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Physical properties of MgO partially stabilized ZrO₂ films deposited by coevaporation

F. TCHELIEBOU, A. BOYER and E. CHARLES

Centre d'Electronique de Montpellier, Laboratoire associé au CNRS URA 391, Université Montpellier II, Sciences et Technique du Languedoc, Place Eugène Bataillon, 34095 Montpellier cedex 5, France

Abstract

ZrO₂ films partially stabilized with MgO in the concentration range 7.6 - 26.1 mol % of MgO have been investigated. The deposition were achieved by coevaporation using a double hearths electron-gun. X-rays diffraction patterns displayed polycrystalline structure. Cubic phase appears from 11.1 mol % MgO. The dielectric constant and the ac conductivity increase to maxima for 14.5 mol % MgO content whatever is the temperature in the range 27°C-700°C. It was also found that the film refractive index exhibits the same behaviour.

I- INTRODUCTION

Zirconia in thin-film form is needed for a variety of applications. It is widely used as thermal barrier and corrosion-resistant coating. ZrO₂ thin films are also used in the fabrication of high temperature sensors (0-800°C) in thin film technology : fluxmeters, thermocouples, mechanical sensors etc...

However structural properties of ZrO₂ is temperature dependent. At ambient, zirconia crystallizes into a structure with a monoclinic lattice. With a temperature (or pressure) increase, the material undergoes a phase transition to yield tetragonal structure. At a higher temperature (or pressure), tetragonal structure becomes a cubic structure. The large volume change associated with the phases transformations is a serious drawback for its optical and mechanical properties. Fortunately it is possible to stabilize zirconia in one of the two high symmetry phases : tetragonal or cubic by adding an appropriate amount of an oxide stabilizer such as Y₂O₃, CeO₂, In₂O₃ or SiO₂, reverse transitions are then inhibited.

II- EXPERIMENTAL SET-UP

Fig.1 shows the synoptic scheme of the deposition chamber. Targets are pellets of ZrO₂ and MgO positionned in the system in separate electron gun hearths. Substrates are 10mmx10 mm nickel rectangles. They were annealed in air during 2 hours, then optically polished. Five substrates were fastened at equal distance on a furnace, directly above two evaporating crucibles. Owing to this disposition, an oxide stabilizer concentration zone was achieved in a single experiment. The base pressure in the chamber was 10⁻⁸Torr.. The substrates were heated to 400°C, oxygen pressure during deposition was 4.10⁻⁵Torr.. The evaporation rates were controlled by two independent quartz monitors. The crystalline phases were deduced from X-ray diffraction spectra. The refractive indices were computed on the basis of the Fresnel formalism, using reflectance measurements performed with a Beckmann 5240 spectrophotometer. Dielectric constant and a.c. conductivity measurements were measured in vacuum using an impedance analyzer (LCR 4275A

III- RESULTS

a- Structural properties

X-Ray diffraction spectra as a function of the MgO oxide stabiliser molar fraction, are shown on Fig.2 for molar fraction ranging between 7.6% and 26.1% and for diffraction angle ranging from 10° to 20° . Diffraction is maximal for crystallization directions $(-1,1,1)$ for monoclinic phase, $(1,1,1)$ for cubic phase and $(0,0,3)$ for tetragonal phase which appears at diffraction angle $\theta \approx 26^\circ$. This zoom on the spectra field enables us to follow the different crystallization evolution as a function of stabilization. The cubic phase appears from 11.1 mol % MgO. It was also found that the cubic lattice parameter a_c of the stabilized ZrO_2 and the parameter of the tetragonal phase c_t varie less with the amount of MgO. These findings are in agreement with the results reported by Mari Lou Balmer *et al* [1].

b - Optical properties.

Refractive indices n were computed on the basis of the Fresnel formalism from reflectance curves. Fig.3 shows the mixed ZrO_2 -MgO n as a function of MgO content. It was found that n of the alloy varies with the amount of MgO, up to a maximum of 2.3 for 14.5 mol% MgO. At molar fraction of MgO higher than 14.5%, a monotonic decrease of index is noted. This could be attributed to the lattice transformation to the cubic symmetry [2]. An additive ion which is not iso-valent with zirconium produces oxygen-defects. Both resulting non-stoichiometry and porosity could influence the film refractive index. Packing density was computed using Bragg-Pippard approach of refractive index developped by Harris *et al* [3]; it ranges from 0.8 to 0.9.

c - Dielectric properties.

The electrical properties of interest investigated are the dielectric constant ϵ and conductivity σ_{ac} as functions of both frequency and temperature. Fig.3(a) and 3(b) are plots of ϵ and log of σ_{ac} as functions of MgO content over the concentration range achieved (7.6-26.1%) at $T=500^\circ C$. ϵ is reported to increase up to maxima corresponding to 14.5 mol% MgO for all frequencies under consideration (10KHz-1MHz), then decreases with increasing additive content. Electrical conductivity increasing is due to both oxygen vacancies introduced in the crystal lattice in order to preserve electrical neutrality during stabilization and the presence of grain boundaries and/or impurities. It decreases in value at high concentration because of the aggregation of vacancies[4]. The σ frequency dependence leads to a conduction process due to electron hopping (Correlated Barrier Hopping)[5]. It is striking that according to the phase diagram of the system ZrO_2 -MgO [6], 14 mol% is the lowest MgO concentration required to stabilize the cubic phase.

CONCLUSION

MgO was used to inhibit the reverse phase transitions in ZrO_2 . Structural, optical and dielectric properties were investigated with the MgO content as the main parameter, at $T=500^\circ C$. Samples were partially stabilized in the cubic phase from 11.1 mol% MgO. It was found that at this temperature as at $27^\circ C$, dielectric constant and ac conductivity were optimized for many frequencies. Film refractive index increases to a maximum of 2.3 for 14.5 mol% MgO. Packing density lay in the range 0.8 to 0.9. From these results, technological applications could be improved.

Fig.1- Schematic diagram of the dual-electron beam deposition system.

Fig.2- Diffractometer scans of ZrO_2 - MgO as a function of mole fraction of MgO stabilizer.

Fig.3.- Mixed ZrO₂-MgO film refractive index as a function of MgO content.

Fig.4(a).- Dielectric constant at T=500°C as a function of MgO content in the system ZrO₂-MgO.

Fig.4(b).-Log of ac conductivity at T=500°C as a function of MgO content in the system ZrO₂-MgO.

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