

Pressure studies of ZrO_2 - Al_2O_3 films grown by magnetron sputtering

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High-pressure studies have been performed on the free-standing films of ZrO_2 - Al_2O_3 with [Zr]:[Al] atomic ratio of 64:36 with use of energy-dispersive x-ray diffraction techniques and synchrotron radiation. As initially deposited in the magnetron sputtering system, the films are amorphous. The tetragonal phase which is stabilized upon annealing in air at 1000°C resembles the high-temperature tetragonal phase. This phase is more compressible than the high-pressure tetragonal phase and is stable up to 16.0 GPa. At room temperature, the amorphous films do not crystallize under application of pressures up to 25.0 GPa.

INTRODUCTION

Zirconia, ZrO_2 , because of its high refractive index, high melting temperature, and corrosion-resistant properties has a wide vista of applications.¹ ZrO_2 forms in different crystallographic phases under different conditions of temperature and pressure; five different phases have been identified so far. At ambient pressure and temperature, ZrO_2 is monoclinic. At atmospheric pressure and elevated temperatures it undergoes two transitions: between 950 and 1250°C, it transforms to a tetragonal-I lattice (space group $P4_2/nmc$), and at 2370°C, to a cubic fluorite structure (space group $Fm3m$).^{2,3} At elevated pressure and room temperature, two other phases are formed: ZrO_2 tetragonal-II and an orthorhombic ZrO_2 . The first high-pressure phase was identified by some investigators to be orthorhombic.⁴⁻⁶ While others reported it to be the same as high-temperature tetragonal with a second phase of orthorhombic symmetry at a higher pressure,⁶⁻¹⁰ the most recent work by Ming *et al.*¹¹ and Block *et al.*¹² suggested that the first high-pressure phase is a tetragonal-II phase which is different from the high-temperature tetragonal-I. Although tetragonal-I and -II phases are very similar, they can be distinguished through Raman spectra and x-ray diffraction.^{11,12} These results were further confirmed by Alzyab *et al.*¹³ The phase diagram for these and other phases have also been reported.¹²

In applications which involve thin-film coatings of ZrO_2 , often cracking results upon cooling from a temperature above 1150°C to room temperature because of the volume change which accompanies the high-temperature tetragonal to monoclinic phase transition. This transformation can be inhibited by alloying with appropriate oxides, e.g., CeO_2 , Y_2O_3 , and Al_2O_3 . Al_2O_3 is not soluble with ZrO_2 and alters the phase stability through constraint. The phase stability of ZrO_2 - Al_2O_3 films grown by magnetron sputtering techniques have been recently discussed in two articles by the present authors.^{14,15} The high-temperature tetragonal phase is stabilized for [Zr]:[Al] atomic ratios up to 0.76:0.24. Samples with higher than 0.76 Zr content nucleate in the monoclinic phase. In all cases as deposited films were amorphous

and nucleated in either tetragonal or monoclinic phases only when annealed in oxygen at 1000°C. In this paper we report the high-pressure studies of free-standing films of amorphous and tetragonal-I stabilized ZrO_2 . A comparison of volume compressibility of high-temperature tetragonal-I and high-pressure tetragonal-II phases is made to understand their response to pressure, despite their close structural relationship.

EXPERIMENTAL RESULTS

Free-standing films of ZrO_2 - Al_2O_3 were deposited on a substrate of NaCl. The substrate was then dissolved in distilled water. The film and a freshly ground fine powder of NaCl were contained in an Inconel gasket between a pair of opposed diamond anvils. Heterochromatic synchrotron radiation was used to illuminate the pressure chamber and the scattered photons were analyzed at a fixed diffraction angle of $2\theta = 18.0^\circ$ with a Ge detector. The pressure was estimated from the measured shift in the NaCl(200) diffraction peak and using Decker's equation of state.¹⁶ Additional experimental details are given elsewhere.¹⁷

RESULTS AND DISCUSSION

At room temperature, ZrO_2 transforms from its normal monoclinic phase to a tetragonal phase at a pressure of about 5.0 GPa, and to an orthorhombic phase at about 15.0 GPa. Ming and Manghnani have shown the close relationship between tetragonal-I and -II phases in that the high-temperature tetragonal phase could be indexed based on high-pressure tetragonal phase with $c_{II} = c_I$ and $a_{II} = \sqrt{2}a_I$. However, tetragonal-II cannot be indexed on the basis of tetragonal-I because of the additional peaks with d spacings of 2.267 Å (201,210), 1.718 Å (300,212), 1.604 Å (301,310), and 1.427 Å (203) as reported in Ref. 11. On the other hand, Block *et al.*¹² reported two additional peaks of 5.10 Å (100) and 3.608 Å (101). The tetragonal phase we obtained after annealing a film of [Zr]:[Al] atomic ratio of 64:36 in oxygen atmosphere did not show the presence of any of the above d spacings and agreed one to one, with that of the high-temperature tetragonal phase I. A piece of as-deposited film of the

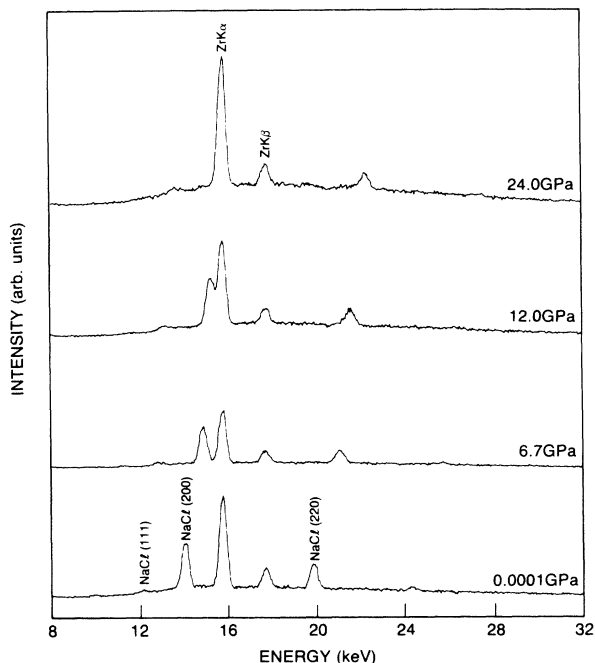


FIG. 1. EDXD spectra of amorphous $ZrO_2Al_2O_3$ film as a function of increasing pressure. The [Zr]:[Al] atomic ratio is 64:36.

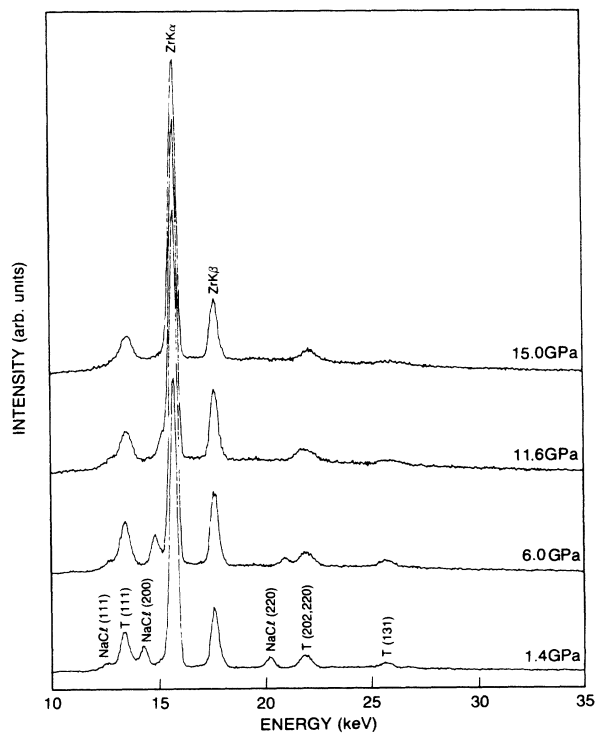


FIG. 2. EDXD spectra of $ZrO_2-Al_2O_3$ film as a function of increasing pressure. The [Zr]:[Al] atomic ratio is 64:36.

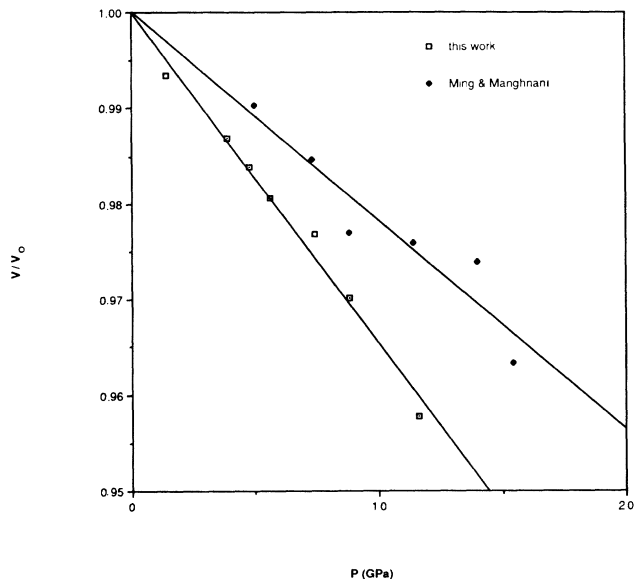


FIG. 3. V/V_0 as a function of increasing pressure. Open square with a dot is our data on tetragonal-I whereas solid squares are the data of Ming and Manghnani on tetragonal-II.

same composition was subjected to pressures above 25.0 GPa. Figure 1 shows the series of spectra as a function of increasing pressure up to 25.0 GPa. Although crystallization could be induced by the application of pressure, as in the case of Si and Ge,¹⁸ no evidence of crystallization was seen in the case of amorphous ZrO_2 . The amorphous film of the same composition when subjected to annealing at 1000°C crystallized in 2 h in the tetragonal-I phase. Figure 2 shows the diffraction spectra as a function of increasing pressure for the crystallized film up to a pressure of 15.0 GPa. In contrast to pure ZrO_2 where the tetragonal-II phase transforms to an orthorhombic phase at a pressure of 15.0 GPa, the high-temperature tetragonal phase I remains stable even under a pressure of 16.0 GPa. The reduced volume V/V_0 is plotted as a function of pressure in Fig. 3 and compared with the data of high-pressure tetragonal-II phase of pure ZrO_2 reported by Ming and Manghnani.¹¹ A linear-least-squares fit to the data gives the slope values of $-3.5 \times 10^{-3} \text{ GPa}^{-1}$ and $-2.2 \times 10^{-3} \text{ GPa}^{-1}$ for high-temperature and high-pressure tetragonal phases, respectively. This indicates that the high-temperature tetragonal phase I is more compressible than the high-pressure tetragonal phase II.

CONCLUSION

The following conclusions can be drawn from this study. (i) The tetragonal phase formed in the $ZrO_2-Al_2O_3$ film is the high-temperature tetragonal phase. It is more compressible than the high-pressure tetragonal phase and does not transform to orthorhombic or tetragonal-II even up to 16.0 GPa. The difference in compressibility is another aspect that distinguishes the tetragonal-I and -II phases. (ii) The amorphous film of ZrO_2 with [Zr]:[Al] atomic ratio of 64:36 does not crystallize even up to pressures of 25.0 GPa.

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