PHASE ANALYSES FOR DUAL ION BEAM DEPOSITED ZrO_2 FILMS ON NaCl SUBSTRATE*

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ABSTRACT

ZrO_2 films on NaCl(100) substrate produced by oxygen ion bombardment and argon ion sputtering of Zr are analysed using TEM, XRD and XPS. The result of TEM shows that only cubic phase exists for the ZrO_2 film produced by oxygen ion bombardment with $30\mu A/cm^2$ and 200eV, while the XRD result shows that there seems to exhibit a small quanitity of monoclinic phase apart from cubic one under the production condition of oxygen ion of $25\mu A/cm^2$, 100eV.

Keywords ZrO_2 film, Dual ion beam deposition, Ion Sputtering, TEM, XRD, XPS

1 INTRODUCTION

ZrO_2 is a high refractive index material with low loss and low scatter in the infrared region, and also an insulating material with a large relative dielectric constant of ~18 and a relatively wide energy gap of ~5eV, so ZrO_2 has many important applications in science and technology.

ZrO_2 cystallizes in different polymorphs under different conditions of temperatures and pressures. 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 and 1250°, it transforms to a tetragonal phase (space group $P4_2/nmc$), and at 2370°C, to a cubic fluorite structure (space group Fm3m). The other two phases exist at elevated pressures.

The methods used for depositing ZrO_2 films include vacuum evaporation, ion beam assisted evaporation, reactive magnetron sputtering and dual ion beam deposition techniques. As a high quality solid thin film producing technique, the stability and reproducibility are the most important factors. In the dual ion beam technique, direct measurement and control are available for the fundamental deposition parameters such as metal atom arrival rate, reactive species arrival rate (as ions), energy of arrival of the reactive species, and the direction of arrival of both metal and reactive species.

In this work, zirconia films are produced using a dual ion beam technique; phase structure analyses in the stoichiometric ZrO_2 films are reported using transmission electron microscopy (TEM) and X-ray diffraction (XRD). Previous investigation of ZrO_2 films includes TEM work on ZrO_2 films formed anodically[4] and by thermally forming

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oxides on zirconium[5], and XRD work on ZrO_2 films formed by e-beam evaporation[6], by reactive sputter deposition[7], and by ion-assisted deposition[8]. Less well study has been published on TEM abd XRD of dual ion beam deposited ZrO_2 films.

2 EXPERIMENTAL

The zirconia thin film samples are deposited by a dual ion beam technique at room temperature. The dual ion beam deposition system is shown schematically in Fig.1. Two Kaufman ion sources are used to supply metal atoms and reactive ions to the substrate. In the experiments, the zirconium target is sputtered by 1 keV Ar^+ ion beam and the reactive oxygen ion flux at 200eV or 100eV is supplied to the growing films, which can control the film composition through changing the beam current. The base pressure in the chamber before deposition is below 10^{-4} Pa (about $5\times10^{-5}\sim7\times10^{-5}$ Pa) and during the deposition is $2\times10^{-2}\sim4\times10^{-2}$ Pa.

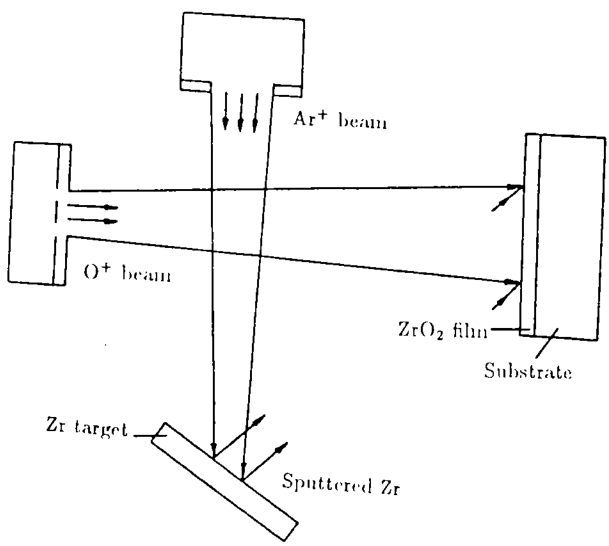

Fig.1 Schematic diagram of a dual ion beam deposition system

Films to be examined by TEM with a H-700H transmission electron microscopy are deposited on the cleaved (100) face of NaCl substrate and are floated off in distilled water and transferred to electron microscope copper grids.

X-ray diffraction patterns are recorded for the deposited ZrO_2 films on NaCl(100) substrate using a D/Max-RA X-ray diffractometer. Cu $K\alpha$ radiation of 40kV is used with a nickel monochromater filter. The detector angle is incremented in 0.02° steps. Data are gathered over a angle range from $2\theta=15°$ to 80°.

Stoichiometric formation of ZrO_2 films is measured by X-ray photoelectron spectrometry (XPS) using a VG scientific ESCALAB MKII system with AlK_α radiation (1486.6eV, 10kV, 20mA). The vacuum in the analysing chamber is better than 6×10^{-9}Pa.

3 RESULTS AND DISCUSSION

Fig.2 shows the Zr3d spectrum with XPS measurement for the bulk of the dual ion beam deposited zirconia film on NaCl (100) substrate. Except for the surface and the interface region between film and substrate stoichiometric ZrO_2 of the bulk of the film was formed. This spectrum resolved into the spin doublets $Zr3d_{5/2}$ and $Zr3d_{3/2}$ at binding energies of 182.2 and 184.3eV, respectively, is resulted from ZrO_2. It has been found that the stoichiometric ZrO_2 film could be produced under the reactive oxygen ion beam curent density of 25-35μA/cm^2. The results are also confirmed by RBS depth analysis[9].

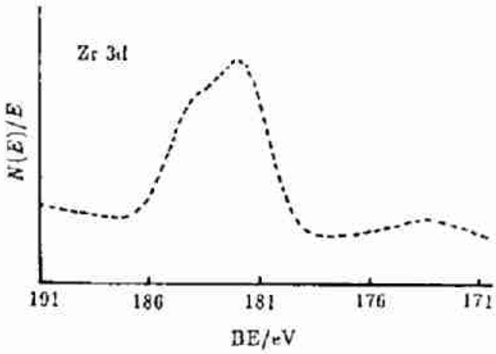

Fig.2 Zr3d spectrum for the bulk of the films under the reactive oxygen ion beam current density of 25μA/cm^2

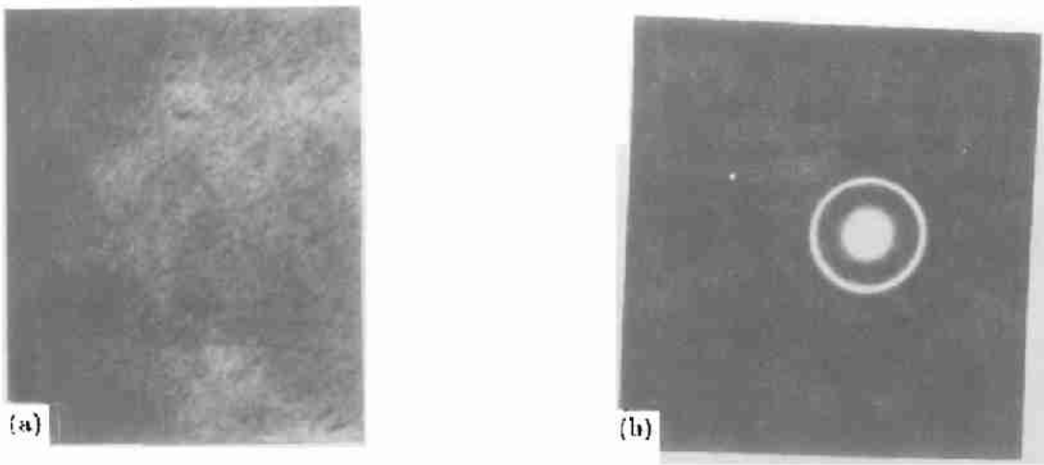

Fig.3 TEM image and corresponding diffraction patterns of selected region in the ZrO_2 film (a) bright field image, (b) electron diffraction pattern of (a)

Fig.3 shows TEM micrographs of the film with reactive oxygen ion beam current density of 30μA/cm^2 and an energy of 200eV, and the fitting of crystalline structure in Fig.3 is shown in Table 1. It can be found from Fig.3(a) that the film contains a uniform fine-grained microstructure with crystalline size of about 20nm. After examining the selected area diffraction patterns and calculation that the lattic parameter (a=0.535nm) measured according to the diffraction rings shown in Fig.3 (b) is greater than that (a=0.515nm) reported by Mckenzie et al[10], where the films were produced in vacuum from an electron beam hearth with simultaneous oxygen ion bombardment on the glass substrate at room temperature.

Fig.4 shows XRD pattern of the ZrO_2 film on NaCl(100) substrate with a oxygen ion beam current density of 25μA/cm^2 and an energy of 100eV. It can be seen that in addition to the main component cubic phase there seems to exhibit a small quantity of monoclinic phase. This is similar to the situation in Ref.[10], where some weak peaks which could not be indexed according to the cubic fluorite structure, however the Raman spectrum provides an indicator of the presence of monoclinic and cubic phase.

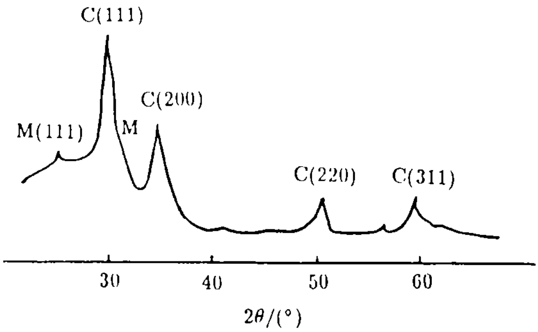

Fig.4 X-ray diffraction pattern of ZrO_2 films grown with reactive oxygen ion beam current densities of 25μA/cm^2 on NaCl(100) substrates, where C and M denote cubic and monoclinic, respectively

Table 1
Assignment of phase structure of the ZrO_2 film in Fig.3

No. of diffraction ring	1	2	3	4
$R=D/2$ (mm)	7.4	8.5	12.1	14.2
$(R_j^2/R_i^2)\times 3$	3.00	3.46	8.02	11.05
(hkl)	111	200	220	311
Measured d/nm	0.308	0.268	0.168	0.160
Stantard d/nm[11]	0.293	0.255	0.1801	0.1534
Deviation/nm	0.015	0.013	0.008	0.007

4 CONCLUSIONS

The ZrO_2 films deposited by the dual ion beam technique with suitable technological parameters reveal that

4.1 According to the results of XPS measurement, the dual ion beam technique with suitable oxygen ion bombardment current intensity and Zr sputtering deposition rate by Ar^+ could produce stoichiometric ZrO_2 films.

4.2 With the parameters in this experiment, crystalline structure could be formed in uniform fine-grain pattern.

4.3 The predominant metastable cubic phase with a small quantity of monoclinic one existed for the ZrO_2 films on NaCl(100) substrate produced by a dual ion beam processing at room temperature.

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