To get a better view on the ballistic contribution of each individual target also pure zirconium and yttrium thin film were simulated (see Fig. 5, bottom and side images).

For the pure thin films, a straightforward influence of scattering is noticed, i.e. an increase of the pressure and/or of the distance produces less tilted columns. Similar results have been previously reported [16,17], however only for the influence of the pressure. For the mixed compositions (central images highlighted by a stripped box in Fig. 5), two trends can be seen. First, at low pressure and whatever the Y target–substrate distance, the columns at the yttrium side have a higher yttrium concentration which is consistent with the STEM-EDX results reported in Ref. [4]. At high pressure, except for 80 and 120 mm, the yttrium is more equally distributed in the zirconium columns. A second trend is related to the columnar tilt. For both pressures, a gradual change of the columnar tilt, starting from the pure Zr thin film (bottom figures) is noticed when the Y target–substrate distance is increased. Hence, the target which provides most atoms to the substrate defines the columnar tilt.

The simulations allow to understand the different behaviour of the tilt angle at high pressure as compared to the low pressure experiment. It is important for the discussion that Simul3D simulation do not account for any lattice parameter changes. Or stated differently, the microstructure is purely defined by the impact angle of the atoms, shadowing effects, and a limited diffusion. It means that any difference with experimental results will find its origin in the effects induced by the energy of the particles and the crystal structure of the material. The Simul3D simulation shows at

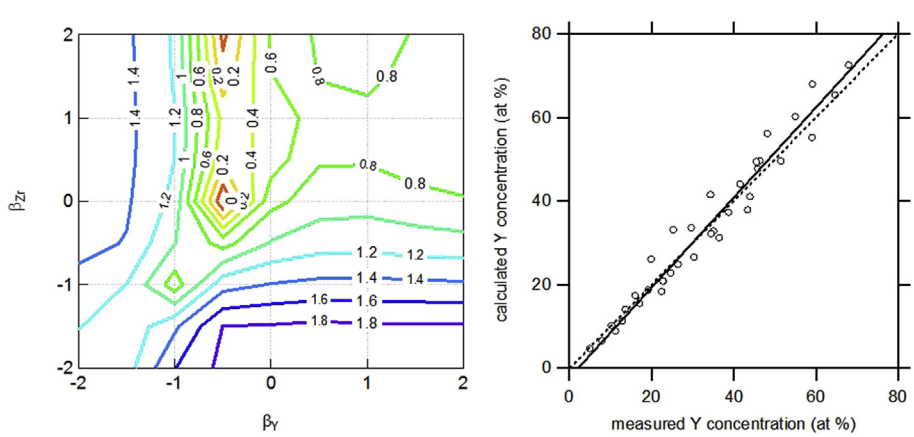

Fig. 3. Left. Optimization of the angular distributions for Zr and Y. The figure shows the relative error between the measured and simulated composition as a function of β for Zr and Y. β defines the angular distribution of the sputtered atoms as defined by Eq. (1). Right. Correlation between the measured and simulated composition for the optimized condition, i.e. $\beta_Y = -0.5$ and $\beta_{Zr} = 0$. The striped line corresponds to the 1:1 correlation, while the full line is a linear fit through the data points.

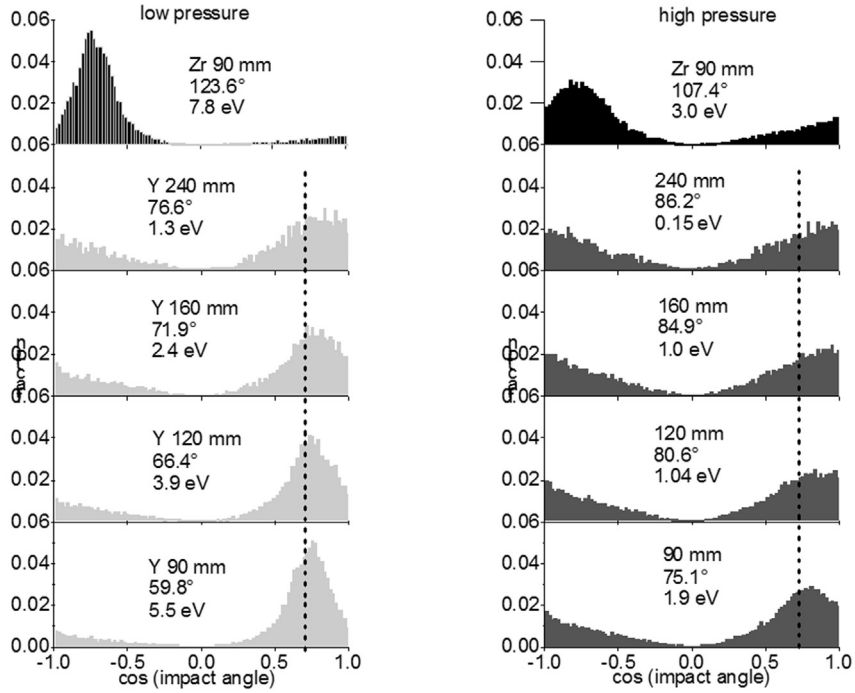

Fig. 4. The calculated impact angle distribution of yttrium atoms (4 bottom figures) on the central position of the substrate at different target-substrate distances at low pressure (0.5 Pa, left), and at high pressure (0.95 Pa, right). The top figure shows the calculated impact angle distribution for the zirconium atoms. The given angle per distribution is the average impact angle, while the energy is the average energy of the impinging atoms. The dashed line shows the impact angle 45°, or the angle between the normal on the target and the one on the substrate.

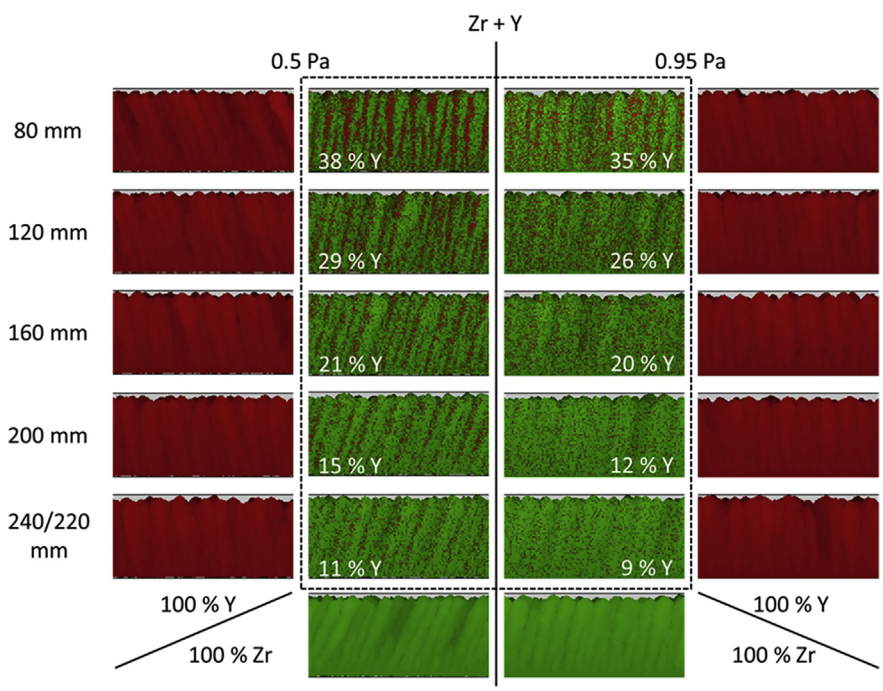

Fig. 5. The simulated microstructure for YSZ thin films at different Y target to substrate distances for low and high pressure. The bottom two images, in green, show pure zirconium films deposited at 0.5 and 0.95 Pa. The outermost images (both left and right), in red, represent pure yttrium films deposited at different pressures and for the different distances. The ten images highlighted by a stripped box (green and red for Zr and Y respectively) in the centre, show the simulation results with the experimental compositions for the two used pressures and the different distances. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

low pressure a limited influence on the columnar tilt at high yttrium concentration or short Y-target-substrate distances (80 mm). But the compositional gradient over the column is clearly present and will result, as discussed in the introduction, in a different lattice expansion between both sides of the column. This difference results in a columnar tilted microstructure. Increasing

the Y-target-substrate distance reduces the yttrium composition. Consequently the lattice induced tilt will diminish. According to Simul3D, this trend is balanced by the ballistic effect which provokes an increase of the tilt towards the Zr target which is however not experimentally observed. This discrepancy is understandable as a ballistic aggregation model will be less accurate when the adatoms have a higher energy. At high pressure, the yttrium atoms arrive at both sides of the column. Scattering reduces clearly the compositional gradient over the columns, and even if the composition changes, the distribution of the yttrium atoms in the column remains more or less homogeneous, except at short yttrium target–substrate distances (80 mm, see Fig. 4, and Fig. 5). Hence, at large yttrium target–substrate distance, the columnar tilt will be defined by the effects accounted for in the Simul3D model (see Fig. 5). At higher Y content, or short Y-target-substrate distances, the latter effect will diminish. Moreover, when both targets supply approximately the same amount of atoms, straight columns are expected. In that case the pressure-distance product becomes however sufficiently small which results in a preferential direction of the yttrium atoms, and hence it can be expected that the lattice parameter effect overrules again the ballistic effect. This results then in a tilt of the column in the direction of the zirconium target. But as the Simul3D simulations show, the effect will be weaker. Hence, as found in the experiments, a less clearly defined columnar (or (200) pole) should be noticed at higher yttrium concentrations.

In summary, the noticed fixed columnar tilt, irrespective of the Y content, at high pressure during the deposition of YSZ by dual magnetron sputtering finds it origin in the combination of a lattice expansion and a ballistic effect. The latter effect could only be elucidated by the successful application of a Monte Carlo simulations.

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