PHYSICAL REVIEW B VOLUME 39, NUMBER 9 15 MARCH 1989-II

Phase stability of ZrO_2-Al_2O_3 thin films deposited by magnetron sputtering

S. B. Qadri*
Condensed Matter Physics Branch, Condensed Matter and Radiation Science Division,
Naval Research Laboratory, Washington, D.C. 20375-5000

C. M. Gilmore and C. Quinn
School of Engineering and Applied Science, George Washington University, Washington, D.C. 20052

E. F. Skelton and C. R. Gossett
Naval Research Laboratory, Washington, D.C. 20375-5000

(Received 8 September 1987; revised manuscript received 6 September 1988)

Thin films of ZrO_2-Al_2O_3 were deposited on a variety of substrates by reactive magnetron sputtering. Nucleation and stability of the cubic, tetragonal, and monoclinic phases of ZrO_2 were investigated over the entire composition range. As deposited films were all amorphous. Annealing in air at temperatures up to 1000 °C for several hours resulted in the crystallization and evolution of ZrO_2 phases. X-ray diffraction studies suggested that films with [Zr]:[Al] atomic ratios up to 70:30 nucleated first with the zirconia in the cubic phase with subsequent transformation to a tetragonal phase as a function of annealing time. These results are consistent with the recent theoretical predictions that the cubic phase is unstable with respect to tetragonal and orthorhombic phases at lower temperatures. Observed decreases in volume of the monoclinic ZrO_2 phase with increasing Al_2O_3 content suggest an internal compression that reduces the volume of the monoclinic cell to that of the tetragonal unit cell, at which point the tetragonal structure is then observed.

I. INTRODUCTION

Zirconia (ZrO_2), because of its high refractive index, high melting temperature, hardness, and corrosion-resistant properties, has many important applications in science and technology. ZrO_2 crystallizes in different polymorphs under different conditions of temperature and pressure. Five different phases have been reported in literature.[1-3] At ambient conditions, ZrO_2 is monoclinic (space group $P2_1/c$), at higher temperatures, between 950 °C and 1250 °C, it transforms to a tetragonal phase ZrO_2(II) (space group $P4_2/nmc$), and at 2370 °C, to a cubic fluorite structure, ZrO_2 (III) (space group $Fm3m$). In addition to high-temperature phases at atmospheric pressure, two other phases have been discovered at elevated pressures; ZrO_2 (IV) tetragonal and ZrO_2(V) orthorhombic. ZrO_2(II) and ZrO_2(IV) show a close structural relationship. The phase diagram for different phases has also been reported elsehwere.[2,3]

Neither of the high-temperature phases, ZrO_2(II) or ZrO_2(III), is quenchable. In applications which involve thin film coatings of ZrO_2, cracking results upon cooling from above 1150 °C to room temperature. This is a consequence of 3% volume change which accompanies the tetragonal-to-monoclinic phase transition. The transformation of ZrO_2(II) to ZrO_2(I) can be suppressed by alloying. CeO_2 and Y_2O_3 form solid solutions with ZrO_2 and change the phase boundaries; however, Al_2O_3 is not soluble with ZrO_2 and according to Lange alters the stability through constraint.[4] The theory of retention of the tetragonal phase through constraint has been discussed in a series of articles by Lange.[4] Essentially the critical nucleus size is increased by a constraining matrix having a Young's modulus higher than that of ZrO_2. Al_2O_3 was suggested because of its higher elastic modulus. Furthermore, Lange[5] fabricated a ZrO_2-Al_2O_3 composite series in sintered powder forms. Lange's results, suggested that high proportions of the tetragonal phase of ZrO_2 could only be retained with ZrO_2 fractions from 0 to 10 vol %.

Plasma spraying is often utilized in depositing coatings of the tetragonal phase of ZrO_2 stabilized by Y_2O_3, but because of the many problems with such coatings, the present authors reported results of thin-films deposition of ZrO_2-Al_2O_3 by magnetron sputtering. In our preliminary studies,[6] we reported that as deposited films were all amorphous at room temperature. Upon annealing at 1000 °C these amorphous films ordered into tetragonal or monoclinic phases. We reported that with a Zr:Al atomic ratio of 76:24, the monoclinic phase was obtained, and with an atom ratio of 52:48, it was predominantly tetragonal.[7] More recently, crystallization of zirconia films by thermal annealing was reported by Rujkorakarn and Sites,[8] suggesting the formation of tetragonal and monoclinic phases at 450 °C and the formation of the cubic phase, above 900 °C. They did not characterize their films by x-ray diffraction; their identification was based on Raman spectroscopy.

In this paper, we present the results of the kinetics and nucleation of different polymorphs of ZrO_2 as a function of annealing time for the entire composition range. We discuss the nucleation of the cubic polymorph and its subsequent transformation to the tetragonal phase.

II. EXPERIMENTAL

Thin films of ZrO_2-Al_2O_3 mixtures were grown by reactive magnetron sputtering of a composite target consisting of aluminum and zirconium in an oxygen atmosphere. The details of growth are given elsewhere.[6] A variety of substrates, including fused quartz, single-crystal NaCl, and graphite, were used. To obtain free-standing films of ZrO_2-Al_2O_3 two methods were used: for the case of NaCl the substrate was dissolved in water, whereas graphite substrates were heated to 800 °C at which temperature the substrate evaporated. The chemical composition was determined by Rutherford backscattering (RBS).[9] Annealing was performed in air for different times and temperatures and x-ray diffraction techniques were used to study the structural properties of these thin films. The particle size was also deduced from transmission electron microscopy (TEM).

III. RESULTS AND DISCUSSIONS

As deposited films were all amorphous and stoichiometric. X-ray diffraction patterns of as-deposited films showed no diffraction peaks, other than a very broad scattering peak characteristic of the amorphous phase. The amorphous films were annealed in air at 1000 °C for different period of times. Subsequently, different diffraction patterns, corresponding to different phases, evolved depending upon the chemical composition of the films as well as on the annealing times.

Figure 1 shows the diffraction spectra recorded with Cu $K\alpha$ radiation for all the ZrO_2-Al_2O_3 thin films. In the case of pure Al_2O_3, γ-Al_2O_3 (cubic) was observed. Peaks corresponding to γ-Al_2O_3 were seen for [Zr]:[Al] ratios of 0:100 and 14:86 cases only and were very weak in intensity. The lattice parameters for this phase obtained based on only three peaks were 7.876 and 7.864 Å, respectively, and were in good agreement with the reported value of 7.90 Å.[10] Diffraction spectra (c)–(f) in Fig. 1 show peaks corresponding to the ZrO_2(II) phase; the lattice parameters for tetragonal phases for these samples are given in Table I. Read camera photographs show that these films have preferred orientation along the [111] direction, consequently the intensities of these peaks are slightly different from the high-temperature tetragonal phase. No additional peaks other than those of ZrO_2(II) phase were observed in the diffraction patterns. This phase more resembles the high-temperature phase, rather than the high-pressure tetragonal phase reported by Ming *et al.*[2] In the case of [Zr]:[Al] atom ratio of 14:86, an additional peak with a d spacing of 2.68 Å was observed. We are not able to identify this peak with any of the known phases of ZrO_2 or Al_2O_3 and the origin of this peak is not understood. Films with ratios of 76:24 to 100:0 [Fig. 1(a)] showed monoclinic ZrO_2 only. Our results show no evidence of ordering in the films when annealed at 500 °C in air, this is in disagreement with results reported by Rujkorakarn and Sites for pure ZrO_2 films deposited by a similar technique.[8] None of the films showed any ordering, even after annealing for 72 h in air at 500 °C or 800 °C.

Films with higher Al content took longer time for crystallization. These times ranged from 48 to 72 h. On the other hand, films with higher Zr content showed ordering in 2–6 h. The film with a [Zr]:[Al] atom ratio of 68:32 crystallized in 2 h, whereas films with 58:42 ratio crystallized in 6 h. Thus with increasing Zr composition, films crystallized in shorter annealing times. This is consistent with the notion that the formation of tetragonal phase is associated with the particle size and that diffusion rates in zirconia are higher than in alumina. The effect of long-time annealing was to make the film more crystalline with diffraction peaks being well defined and narrower in width.

The cubic and tetragonal polymorphs of ZrO_2 are closely related to each other. The high-temperature cubic phase has the fluorite structure, whereas the tetragonal and monoclinic phases are distortions of this phase. In films where the monoclinic phase was not stable, the initial phase formed was cubic. Figure 2 shows that the amorphous film with a [Zr]:[Al] ratio of 68:32 crystallized first in the cubic phase after annealing for only 2 h. Upon annealing for 70 h, some of the peaks split into two

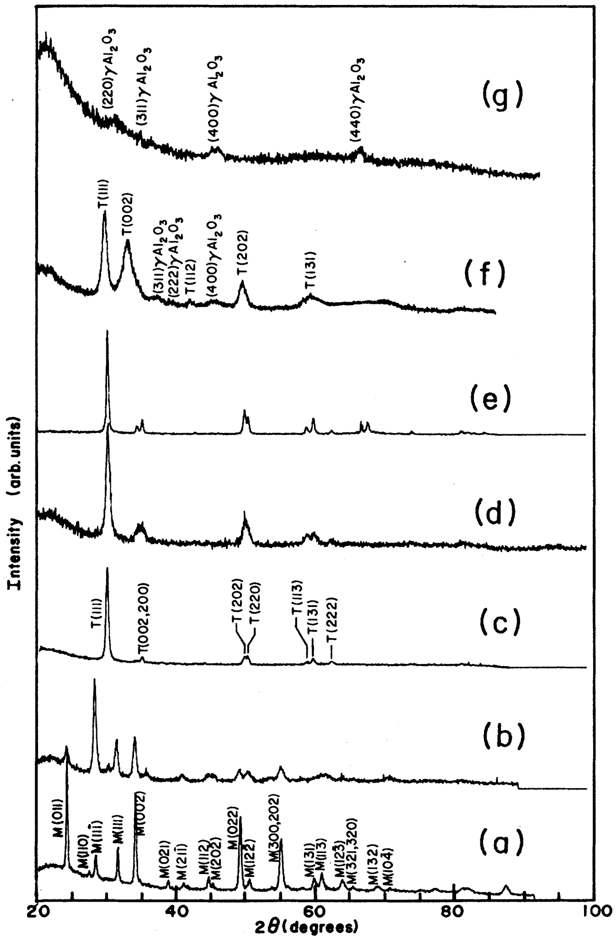

FIG. 1. 2θ-diffraction scans for ZrO_2-Al_2O_3 films with [Zr]:[Al] ratios of (a) 100:0, (b) 76:24, (c) 68:32, (d) 52:48, (e) 45:55, (f) 14:86, (g) 0:100.

TABLE I. Unit-cell parameters and volumes of ZrO_2-Al_2O_3.

[Zr]:[Al]	a (Å)	b (Å)	c (Å)	β	V (Å^3)	t (Å)	Phase
100:0	5.3225	5.1702	5.2890	98.9°	143.8	500	ZrO_2(I)
76:24	5.1639	5.0937	5.3352	99.2°	138.6	250	ZrO_2(I)
68:32	5.0930		5.1890		134.6	220	ZrO_2(II)
42:48	5.0890		5.1620		133.7	156	ZrO_2(II)
45:55	5.0790		5.1890		133.9	376	ZrO_2(II)
14:86	5.1090		5.1250		133.7	150	ZrO_2(III)
14:86	7.8640				486.3		γAl_2O_3
0:100	7.8760				488.5		γAl_2O_3

peaks, indicating a tetragonal distortion of the cubic phase and the formation of tetragonal phase. Similarly in the case of a [Zr]:[Al] ratio of 14:86, the initial phase formed was cubic when annealed for 48 h.

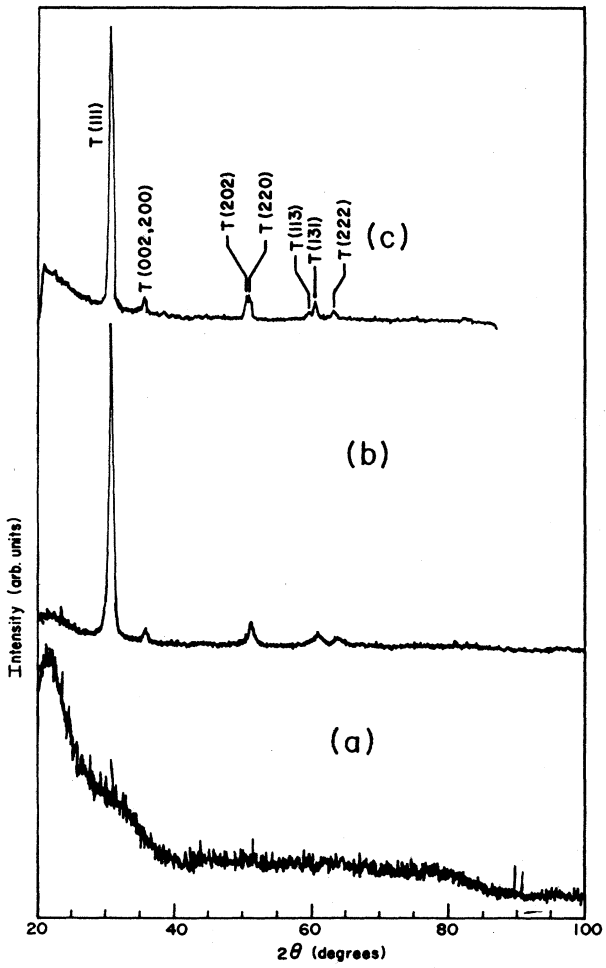

FIG. 2. 2θ scans for a film of a [Zr]:[Al] ratio 68:32 as a function of annealing time at 1000 °C: (a) as-deposited film, (b) after 2 h of annealing, and (c) after 70 h of annealing (tetragonal distortion is evident by the splitting of the peaks).

The monoclinic phase was retained for films where the Al content was less than 30 at. %. In our previous work[7] we reported the presence of one weak diffraction peak of monoclinic phase for 52:48 [Zr]:[Al]. Since then we made a new film for the same composition and more films with up to ratios of 68:32 and found no traces of the monoclinic phase in diffraction spectra. The slight trace of monoclinic phase in our previous film could be explained based on the nucleation of one or two grains of monoclinic phase. It is further evident from Table I that the unit-cell volume for pure ZrO_2 is 143.8 Å^3, in agreement with the pubished value in the literature, whereas for a 76:24 ratio film the unit-cell volume decreased by about 4% to 138.6 Å^3 and approaches the unit-cell volume for tetragonal phase. This suggests that with increasing Al the ZrO_2 is under a state of compression and undergoes a transformation to the tetragonal phase when the Al content is close to 30%, at which point the monclinic cell volume decreased to the volume of the tetragonal unit cell. This observation may explain why in this work the tetragonal phase of ZrO_2 was retained up to a 68:32 ratio; whereas Lange observed the tetragonal phase only up to a 10:90 ratio.[5] There was no report of a volume change in ZrO_2 by Lange.[5] Since it is reported that there is only a small amount of solubility of Al_2O_3 in ZrO_2, it is unlikely that the change in unit lattice parameters or the unit-cell volume is due to substitutional effects.[1]

In order to correlate the formation of the tetragonal phase with the grain size, the grain size of each film was determined by measurement of the breadth of (111) diffraction in the case of tetragonal phase and the $(11\bar{1})$ peak for the monoclinic phase. A standard silicon powder with a known grain size of 1–2 μm was used as a reference to determine the line broadening due to instrumental effects such as the divergence of the incident beam and the width of the x-ray source. The grain size was determined using the Scherrer equation and the broadening of the diffraction peak arising due to grain size. The grain size t for each composition is also listed in Table I. As can be seen from the table, the grain size ranges from 150 to 500 Å and to within accuracy of our measurements, there is no systematic change with composition.

These results are in reasonable agreement with those obtained by TEM measurements. A typical particle size obtained from TEM results was of the order of 0.05 μm for a film with a [Zr]:[Al] atomic ratio of 52:48. In all films, the width of the diffraction peaks narrowed under long-term annealing and the value of the grain size approached 500 Å. These results suggest that the formation of tetragonal or monoclinic phases is independent of the grain size, but is mostly dependent on the composition of the films. Furthermore since the tetragonal is retained in the case of free-standing films, it presumed that the formation of tetragonal phase is not due to stresses induced by the substrate material. Since the unit-cell volume for films with monoclinic phase decreased with increasing aluminum composition, it suggests that zirconia is being compressed by the surrounding alumina matrix. This compression may arise due to large difference in thermal expansion between ZrO_2 and Al_2O_3. Zirconia has a much higher thermal expansion than alumina and would contract more on cooling. Since it is uniformly surrounded by alumina matrix it gets compressed when cooled down from high temperatures. The advantage of using magnetron sputtering is that we can mix zirconia and alumina at an atomic scale. This compression may not be present in the pressed and sintered powders of Lange.[5]

IV. CONCLUSIONS

The structure of the ZrO_2-Al_2O_3 films as initially deposited, showed no evidence of long-range order. When annealed at 500 °C even up to 70 h, there was still no evidence of crystallization. However, as the annealing temperature was increased to 1000 °C, and if the [Zr]:[Al] atom ratio was less than 76:24, the ZrO_2 component crystallized in the cubic phase initially. Further annealing at this temperature resulted in conversion to the high-temperature tetragonal phase (II). The high-temperature tetragonal phase was stable and did not transform to the monoclinic phase under long-term annealing. Films with a [Zr]:[Al] atom ratio from 76:24 to 100:0 nucleated in the monoclinic phase. γ-Al_2O_3 was observed in films with pure Al_2O_3 and for films with [Zr]:[Al] ratios between 14:86 to 0:100. There was no evidence of ordering in Al_2O_3 for higher Zr compositions for the short-term heat treatments utilized. The volume decrease in the monoclinic phase of ZrO_2 with increasing amounts of Al suggests an internal compression that eventually reduces the monoclinic volume to that of the tetragonal phase resulting in the formation of tetragonal zirconia.

---

[*] Permanent address: Sachs/Freeman Associates, Inc., Landover, MD 20785.

[1] E. M. Levin and N. F. McMurdie, in *Phase Diagrams for Ceramists,* edited by M. K. Reser (The American Ceramic Society, Columbus, OH, 1975), p. 76.

[2] L. C. Ming and M. H. Manghnani, in *Solid State Physics Under Pressure,* edited by S. Minomura (Terra Scientific, Tokyo, 1985), pp. 135–140.

[3] S. Block, J. A. H. Da Jornada, and G. J. Piermarini, J. Am. Ceram. Soc. **68**, 497 (1985).

[4] F. F. Lange, J. Mater. Sci. **17**, 225 (1982).

[5] F. F. Lange, J. Mater. Sci. **17**, 247 (1982).

[6] C. M. Gilmore, C. Quinn, E. F. Skelton, C. R. Gossett, and S. B. Qadri, J. Vac. Sci. Technol. A **4**, 2598 (1986).

[7] C. M. Gilmore, S. B. Qadri, C. Quinn, C. R. Gossett, and E. F. Skelton, J. Vac. Sci. Technol. A **5**, 2085 (1987).

[8] R. Rujkorakarn and J. R. Sites, J. Vac. Sci. Technol. A **4**, 566 (1986).

[9] C. R. Gossett, Nucl. Instrum. Methods **168**, 151 (1980).

[10] H. P. Rooksby, in *X-ray Identification and Crystal Structures of Clay Minerals* (Mineralogical Society, London, 1951), p. 264, and American Society for Testing and Materials (ASTM) Card. No. 10-425.