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Structural and Optical Properties of RF Magnetron Sputtered Yttria-Stabilized Zirconia Thin Films

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고주파 마그네트론 스퍼터링에 의해 제조된 이트리아 안정화 지르코니아 박막의 조직 및 광학적 특성

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Abstract – The effects of the O_2 concentration in the sputtering gas mixture, substrate temperature and Ar pressure on the structural and optical properties of 3 mol% YSZ and 8 mol% YSZ thin films deposited by RF magnetron sputtering were investigated. The films were observed to have various crystal structures with different compositions in accordance with the type of the target materials. The size of fine grain-like particles decreased with increasing the O_2 concentration in the sputtering gas in the case of 3 mol% YSZ, while it increased in the case of 8 mol% YSZ. However, the average optical transmission of 8 mol% YSZ, despite of thicker thickness, was higher than that of 3 mol% YSZ. Furthermore, the values of refractive index of 3 mol% YSZ increased with increasing the O_2 concentration in the sputtering gas on the contrary to those of the 8 mol% YSZ. However, the transmission spectra of 8 mol% YSZ films were not strongly influenced by the substrate temperature and Ar pressure, whereas the refractive index of the YSZ films were strongly affected by the sputtering parameters.

요 약 – 고주파 마그네트론 스퍼터링법에 의해 제조된 3 mol%와 8 mol% YSZ 박막의 스퍼터링 가스 내의 산소농도, 기판온도 및 Ar 압력에 따른 조직 및 광학적 특성을 조사하였다. 제조된 박막과 타게트의 결정구조는 서로 상이하게 나타났다. 3 mol% YSZ 박막의 경우 스퍼터링 가스 내의 산소농도가 증가함에 따라 grain-like particle의 크기가 감소하였지만 8mol% YSZ 박막의 경우는 증가하는 경향을 보여주었으며, 8 mol% YSZ 박막의 투과율은 3 mol% YSZ 박막의 두께보다 더 두꺼운 두께에도 불구하고 더 높았다. 3 mol% YSZ 박막의 굴절률은 스퍼터링 가스 내의 산소농도가 증가함에 따라 증가하였지만 8 mol% YSZ 박막의 경우는 감소하는 경향을 보여주었다. 또한 8 mol% YSZ 박막의 투과율은 기판온도 및 Ar 압력에 크게 영향을 받지 않았지만 굴절률은 큰 영향을 받았다.

1. Introduction

Zirconia(ZrO_2) is of current interest as a high refractive index material in optical coatings since its absorption is low in a broad spectral region from near-UV to mid-IR. In addition to having a large optical band gap and a high laser damage threshold, it is hard, durable and easily available. It appears suitable for making high reflecting mirrors, laser gyros, broadband interference filters, and refractometer prisms[1-4]. Like many oxides, zirconia crystallizes into different polymorphs when it is subjected to different thermal cycles. The zirconia crystal structure is temperature-dependent. The phase transition is a limiting factor because of the large volume variation associated with it(3~

6%), but it can be inhibited by adding a convenient amount of other oxides, such as Y_2O_3, MgO etc.[5]. The thin films obtained are therefore resistant to environmental influences. However, the optical application of zirconia suffers from two serious drawbacks: variation of the refractive index with thickness and high optical loss, especially scattering[6, 7]. Generally, the optical losses are structure- and/or impurity-related and act as performance-limiting factors[7].

A composite thin film made from the mixture of two or more pure materials has new properties (e.g. optical, mechanical, structural and electrical properties) which pure materials do not have. This idea is adopted by this work to improve various properties of zirconia thin films for thin film optics.

In the present work, zirconia materials partially and totally stabilized with 3 mol% and 8mol% yttria(Y_2Oa_3), respectively, were studied to assess the effects of deposition parameters, such as the O_2 concentration in the sputtering gas, substrate temperature and gas pressure, on the structural and optical properties of the materials.

2. Experimental procedures

Yttria stabilized zirconia(YSZ) thin films were deposited on glass and silicon substrates by RF magnetron sputtering; selection of the particular substrate for each specimen depended on the characteristic properties to be studied. The base pressure was below 5×10^{-6}torr before introducing sputtering gases for the plasma discharge, and the target was sputter-cleaned for approximately 20 min before deposition. The plasma atmosphere was pure Ar and a mixture of Ar and O_2 gases and the sputtering pressure used was 5×10^{-3}torr.

The compositions of the sputtering targets 3 inches in diameter were 3 mol% and 8 mol% YSZ of 99.95% purity. Spectrographic analysis showed that all the impurities present were less than 0.01% by weight except for Ti(0.02%). The result of X-ray diffraction measurements indicated that the 3 mol% and 8 mol% YSZ targets had tetragonal zirconia with a small trace of monoclinic phase and cubic zirconia with a small trace of tetragonal phase, respectively. In this study, the deposition parameters were O_2 concentration in the sputtering gas, substrate temperature and concentration of yttria in the targets. To characterized the properties of the films deposited under various conditions, the following measurements were carried out; film thickness and roughness by alpha step(Tencor, α-step 200), film structure and morphology by XRD (Rigaku, RAD-C), SEM(JEOL, JSM-35CF) and TEM(JEOL, JEM-2000EX II), film composition by XPS(V. G. Scientific, ESCALAB 220i), refractive index by ellipsometer(Gaertner Sci., L 116B-85B) and optical transmission by spectrophotometer (Perkin-Elmer, Lambda 9 UV/VIS/NIR).

3. Results and Discussion

The Y and Zr contents in the YSZ films and those of the sputtering targets determined by XPS is shown in Table I, where the sputtering yield of Zr is observed to be higher than that of Y during RF magnetron sputtering. Fig. 1 shows a wide scan XPS spectrum of a as-deposited 8 mol% YSZ film in the 0-1000 eV range. The major peak lines are O 1s, Zr 3p, Zr 3d, Zr 4p, Y 3p and Y 3d in

Table 1. XPS analysis of sputtering targets and deposited films

Sample \ Content	Zr (at. %)	Y (at. %)
8 mol% YSZ target	84.15	15.85
8 mol% YSZ film (0% O_2)	90.73	9.27
8 mol% YSZ film (10% O_2)	94.03	5.97
8 mol% YSZ film (20% O_2)	93.11	6.89
3 mol% YSZ target	92.75	7.25
3 mol% YSZ film (0% O_2)	97.69	2.31
3 mol% YSZ film (10% O_2)	98.45	1.55
3 mol% YSZ film (20% O_2)	98.31	1.69

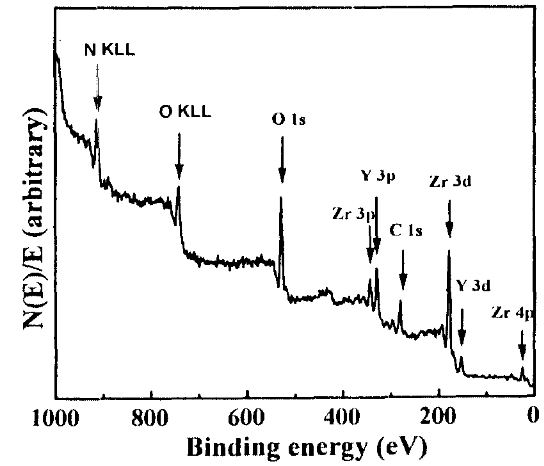

Fig. 1. XPS spectrum of 8 mol% YSZ film(0% O_2).

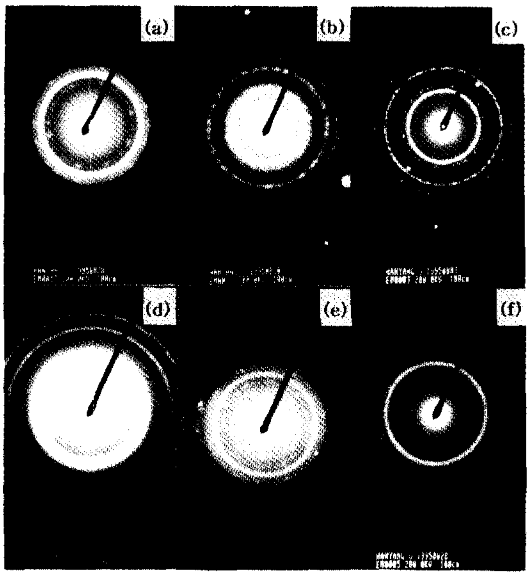

Fig. 2. Electron diffraction patterns of 3 mol% YSZ((a) 0% O_2, (b) 10% O_2, (c) 20% O_2) and 8 mol% YSZ((d) 0% O_2, (e) 10% O_2 (f) 20% O_2) films.

the spectrum. It can be seen that C 1s line appears in addition to the major compositional elements of the films. The carbon is believed to come from the residual gases such as CO and CO_2 in the vacuum chamber.

The electron diffraction patterns for the 3 mol% and 8 mol% YSZ films sputter deposited on silicon substrates at different O_2 concentrations are

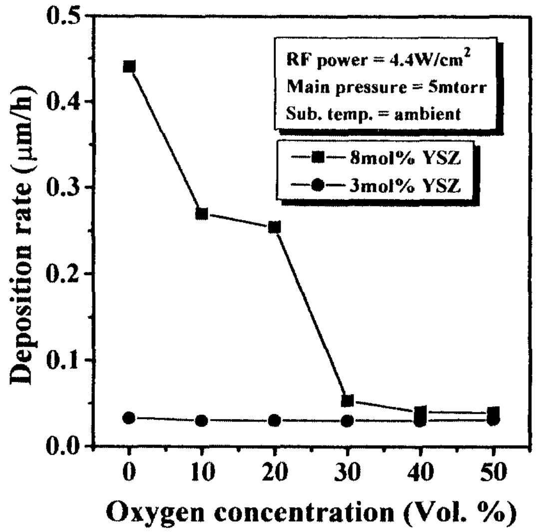

Fig. 3. Effect of O_2 concentration on deposition rate.

shown in Fig. 2. The result shows that 8 mol% YSZ films have a tetragonal structure independent of O_2 concentration while 3 mol% YSZ films have a monoclinic structure in 0% O_2 concentration and a monoclinic structure with a small trace of tetragonal (111) phase with O_2 concentrations above 10%.

Fig. 3 shows that at a constant sputtering pressure(5×10^{-3}torr) the deposition rate of 8 mol% YSZ falls down rapidly with increasing the O_2 concentration in the Ar-O_2 gas mixture but that of 3 mol% YSZ remain low and almost constant. It is difficult to pinpoint the exact mechanism responsible for the constant and the sudden decrease in the deposition rate of 3 mol% YSZ and 8 mol% YSZ, respectively, with the introduction of O_2 gas, because sputtering of YSZ targets in the presence of Ar-O_2 gas mixture is very complex, involving a number of processes causing changes in discharge conditions. These processes are (a) oxidation of YSZ target surface; (b) sputtering of metal oxide molecules from target; (c) gettering of O_2^- ions and O_2 atoms by the YSZ films on the substrate, and (d) the reactions between sputtered material with Ar-O_2 gas mixture are highly complex. However,

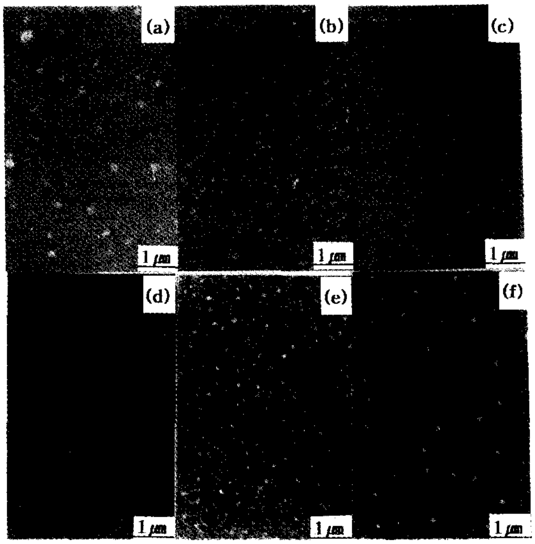

Fig. 4. SEM micrographs of 3 mol% YSZ((a) 0% $_2$, (b) 10% O_2, (c) 20% O_2) and 8 mol% YSZ((d) 0% O_2, (e) 10% O_2, (f) 20% O_2) films.

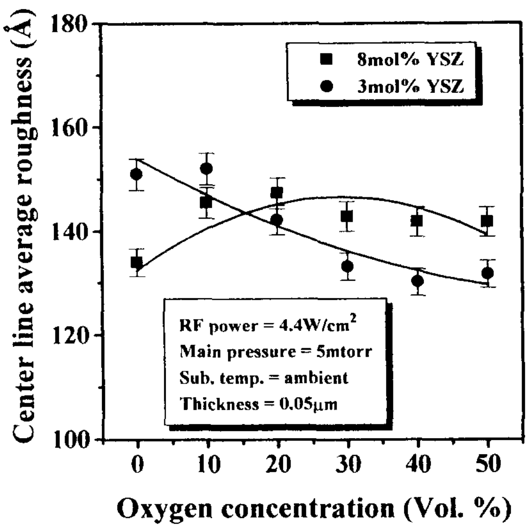

Fig. 5. Surface roughness as a function of O_2 concentration.

it is thought that the decrease in the sputtering rate of 8 mol% YSZ with increasing the O2 concentration is caused in part by a decrease in the oxygen vacancy on the surface of the target. With the O_2 concentrations over 30%, the sputtering rate remains low independently of the O_2 concentration, indicating a saturation of the target surface oxidation, while the sputtering rate of 3 mol% YSZ having fewer oxygen vacancies was independent of the O_2 concentration. Throughout the O_2 concentration range, the deposition rate of 8 mol% YSZ was faster than that of 3 mol% YSZ, probably due to the lower hardness and other mechanical strengths of 8 mol% YSZ target, giving high sputtering yield.

Blackening of the surface of the target was observed in an atmosphere of pure Ar, presumably due to reduction of the materials, but this could be reduced considerably by the addition of O_2 to the sputtering gas. Surface blackening was negligible when an equivolume mixture of O_2 and Ar was used.

It is known that the texture of YSZ films depend on the yttria content, bombardment during deposition and heat treatment[8]. The micrographs in Fig. 4 were obtained with the O_2 concentrations ranging from 0% to 20% in the sputtering gas and with the two materials(3 mol% and 8 mol% YSZ). In the figure, we can observe that under the identical as-deposited condition(0% O_2) the film surface is smoother and the size of fine grain-like particles is smaller in the films with higher yttria content(8 mol% YSZ) than in those with lower content(3 mol% YSZ). This result shows that the presence of the yttria dopant inhibits atomic mobility during film growth, producing a finer texture and smoother surface when the yttria concentration is increased.

Also, it is shown that in the case of 3 mol% YSZ, the size of fine grain-like particles decreases with increasing the O_2 concentration in the sputtering gas. The decrease can largely be attributed to the decrease in the energy transferred to the growing particles from high-energy gas species in the Ar-O_2 sputtering gas. On the contrary, in the case of 8 mol% YSZ, the size of the particles increased with increasing the O_2 concentration in the sputtering gas. The result can be attributed to the reduced atomic diffusion when the yttria con-

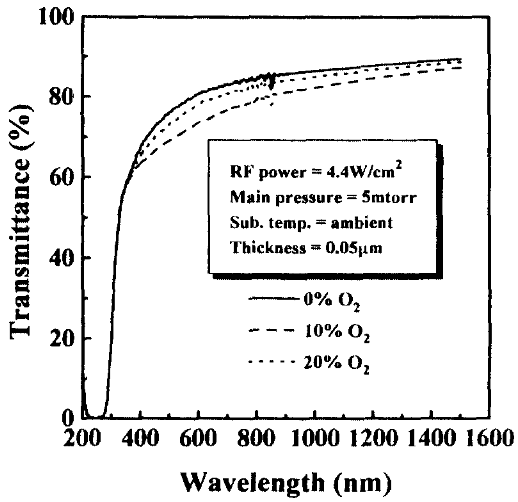

Fig. 6. Transmittance spectra of 3 mol% YSZ films sputter deposited on glass substrates at different O_2 concentrations.

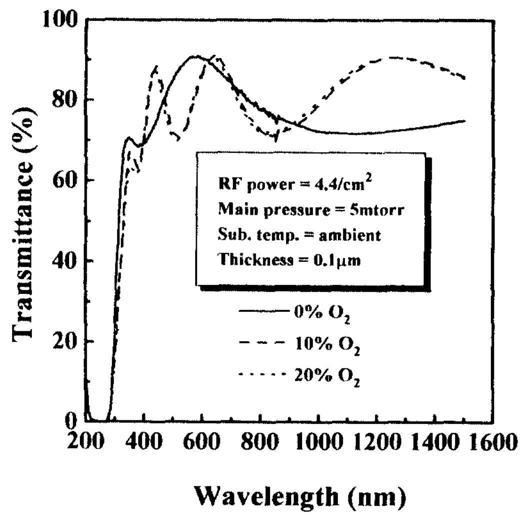

Fig. 7. Transmittance spectra of 8 mol% YSZ films sputter deposited on glass substrates at different O^2 concentrations.

centration is as high as 8 mol%.

The morphology of the films was also characterized on the basis of the profile of their surface roughness, obtained by alpha step analysis. The center line average roughness related to this analysis is given in Fig. 5. From this Fig. 5, we observed that the mean roughness of the 3 mol% YSZ decreased with the O_2 concentration in the sputtering gas, whereas 8 mol% YSZ increased. This result is in accordance with SEM micrographs of Fig. 5.

The optical transmission properties of 3 mol% and 8 mol% YSZ films were compared with each other in the wavelength range from 200 to 1500 nm in terms of the O_2 concentration in the sputtering gas in Figs. 6 and 7. The transmission of the 3 mol% and 8 mol% YSZ films was not improved by increasing the O_2 concentration, however, the spectra pattern was strongly influenced by the introduction of O_2. In particular, only one absorption peak appears in the transmission spectrum of the 8 mol% YSZ films for the case of 100% Ar gas, but several peaks appear introduction of O_2 in the sputtering gas. The transmission spectra are known to depend on the factors such as surface roughness, grain boundaries, voids, internal strain, scattering of free electrons at the film surface, etc.[9, 10].

Fig. 8 shows the average transmission and absorption coefficient in the visible wavelength range as a function of O_2 concentration. The absorption coefficient, β, is given by

$$T = \exp(\beta - x), \qquad (1)$$

$$T(\lambda) = \sum_{i=380}^{780} T_i / 401 \qquad (2)$$

where T, T_i and x are average transmission, that is, average fraction of light transmitted in the wavelength range from 380 to 780 nm, transmission at each wavelength and YSZ film thickness, respectively[11]. In the visible wavelength region (380 to 780 nm), the average transmission values for the three O_2 concentrations(0, 10 and 20%) fall in the range from 71% to 78% for the 3 mol% YSZ films and from 80% to 83% for the 8 mol% YSZ films. Thus, the average transmission of 8 mol% YSZ, despite of thicker thickness depicted Figs. 6 and 7, was higher than that of 3 mol% YSZ. This result is due to the lower absorption

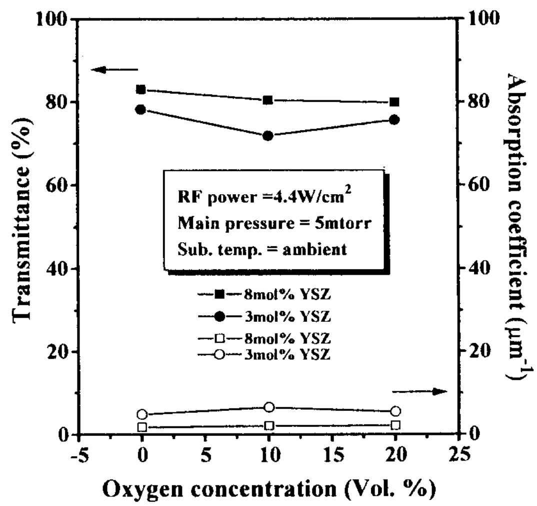

Fig. 8. Average transmittance and absorption coefficient in the visible range as a function of O_2 concentration.

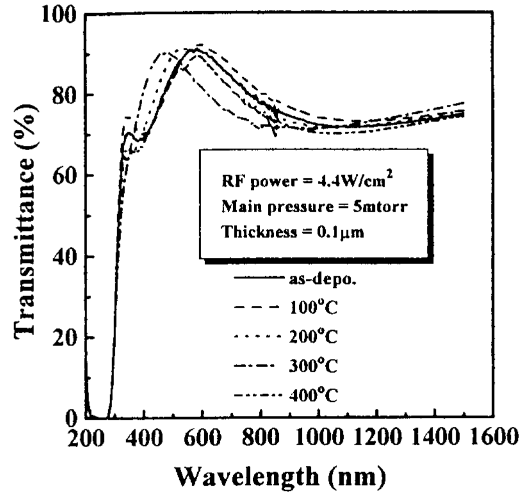

Fig. 10. Transmittance spectra of 8 mol% YSZ films sputter deposited on glass substrates at different substrate temperatures.

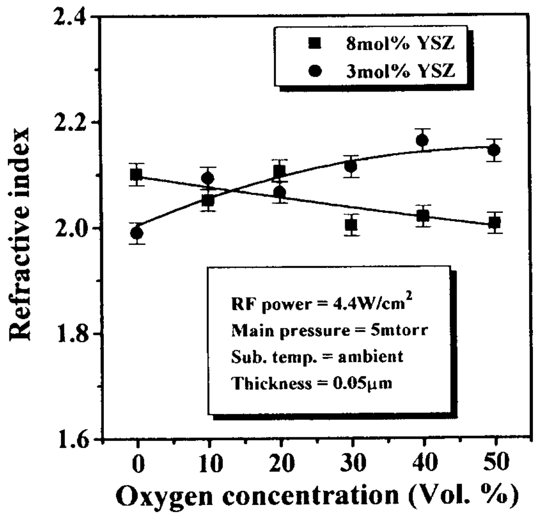

Fig. 9. Refractive index as a function of O_2 concentration (λ=632.8 nm).

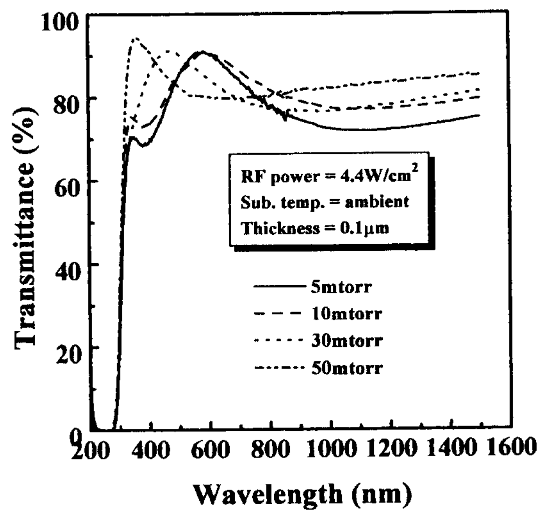

Fig. 11. Transmittance spectra of 8 mol% YSZ films sputter deposited on glass substrates at different Ar pressures.

coefficient of 8 mol% YSZ than that 3 mol% YSZ.

Fig. 9 shows variation of refractive index with the O_2 concentration determined by spectroscopic ellipsometry(Gaertner Sci., L116B-85B) and the measurements of refractive index were carried out using GC5A + Sub CA + SC6A + SC7A automatic ellipsometry program for IBM PC. The values of refractive index of 3 mol% YSZ increased with increasing the O_2 concentration in the sputtering gas while the reverse is true for the 8 mol% YSZ. The result shows that the values of the refractive index were low in the 8 mol% YSZ material due to the presence of a very strong tetragonal (111) phase of the nearest inner ring in the electron diffraction patterns of Fig. 2. But, variations of O_2 con-

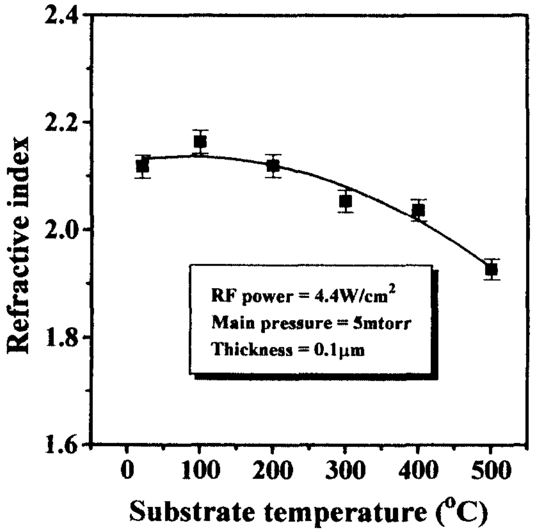

Fig. 12. Refractive index of 8 mol% YSZ films as a function of substrate temperature (λ=632.8 nm).

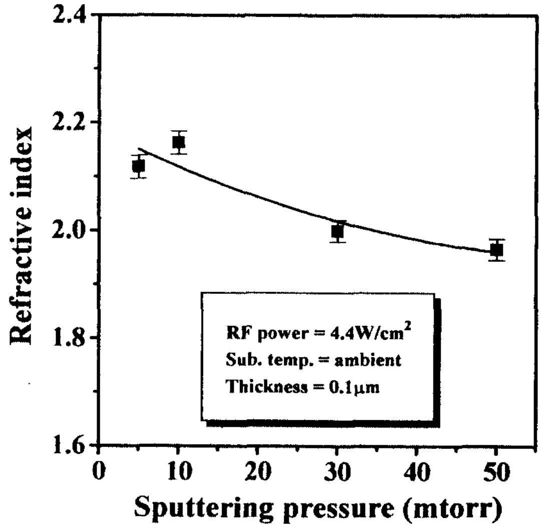

Fig. 13. Refractive index of 8 mol% YSZ films as a function of Ar pressure (λ=632.8 nm).

centration in the sputtering gas had less effect on the compactness (or packing density) of the 8 mol% YSZ films than that of the the 3 mol% YSZ films.

Figs. 10 and 11 show transmission spectra of the 8 mol% YSZ films deposited on glass substrates at different substrate temperatures and Ar pressures. The average transmission at different substrate temperatures were in the range from 81% to 83% and the average transmission at different Ar pressures were in the range from 83% to 85%. The transmission spectra are not strongly influenced by the substrate temperature and Ar pressure.

Figs. 12 and 13 show variation of the refractive index of 8 mol% YSZ films with the substrate temperature and the Ar pressure. The values remains almost the same with increasing the substrate temperature up to 200°C but decreases remarkably at temperatures above 200°C, while the values decreased with increasing Ar pressure. This result tells that these sputtering parameters affect the compactness and phase of the 8 mol% YSZ films.

4. Conclusions

We have studied the effects of the O_2 concentration in the sputtering gas mixture, substrate temperature and Ar pressure on the structural and optical properties of the 3 mol% YSZ and 8 mol% YSZ films. The films were observed to have various crystal structures with different compositions in accordance with the type of the target materials. The size of fine grain-like particles decreased with increasing the O_2 concentration in the sputtering gas in the case of 3 mol% YSZ, while it increased in the case of 8 mol% YSZ. However, the average optical transmission of 8 mol% YSZ in the visible range, despite of thicker thickness, was higher than that of 3 mol% YSZ. Furthermore, the value of the refractive index of 3 mol% YSZ increased with increasing the O_2 concentration in the sputtering gas while that of the 8 mol% YSZ decreased. Also, the transmission spectra of 8 mol% YSZ films were found to be not strongly influenced by the substrate temperature and Ar pressure. The value of the refractive index remains the same with increasing the substrate temperature up to

200°C but decreases greatly at temperatures above 200°C, while it decreased with increasing Ar pressure.

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