EFFECT OF RF MAGNETRON SPUTTERING CONDITIONS ON MICROSTRUCTURE AND X-RAY CHARACTERISTICS OF YTTRIA-STABILIZED ZIRCONIA THIN FILMS

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Zirconia thin films were deposited on glass substrates by rf magnetron sputtering directly from an oxide target. It was found, that zirconia growth is strongly dependent on sputtering power and pressure. At low power and high pressure, zirconia grows preferentially in the (200) direction with columnar microstructure. On the contrary high power and low sputtering pressures promote the growth of randomly oriented, polycrystalline zirconia. Increasing the argon flow at constant power and sputtering pressure again favours preferential growth of the zirconia layers however not in the (200) direction as before, but in the (111) direction.

1. INTRODUCTION

As is generally known, growing of high quality YBCO thin films on different substrates requires the use of intermediate buffer layers. The buffer layer must be lattice matched with both substrate material and YBCO, and be chemically stable up to the processing temperatures of YBCO thin films. These conditions are fulfiled by yttria-stabilized zirconia (YSZ). Epitaxial YSZ is grown by different techniques such as sputter deposition, electron beam deposition, pulsed laser deposition and different CVD methods. In the Department of Solid State Sciences of the University of Gent, rf magnetron sputter deposition techniques for the different target materials are developed.

As it was described earlier [1], in the case of a metallic target and reactive rf magnetron sputtering, translucent cubic zirconia layers grow preferentially in the (200) direction with columnar microstructure independently on the oxygen flow,

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substrate material, argon to oxygen flow ratios and almost the whole range of sputtering pressures studied. The heating of the substrate does not change the crystallographic structure of zirconia, but strongly affects its orientation. With increasing temperature, the zirconia crystallographic orientation changes from a preferential (200) direction to a random orientation typical for a polycrystalline state.

In this study, an yttria stabilized zirconia target was used. Because of its higher melting point and bonding energy as compared to the metallic target, the argon ions in rf plasma require more energy to sputter effectively the target material. According to the results of Liu et al. [2], the mean argon ion bombardment energy in an rf plasma increases linearly with increasing rf power and for a given power decreases with increasing sputtering pressure because of the increasing number of collisions in the sheath. In relation to these conclusions, the main subject of this work was to determine the influence of the sputtering pressure and the rf power on the deposition speed and on the phase composition and microstructure of the grown YSZ layers.

2. EXPERIMENTAL

For the deposition of YSZ thin films an rf magnetron sputter deposition system was used [1]. The magnetron sputtering source was an US "Inc.2" sputtergun. As a target, an oxide (ZrO_2+7 mol.% Y_2O_3) disc with a diameter of 50 mm and a thickness of 6 mm (produced by Institute of Electronic Materials Technology, Warsaw, Poland) was used. The sputtering source was driven by a 13.56 MHz rf power supply (Huttinger PFG 600RF). Glass microslides were used as substrates. The substrate was mounted on a rotatable substrate holder equipped with a resistive heater. Before deposition the system was pumped down to a base pressure of 1×10^{-3} Pa. The pressure was measured at the bottom of the system by respectively Pirani and Penning pressure gauges. Argon as a sputtering gas was introduced through a stainless steel tube at the bottom of the system and the flow was controlled by a standard mass flow controller.

The typical conditions during sputter deposition are summarized in table 1.

Table 1. Typical sputtering conditions.

Argon flow	2.0 sccm
Sputtering pressure	0.11Pa
rf power	50W
DC bias	-10V
Target-substrate distance	50mm
Substrate temperature	0-530°C

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Experiments with different sputtering pressures (0.1-3.0 Pa) and argon flows (5-22 sccm) were realized.

The deposition speed of the YSZ layers was determined by measuring both the thickness (Talystep-Rank Taylor Hobson) of the deposited layers and the corresponding deposition time.

The phase composition of zirconia was measured by X-ray diffraction (Siemens diffractometer Kristalloflex D 5000). The measurements were carried out in the 2 θ angle range 20-65° at 293K using monochromatized $CuK_{\alpha 1}$ radiation in steps of 0.06 deg min^{-1}.

The free and fractured surfaces were examined by scanning electron microscopy (Zeiss DS 962).

To monitor the degree of oxidation of zirconia films XPS (Perkin-Elmer PHI 5500 ESCA system) and RBS were used. RBS measurements were made with a 2MeV He^{4+} beam produced by the Van der Graaf accelerator of the Institute of Electronic Materials Technology (Warsaw, Poland). The He^{4+} probe has a cross-section of approximately 0.5 mm^2 (ϕ=0.8 mm) at a working pressure of 1.33×10^{-4}Pa. Backscattered particles were counted by a solid state detector (Ortec type) at an angle of 165° with a 15 keV resolution.

The optical transmittance of the layers was measured by a 8451A Diode Array Spectrophotometer (Hewlett Packard).

3. RESULTS AND DISCUSSION

As can be seen from Fig.1, the deposition speed of YSZ layers is strongly dependent on the sputtering pressure. At the higher pressures ($\geq$ 0.7 Pa), resulting in smaller mean free path lengths of the sputtered atoms, more scattering of the sputtered species occurs and consequently a decrease of the deposition speed is observed. On the contrary, a decrease of the sputtering pressure down to 0.11 Pa, favours an increase of the mean argon ion bombardment energy, yielding a continuous increase of the deposition speed. The maximum speed of deposition occurs for the lowest possible pressure compatible with a sustained plasma. Surprisingly the highest speed of zirconia deposition corresponds with the lowest dc bias value (Fig.1). In the whole range of sputtering pressures, dc bias values are inversely proportional to the values of deposition speed.

Independent of the sputtering pressure, translucent, good adhering and fully oxidized zirconia layers were obtained without any additional oxygen supply to the system. X-ray diffraction measurements showed that zirconia is in the cubic form, but its orientation is related to the sputtering pressure used. Similarly to earlier results, at higher sputtering pressures ($\geq$ 0.7 Pa) zirconia grows with a prefered (200) orientation (table 2). However, decreasing the pressure leads to a change in crystallographic

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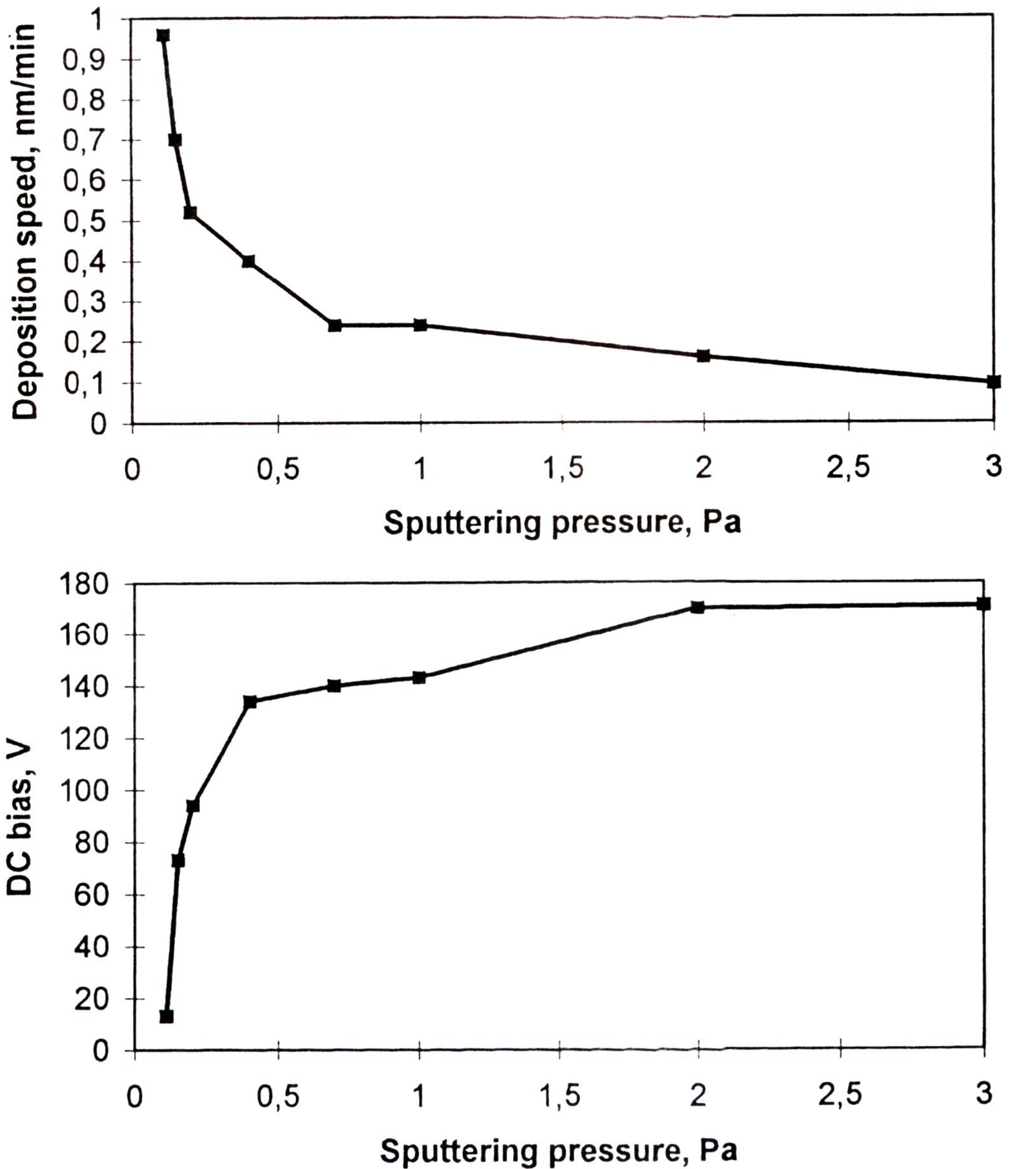

Fig.1. Deposition speed of YSZ layer and DC bias as a function of sputtering pressure (argon flow: 2 sccm, rf power used: 50 W).

orientation of the zirconia layers. The lower the sputtering pressure, the more intensive the (111) peak of zirconia can be observed. At a pressure of 0.15 Pa, the (111) peak becomes the most intensive diffraction peak, however the corresponding X-ray diffraction diagram of the layer is getting completely random in character, typical for

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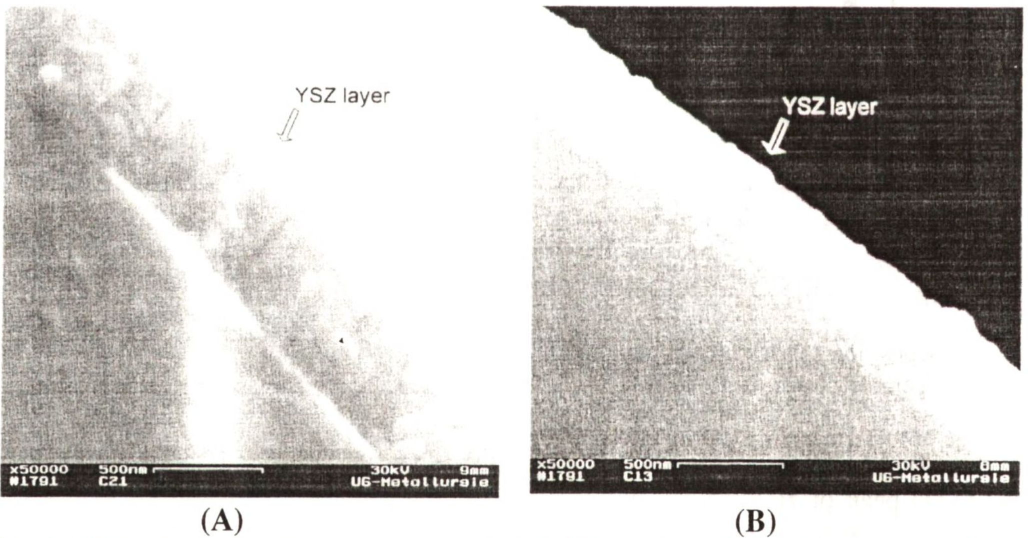
Table 2. Effect of sputtering pressure on X-ray characteristics of YSZ layers (argon flow: 2 sccm, power: 50 W).

Sputtering pressure, Pa	Intensities of main c-ZrO_2 peaks			
	(111)	(200)	(220)	(311)
1.0	0	100	0	0
0.7	0	100	0	0
0.4	53.6	100	48.7	24.3
0.25	52.0	100	64.0	28.0
0.20	87.5	100	62.5	50.0
0.15	100	55.5	51.8	29.6
0.11	100	41.8	46.5	27.9
Intensities for theoretical random orientation	100	17	32	16

polycrystalline material. Together with the change of X-ray characteristics of the layers prepared at a decreasing sputtering pressure, a change of the microstructure is also observed. From a columnar type of growth, typical for the preferentially oriented layers obtained at pressures of 0.7 Pa and higher, the microstructure of zirconia changes to a polycrystalline one when the sputtering pressure is decreased (Fig. 2).



(A) (B)

Fig.2. SEM micrograph of a cross-section of an YSZ layer on a glass substrate prepared at a sputtering pressure of 0.7 Pa (A) and 0.11 Pa (B) (argon flow: 2 sccm, rf power used: 50 W).

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X-ray results of the layers show that low energy argon ions and sputtered atoms, typical for the higher sputtering pressures promote lower density (200) zirconia plane. On the contrary at lower pressures where higher energy spieces are available, the energy is used to recrystallize the grown layer into random oriented polycrystalline material.

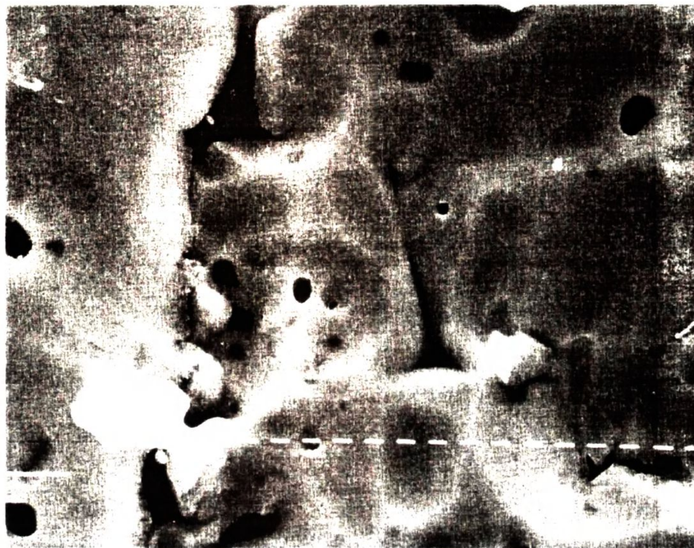

Fig. 3. SEM micrograph of the zirconia target surface after 300 h deposition experiments (black part) - magnification: 2500x.

During deposition of the YSZ layers (at 2 sccm argon flow) a change of the target surface colour was observed. Originally yellowish in colour, from one deposition to another the target was getting more and more brown and black in colour. This effect points in the direction of preferential oxygen sputtering from the target surface. The thickness of the reduced surface layer is estimated as about 0.5 mm. The surface of the oxide target after about 300 h deposition experiments is shown in Fig.3.

Table 3. Effect of substrate heating on X-ray characteristics of YSZ layers and (Zr+Y)/O ratio (RBS measurements) for two different sputtering pressures (rf power: 50 W, argon flow: 2 sccm).

Sputt. pressure, Pa	Substr. temp., °C	Intensities of main c-ZrO_2 peaks				(Zr+Y)/0 ratio
		(111)	(200)	(220)	(311)	
0.7	Floating temp.	0	100	0	0	0.500
	530	100	15.1	0	3.0	0.585
0.11	Floating temp.	100	41.8	46.5	27.9	0.500
	530	100	33.3	0	~1.0	0.541

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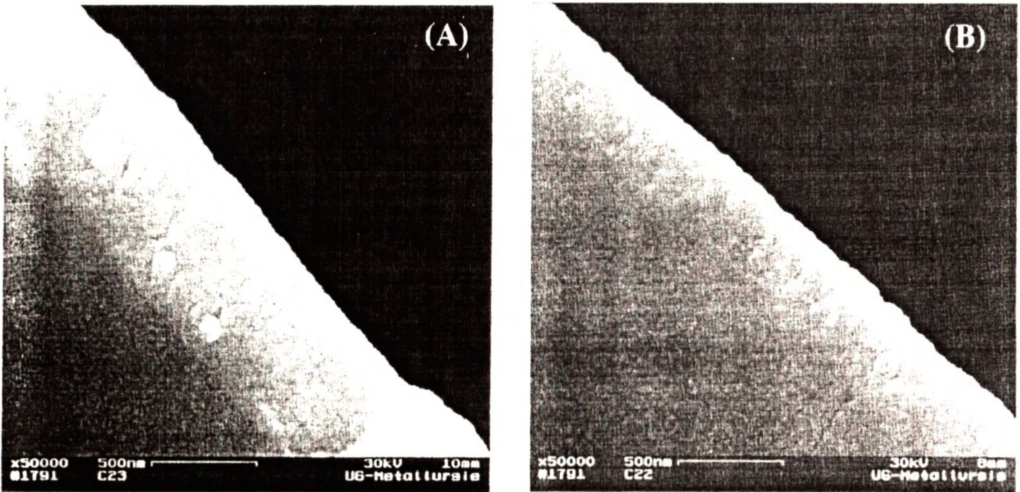

Fig.4. SEM micrograph of a cross-section of an YSZ layer on a glass substrate prepared at a substrate temperature of 530 °C and sputtering pressures: 0.7 Pa(A) and 0.11 Pa(B) (argon flow: 2 sccm, rf power used: 50 W).

Irrespective the sputtering pressure (energy of sputtered particles), heating of the substrate leads to a change of X-ray characteristics and microstructure of the zirconia layers (table 3 and Fig.4). X-ray diffraction diagrams of the layers become completely random in character, typical for polycrystalline material (table 3). This is also confirmed by observing the microstructure of the layers (Fig.4). As can be seen from Fig.4A, a zirconia layer prepared at 0.7 Pa seems to be finer grained than a corresponding layer prepared at 0.11 Pa. This effect needs further investigation and must be ascribed either to the speed of deposition or to the number of oxygen vacancies present in the layers. Parallel with the described change of X-ray

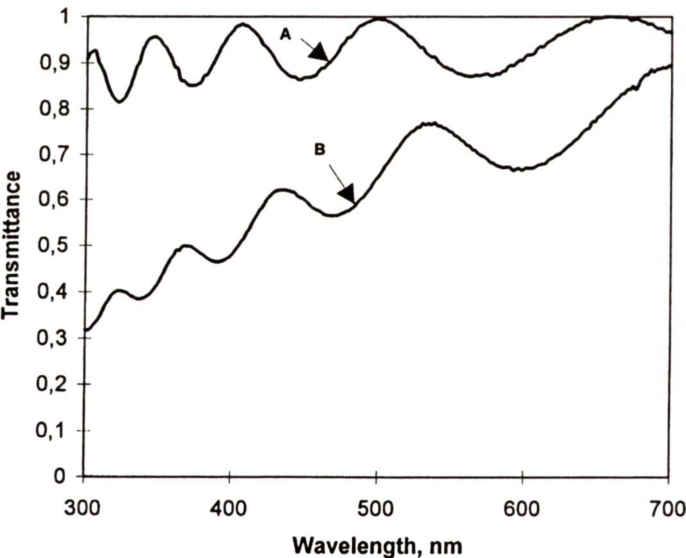

Fig.5. Optical transmittance spectra as a function of substrate temperature: (A) floating temperature, (B) 530°C, for an YSZ layers prepared at a sputtering pressure of 0.11 Pa, argon flow: 2 sccm and rf power used: 50 W.

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diffraction characteristics, the colour aspect of the deposited layers is also changing. The originally transparent water-like layers obtained with a floating substrate temperature are getting more and more greenish and brownish in colour at enhanced substrate temperatures, as is seen from the optical transmittance spectra (Fig.5). The RBS measurements listed in table 3, show that the colour aspect and the decrease of optical transmittance of the layers is due to oxygen deficiency of zirconia created during sputtering.

The importance of the mean argon ion bombardment energy and the energy of the sputtered atoms in the growth of zirconia layers is confirmed by experiments made at a constant sputtering pressure but at increasing sputtering power.

As can be seen from table 4 and 5, an increase of rf power not only increases the

Table 4. Effect of sputtering power on the deposition speed (nm/min) of an YSZ layers for different sputtering pressures.

Sputtering power, W		30	50	75	100
Deposition speed at pressures,Pa	0.11	0.16	0.96	1.14	2.22
	0.7	0.16	0.24	0.51	-

Table 5. Effect of sputtering power on X-ray characteristics of YSZ layers (sputtering pressure: 0.11 Pa, argon flow: 2 sccm).

Sputtering power, W	Intensities of main c-ZrO_2 peaks			
	(111)	(200)	(220)	(311)
30	37.8	100	34.4	20.6
50	100	41.8	46.5	27.9
75	100	44.4	73.7	24.0
100	100	31.4	48.8	25.6

speed of deposition but also influences the X-ray characteristics of the layers. Similarly to experiments with decreasing sputtering pressure at constant power, low energy particles lead to (200) preferential zirconia growth, while higher energy particles build more and more randomly oriented, polycrystalline type YSZ layers. These results are also confirmed by microscopic observations of the layer cross-sections.

A strong effect of argon flow was observed on the zirconia deposition speed and on the X-ray characteristics of the deposited layers (table 6 and 7). An increase of

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Table 6. Effect of argon flow rate on a deposition speed of YSZ layers (sputtering pressure: 0.11 Pa, power: 50 W).

Argon flow rate, sccm	2.0	5.0	10.0	15.0	20.0	22.0
Deposit. speed, nm/min	0.96	1.1	1.35	1.42	1.50	1.42

Table 7. Effect of argon flow rate on X-ray characteristics of YSZ layers (sputtering pressure: 0.11 Pa, rf power: 50 W).

Argon flow rate, sccm	Intensities of main c-ZrO_2 peaks			
	(111)	(200)	(220)	(311)
2.0	100	41.8	46.5	27.9
5.0	100	17.2	27.5	17.2
10.0	100	0	17.5	6.8
15.0	100	0	10.5	2.5
20.0	100	0	10.0	0
22.0	100	0	10.0	0

the argon flow rate, up to 20 sccm, is accompanied by a continous increase of the deposition speed. The observed increase in deposition speed (sputtering pressure was kept constant) can be interpreted as being due to an increase of the degree of argon ionization in plasma. As a result, this leads to an increase of argon ions bombarding the oxide target which in turn increases the speed of deposition. Parallel with the described changes of deposition speed, the X-ray characteristics of the layers are also changing with argon flow.

As can be seen from table 7, the intensity of the (200) zirconia peak decreases systematically and becomes zero at an argon flow rate of 10 sccm. It means that an increase of argon flow changes the zirconia layer growth from a random, polycrystalline growth into a preferentially (111) oriented growth. Similar changes in microstructure of the layers are also observed. For higher argon flow rates, the microstructure of zirconia becomes again columnar in aspect, but (111) oriented. This result is

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not understood for the moment and requires further investigation.

4. CONCLUSIONS

As was shown zirconia layers prepared by rf magnetron sputtering from an oxide target are translucent, fully oxidized without using additional oxygen in the plasma. The deposited layers have a cubic crystallographic structure independently on power and sputtering pressure. However these two parameters (power and pressure) strongly influence the X-ray characteristics and microstructure of the zirconia layers. At a constant power, higher sputtering pressures favour preferential (200) directed columnar zirconia growth while the lower pressures give rise to a random, polycrystalline microstructure.

A similar effect of the sputtering power on the zirconia orientation was observed. Preferential (200) oriented growth is typical for the lower power levels. Higher sputtering power changes the zirconia crystallographic orientation into a random orientation typical for a polycrystalline state.

Increase of argon flow, at a constant power and sputtering pressure, promotes the growth of zirconia into a preferential (111) direction.

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5. REFERENCES

[1] Tomaszewski H., Haemers J., De Roo N., Denul J. and De Gryse R., Thin Solid Films, 1995

[2] Liu J., Huppert G.L., Sawin H.H.: Ion bombardment in rf pressures., J.Appl. Phys., 68 1990 3916

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WPŁYW WARUNKÓW SPUTERINGU MAGNETRONOWEGO NA MIKROSTRUKTURĘ I CHARAKTERYSTYKĘ RENTGENOWSKĄ CIENKICH WARSTW DWUTLENKU CYRKONU STABILIZOWANEGO TLRNKIEM ITRU

Streszczenie

Cienkie warstwy dwutlenku cyrkonu osadzano na podłożach szklanych metodą rf sputteringu magnetronowego bezpośrednio z tlenkowego targetu. Zakłada się, iż wzrost, warstw ZrO_2 jest silnie zależny od mocy i ciśnienia sputteringu. Przy niskich mocach i wysokich ciśnieniach, dwutlenek cyrkonu wzrasta w sposób uprzywilejowany w kierunku (200) wytwarzając mikrostrukturę typu kolumnowego. Wzrost przepływu argonu przy stałej mocy i ciśnieniu ponownie sprzyja ukierunkowanemu wzrostowi warstw dwutlenku cyrkonu, jednak nie w kierunku (200) jak poprzednio, lecz w kierunku (111).

ВЛИЯНИЕ УСЛОВИЙ РФ МАГНЕТРОННОГО НАПЫЛЕНИЯ НА МИКРОСТРУКТУРУ ТОНКИХ СЛОЁВ ОКСИДА ЦИРКОНИЯ СТАБИЛИЗИРОВАННОГО ОКСИДОМ ИТТРИЯ

Краткое содержание

Тонкие слои оксида циркония наносили на стеклянные подложки методом магнетронного напыления с оксидной мишени. Оказалось, что рост слоёв оксида сильно зависит от мощности и давления при напылении. Для низких мощностей и высоких давлений оксид циркония растёт главным образом в направлении (200) с игольчатой микроструктурой. Для высоких мощностей и низких давлений наблюдается рост поликристаллического оксида.

Увеличение потока аргона при постоянных мощности и давлении вызывает рост оксида циркония в основном в направлении (111).

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