Mechanical properties of 3Y-ZrO_2 and 8Y-ZrO_2 films by rf sputtering

Minoru MORIYAMA*, Kiichiro KAMATA**, Hidetoshi SAITO**,
Osamu NISHINO**, Yoshimori KAWAGUCHI**
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Authors prepared 8mol%Y_2O_3-ZrO_2 (8Y-ZrO2) and 3mol%Y_2O_3-ZrO_2 (3Y-ZrO_2) ceramic films by the magnetron-assisted rf sputtering method on the glass substrate. The prperties of hardness, the internal stress and the refractive index etc. were investigated for the prepared films. The hardnesses of 8Y-ZrO_2 and 3Y-ZrO_2 films were 15.6 GPa and 12.9 GPa, respectively. The total compressive stresses for 8Y-ZrO_2 and 3Y-ZrO_2 films at 1 μ m thick on the borosilicate glass substrates were 1280 Nm^{-1} and 1100 Nm^{-1}, and the internal stresses for both films at 0.1 μ m thick were 3.13 GPa and 2.94 GPa, respectively. The fracture toughnesses for the coated substrate with 8Y-ZrO_2 and 3Y-ZrO_2 films were 0.719 $MNm^{-3/2}$ and 1.11 $MNm^{-3/2}$, respectively.

1. Introduction

The pure zirconium oxide (zirconia, ZrO_2) ceramics is apt to fracture by the fine cracks resulting from the volume expansion through cooling at the phase transition (about 900 ～ 1170 ˚ C) from tetragonal to monoclinic phase[1]. But, the highly strengthened and toughened ZrO_2 ceramics, partially stabilized zirconia (PSZ) or full stabilized zirconia (FSZ), is obtained by the addition of Y_2O_3, CaO and MgO ceramics[2,3]. The ZrO_2 ceramics stabilized by Y_2O_3 is called "YSZ (Yttria stabilized zirconium oxide)". In the case of PSZ, the change in the strength and toughness is considered by the following reasons. When the stress is concentrated at the tip of propagated cracks in the meta-stable tetragonal phase, the tetragonal phase is transformed into the monoclinic phase by the applied stress with absorption of strain energy and stress relaxation owing to the volume expansion of the transformation. This is called stress-induced transformation or martensitic transformation[2,3]. The absorption of strain energy brings about the improvements of toughness, and the stress relaxation results in

*Department of Electronics and Control Engineering
**Department of Chemical Engineering in Nagaoka University of Technology

the high strength.

Authors prepared 8mol%Y_2O_3-Zr_2 (8Y-ZrO_2) and 3mol%Y_2O_3-ZrO_2 (3Y-ZrO_2) ceramic films, which were well-known to possess high mechanical properties, by the magnetron-assisted rf sputtering method on the glass substrate. The mechanical properties such as the microhardness, the internal stress, the refractive index and the relationships between the internal stress and the crack length around Vickers indentation were investigated for the prepared films as shown below.

2. Experimental procedure

2-1 Preparation

The films were prepared on the glass substrate by the magnetron-assisted sputtering equipment (2 pole type) under the conditions as shown in table 1. The two kinds of target materials (99.99% pure) of 8mol%Y_2O_3-ZrO_2 and 3mol% Y_2O_3-ZrO_2 were used. The former was the composition of full stabilized zirconium oxide and the latter of partially stabilized zirconium oxide in the phase diagram[4]. The details of preparation and characterization for the films were reported in the another paper[5]. Although both targets were consist of cubic and monoclinic phases, it was found that the prepared films had cubic structure alone from X-ray diffraction analysis. 8Y-ZrO_2 films were oriented to (111) and (220) planes, and 3Y-ZrO_2 films to (111) plane. The compositions of the films were almost same as that of target materials from the measurement of EPMA.

Table 1 : Sputtering conditions.

Total gas pressure	1.0∼10.0 Pa
RF power	120 W
Electrode distance	30 mm
Electrode diameter	76 mm
Substrate temperature	10∼250 °C
Sputtering gas	Ar + O_2 (Pressure ratio 4:1)
Target materials	8mol%Y_2O_3-ZrO_2 3mol%Y_2O_3-ZrO_2
Substrate	Crown glass Borosilicate glass

2-2 Measurement of mechanical properties

2-2-1 Microhardness

The microhardness of the films deposited on crown glass substrate (1.0∼1.2 mm thick) was measured by a Vickers microhardness tester and evaluated with the mean value and standard deviation of 5 samples calculated from

$$Hv = 2\sin 68° \frac{L}{d^2} \quad \text{(Pa)} \qquad (1)$$

Where L is the load (0.049 N), d the diagonal lengths of indentation (m).

2-2-2 Internal stress

The internal stress in the films deposited on a single side of a thin circular borosilicate glass substrate of 15 mm (diameter)×0.139 mm (thickness) was evaluated from radius of curvature of elastic bending with a microstylus profilometer[6,7]. The internal stress (σ_i) was calculated from the next equation[8,9] under the conditions of $t_f<t_s<r_s$.

$$\sigma_i = \frac{E_s t_s^2}{6(1-\nu_s) r_s t_f} \quad \text{(Pa)} \qquad (2)$$

Where, E_s, t_s, ν_s and r_s are the Young's modulus (70.85 GPa), thickness (~0.139 mm), Poisson's ratio (0.23), radius of curvature (m) of the substrate, respectively, and t_f is the film thickness (m). It is difficult to measure the stress distribution in the film. When the whole film is regarded as surface layer with no thickness, the product of internal stress (σ_i) and film thickness (t_f) is called the total stress (S). The total stress corresponds to surface tension (N m^{-1}).

$$S = \sigma_i \cdot t_f \quad \text{(N m}^{-1}\text{)} \qquad (3)$$

2-2-3 Fracture toughness of film

When stress is acting in the surface layer of the substrate, the radial crack length induced around Vickers indentation changes according to internal stress. The crack length extends when surface stress is tensile ($\sigma_i>0$), while it recedes when it is compressive ($\sigma_i<0$) at a constant load of the indenter (9.8N). According to thin-layer surface stress analysis proposed by Lawn and Fuller[10], the relationships between the internal stress of the surface layer and crack length induced by Vickers indenter is given by eq.(4) when the thin layer is smaller than the crack length ($t_f<C$).

$$2\Psi \sigma_i t_f^{1/2} = K_c \left\{ 1 - \left(C_s / C \right)^{3/2} \right\} \quad \text{(N m}^{-3/2}\text{)} \qquad (4)$$

Where Ψ is the crack geometry factor (about 1.0), t_f the thickness (m) of stress layer (i.e., the film thickness in this study), K_c the fracture toughness (Nm$^{-3/2}$) which is often effected by stress layer (film toughness), C_s the radial crack length (m) when the stress layer is absent (i.e., the substrate itself), and C the radial crack length (m) when surface stress is applied.

2-2-4 Refractive index

The refractive index was derived from the interference fringes in the UV transmission absorbance spectra for the YSZ film on the quartz glass substrate[11].

$$n_a = \frac{N \lambda_1 \lambda_2}{2 t_f (\lambda_2 - \lambda_1)} \qquad (5)$$

Where n_a is the mean refractive index between λ_1 and λ_2, λ_1, λ_2 the local maxima of wave length (m) ($\lambda_1 < \lambda_2$), t_f the film thickness (1 μ m), N the number of waves between λ_1 and λ_2. Since the refractive index is basically proportional to the density of the films[12], it is possible to interpret that the refractive index of the films corresponds to the film density.

3. Results and discussion

3-1 Microhardness

Fig.1 shows the effect of film thickness (1～4 μ m) on the Vickers microhardness for the 8Y-ZrO_2 (●) and 3Y-ZrO_2 (○)films, which are sputtered under the condition of the substrate temperature of 250 ℃ and sputtering pressure of 1.0 Pa. The load of indenter is constant at 0.049 N. The hardness of both films increased with the film thickness, and gradually became an inherent value at film thicknesses above 3 μ m. The hardnesses of 8Y-ZrO_2 and 3Y-ZrO_2 films were 15.6 GPa and 12.9 GPa, respectively. The fact that the hardness of 8Y-ZrO_2 films is higher than that of 3Y-ZrO_2 films is seemed to be responsible for the higher density of the films, since 8Y-ZrO_2 films possess the higher refractive index (2.14) than 3Y-ZrO_2 films (1.97). The hardness of sintered ZrO_2 bulk samples is about 12～15 GPa[13,14]. Hence, the hardness of the films prepared by this experiment was comparable to that by the sintering method.

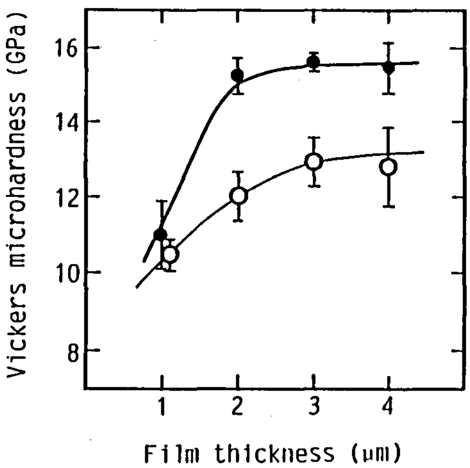

Fig.1 Effect of film thickness on Vickers hardness in 8Y-ZrO2 (●) and 3Y-ZrO2 (○) films. Hardness value of crown glass substrate is 5.3 GPa. Indenter load is constant at 0.049 N.

3-2 Internal stress

Fig.2 shows the effect of film thickness (0.1～1.0 μ m) on the total stress and internal stress in the films on the borosilicate glass substrates under the condition of the substrate temperature of 250 °C and sputtering pressure of 1.0 Pa. The internal stress determined was strongly compressive (negative values) as a whole. The total stress (S) increased linearly with the film thickness. The total stresses for 8Y-ZrO_2 and 3Y-ZrO_2 films at 1 μ m thick were 1280 Nm^{-1} and 1100 Nm^{-1}, respectively. On the other hand, higher internal stresses (σ_i) were acted in thinner films. The internal stresses for 8Y-ZrO_2 and 3Y-ZrO_2 films at 0.1 μ m thick were 3.13 GPa and 2.94 GPa, respectively. The reason for the compressive stress acted in the films is estimated as follows. When the film is deposited by sputtering in rf plasma, the particles (the molecules or ions of target material) collide with the films on the substrate accompanying high speed and kinetic energy (about 10 eV at the maximum). These particles invade the interstitial site of crystal lattice of the films, or strike the atoms of the film surface into the inside to create interstitial atoms. Therefore, these particles bring about the volume expansion of the films and simultaneously induce the compressive stress in the films. This phenomenon is called "peening effect"[15]. Generally, the compressive stress in the films is preferable to the tensile stress from the view point of the prevention of crack occurrence. But extremely high compressive stress is afraid of the lowering in adhesive strength to the contrary[16].

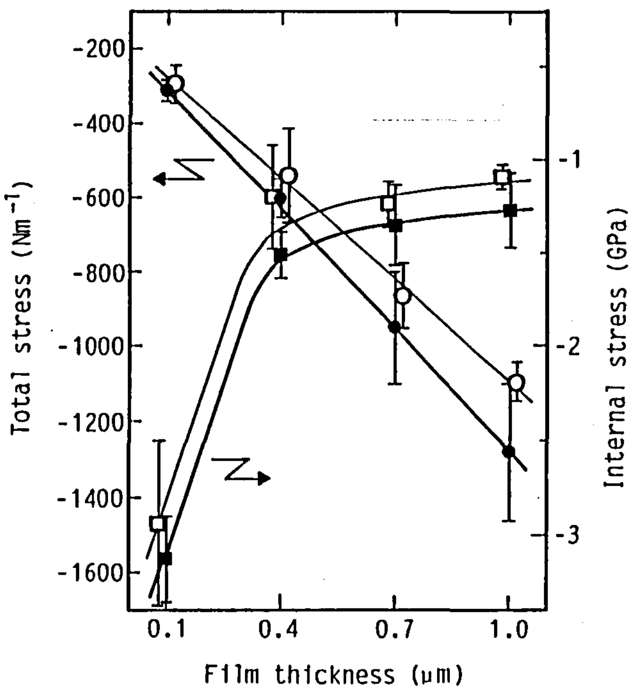

Fig.2 Effect of film thickness on total stress and internal stress in 8Y-ZrO2 (●) and 3Y-ZrO2 (O) films on borosilicate glass substrate.

3-3 Substrate temperature dependence on hardness, internal stress and refractive index

Fig.3 shows the effect of the substrate temperatures (10~250 °C) on Vickers microhardness, total stress, internal stress and refractive index in the films under the condition of the film thickness of 1 μ m and sputtering pressure of 1.0 Pa. The hardness values in this figure (1 μ m thick film) were not the inherent values of the film hardness, because they were obtained at the film thicknesses above 3 μ m (see Fig.1). However these values of hardness were interpreted to show the tendency of microhardness with increasing substrate temperature. The hardness was increased only slightly with increasing substrate temperature. The hardness for 8Y-ZrO_2 films was somewhat higher than that of $3Y\text{-}ZrO_2$ films. This may be also attributable to the higher density of $8Y\text{-}ZrO_2$ films judging from the measurement of the refractive index. The internal stress or total stress was not dependent on the substrate temperature in both $8Y\text{-}ZrO_2$ and $3Y\text{-}ZrO_2$ films. The thermal stress based on the difference of the thermal expansion coefficient between the substrate and film is shown in eq.(6)[17].

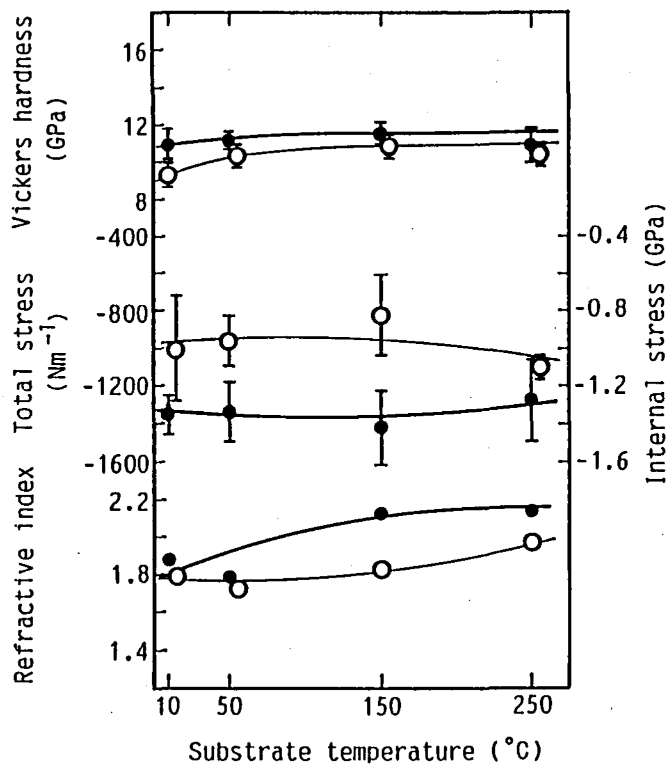

Fig.3 Effect of substrate temperature on Vickers hardness, total stress, internal stress and refractive index in 8Y-ZrO2 (●) and 3Y-ZrO2 (O) films.

$$\sigma_{th} = \frac{E_f}{1-\nu_f}\left(\alpha_s - \alpha_f\right)\Delta T \quad \text{(Pa)} \qquad (6)$$

Where σ_{th} is thermal stress (Pa), E_f, ν_f, α_f are Young's modulus (~210 GPa)[18], Poisson's ratio (~0.31)[18] and thermal expansion coefficient (~9.6×10^{-6}°C^{-1})[18] for the films, respectively, and α_s is the thermal expansion coefficient (~7.7×10^{-6}°C^{-1}) for the substrate. Substituting the above values for the eq.(6) yields σ_{th}= -0.145 GPa (the negative value expresses a compressive stress). Generally, resulting internal stresses (or residual stresses) are the sum of thermal stress and intrinsic stress. Since the measured stress (-0.8~-1.4 GPa) is fairly higher than the predicted thermal stress, the main component of internal stress is considered to be the intrinsic stress in this experiment.

3-4 Total gas pressure dependence on hardness, internal stress, crack length and refractive index

Fig.4 shows the effect of sputtering pressures (1.0~10.0 Pa) on the Vickers microhardness, total stress, internal stress, radial crack length around Vickers indentation and refractive index in the films under the condition of the film thickness of

1.0 μ m and substrate temperature of 250 °C. The hardness in both films lowered with the increase in the sputtering pressure (total pressure). This seemed to be also responsible for the decrease in the density of the films, as the change of hardness was corresponding to that of refractive index. The higher sputtering pressure the film was prepared at, the lower density the film possessed. This is interpreted as follows. When the total pressure in the chamber of the rf sputtering equipment is higher, the density of the films becomes lower as interpreted from the data of the refractive index. Hence, the deposition rate of the films will become higher in appearance[5]. The compressive total stress (internal stress) was decreased at the higher sputtering pressures as shown in Fig.4. This is explained as follows. When the sputtering pressure in the chamber becomes higher, the collision frequency among the molecules or ions are increased. It brings about the shorter mean free path, lower kinetic energy per particle and lower peening effect, which result in the lower compressive stress in the films.

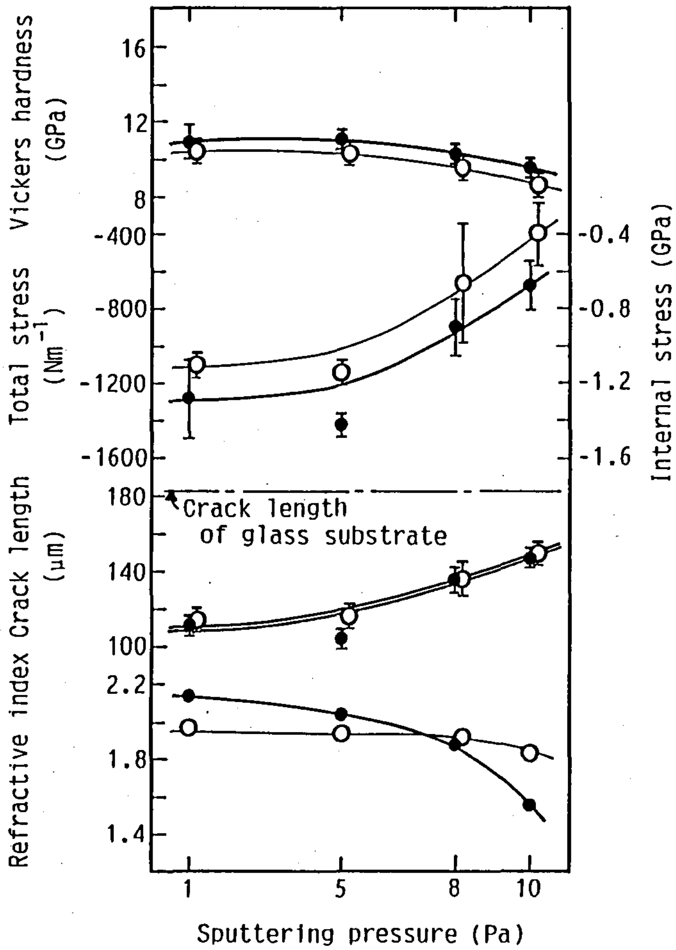

Fig.4 Effect of sputtering pressure on Vickers hardness, total stress, internal stress, radial crack length around Vickers indentation and refractive index in 8Y-ZrO2 (●) and 3Y-ZrO2 (○) films.

3-5 Fracture toughness

Vickers indenter (load 9.8 N) was loaded at the film (1 μ m thick) on the crown glass substrate, and the radial crack length around Vickers indentation was measured. The crack length was shortened at higher sputtering pressures as shown in Fig.4. This change was very similar to that of internal stress. According to the thin-layer surface stress analysis[10], the relationships between the crack length around Vickers indentation and internal stress is expressed in eq.(4). The results of Fig.4 were plotted in Fig.5 by using eq.(4). As shown in Fig.5, linearly proportional relations were obtained for both the films in accordance with the theory. From this relation, the acting internal stress in the films was found to be estimated by the measurement of the crack length of the films with a constant film thickness, concomitantly. The slope of the line will indicate the toughness of the coated substrate, which is affected by film toughness. The calculated toughnesses for the coated substrate with $8Y\text{-}ZrO_2$ and $3Y\text{-}ZrO_2$ films were 0.719 $MNm^{-3/2}$ and 1.11 $MNm^{-3/2}$, respectively. The toughness relating to $3Y\text{-}ZrO_2$ films was slightly higher than that relating to $8Y\text{-}ZrO_2$ films. This reason may be attributable to the stress-induced transformation in $3Y\text{-}ZrO_2$ (partially stabilized zirconium oxide) films.

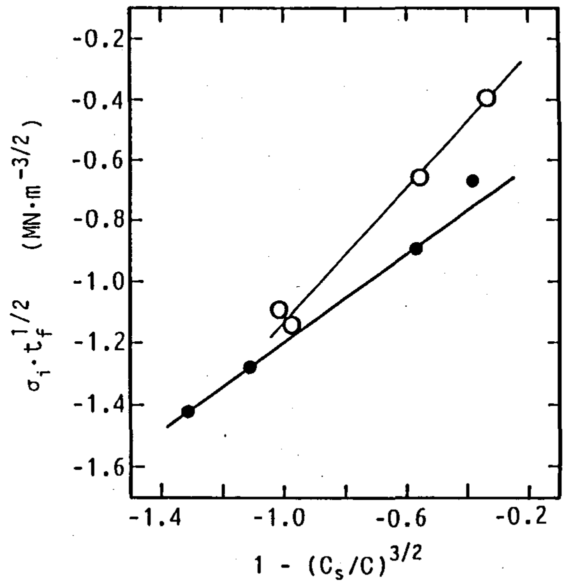

Fig.5 Plots of $\sigma_i t_f$ with $1 - (C_s/C)^{3/2}$ to the equation (4) to investigate the relation between internal stress (σ_i) and radial crack length (C). Slope of linear line is related to the fracture toughness (K_c) of the film.

4. Conclusions

The $8mol\%Y_2O_3\text{-}ZrO_2$ ($8Y\text{-}ZrO_2$) and $3mol\%Y_2O_3\text{-}ZrO_2$ ($3Y\text{-}ZrO_2$) ceramic films were prepared by the magnetron-assisted rf sputtering method on the glass substrate. Their properties were as follows.

(1) The hardnesses of $8Y\text{-}ZrO_2$ and $3Y\text{-}ZrO_2$ films were 15.6 GPa and 12.9 GPa, respectively. The hardness of $8Y\text{-}ZrO_2$ films is higher than that of $3Y\text{-}ZrO_2$ films, since $8Y\text{-}ZrO_2$ films possess the higher density than $3Y\text{-}ZrO_2$ films by the measurement

of refractive index. The hardness of the prepared films was comparable to that by the sintering method.

(2) The total stress and internal stress in the films on the borosilicate glass substrates were strongly compressive (negative values) as a whole, since the particles induced by rf plasma invaded the interstitial site of crystal lattice of the films and brought about the volume expansion of the films

(3) The total stresses for $8Y\text{-}ZrO_2$ and $3Y\text{-}ZrO_2$ films at 1 μ m thick were 1280 Nm^{-1} and 1100 Nm^{-1}, and the internal stresses for both films at 0.1 μ m thick were 3.13 GPa and 2.94 GPa, respectively.

(4) The Vickers hardness, total stress, internal stress and refractive index in both $8Y\text{-}ZrO_2$ and $3Y\text{-}ZrO_2$ films were not strongly dependent on the substrate temperatures (10 ~250 °C).

(5) The Vickers hardness, compressive internal stress and refractive index in both films lowered with the increase in the sputtering pressure (total pressure, 1.0~10.0 Pa). The crack length around Vickers indentation was increased at the higher sputtering pressures because of the lowered compressive internal stress.

(6) The fracture toughnesses for the coated substrate with $8Y\text{-}ZrO_2$ and $3Y\text{-}ZrO_2$ films were 0.719 $MNm^{-3/2}$ and 1.11 $MNm^{-3/2}$, respectively. The toughness for $3Y\text{-}ZrO_2$ films, which have the stress-induced transformation (partially stabilized zirconium oxide), was slightly higher than that for $8Y\text{-}ZrO_2$ films with no transformation.

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