Phase changes of the ZrO_2-12 wt%Y_2O_3 film with Ar^+ irradiation*

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Abstract The zirconia containing 12wt%Y_2O_3 thin films deposited by r.f. magnetron sputtering at 25°C or 400°C, and then bombarded with Ar^+ beam at room temperature were characterized with XRD before and after Ar^+ bombardment. It is found that a series of phases formation and transformation happened, among them the most important event is that T' phase appeared after Ar^+ irradiation and the content of the T' phase increased with the increase of Ar^+ ion doses from 5×10^{15} to 6×10^{16} ions cm^{-2}.

Keywords Magnetron sputtering, ZrO_2-12wt% Y_2O_3 film, Ar^+ irradiation, XRD

1 Introduction

Yttria-stabilized zirconia with a high resistivity and a large relative dielectric constant is a very attractive electrical insulator.[1] It can be used for the fabrication of silicon-on-insulator(SOI) structures or as the buffer layer in high T_c ceramic superconductors on Si to avoid the reaction between Si and the superconductor film.[2]

The polymorphic behaviour of zirconia based ceramics containing less than 20wt% Y_2O_3 still affects its thermal shock-resistance when it is used over a large temperature range. It has been found that there seems a correlation between coating durability and tetragonal phase content in the plasman-sprayed zirconia-yttria coatings.[3] As known well, there are two kinds of tetragonal phases, one is a metastable tetragonal phase (T) with a low yttria content which transforms martensitically to the thermodynamically more stable monoclinic phase, hence is expected to be able to toughen, and another is also a metastable tetragonal phase (T') with a high yttria content which does not transform on cooling to room temperature and lies in the chemical stability. In order to sort out the effects of these phases on the coating performance, it is necessary to go further into such a phase composition. In our previous paper,[4] the zirconia-yttria films containing 8.0wt% Y_2O_3 produced by r.f. magnetron sputtering followed by Ar^+ bombardment at room temperature were microanalysized. In this paper the films containing 12wt%Y_2O_3produced by the same way were characterized with XRD in order to further understand the effects of ion irradiation on the phase formation or transformation.

2 Experimental

ZrO_2 with 12wt%Y_2O_3 films were deposited by r.f. magnetron sputtering on Si substrate at room temperature (25°C) or at 400°C. The chamber had a base pressure of 4×10^{-4}Pa but this pressure increased to 0.3~0.7 Pa during deposition owing to argon plus a little quantity of oxygen feeding the discharge. After deposition, some of these specimens were bombarded at room temperature with 170keV Ar^+ ions to a dose of $(0.5\sim6)\times10^{16}$ ions cm^{-2}, respectively. Phase structure analysis of the films was performed with a D/Max-RA X-ray diffractometer.

3 Results and discussion

The results of the XRD measurements for the ZrO_2-12wt%Y_2O_3 films on Si substrates deposited by r.f. magnetron sputtering are that the films were amorphous when the substrate was at room temperature during deposition; while the films were partially crystallized and still showed a content of amorphous (a) when the substrate temperature was at 400°C, as

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shown in Fig.1. The crystallized part was cubic(C) with a minor quantity of monoclinic (M) phase. The phase structure of the films observed in our experiment agrees with that of previous studied[5], but differs from those of Knoll[6], who observed only a cubic phase in the composition range of 3mol%~15mol%Y_2O_3 for the r.f. diode sputtering deposited YSZ films.

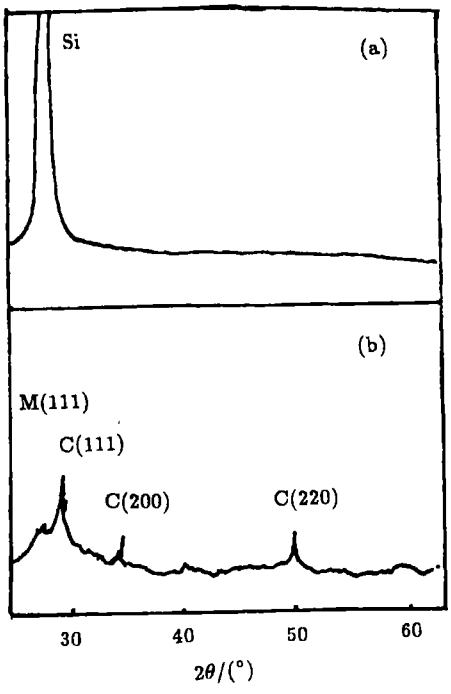

Fig.1 XRD peaks of the ZrO_2-12wt%Y_2O_3 films deposited by r.f. magnetron sputtering at substrate temperature of 25°C (a) and 400°C (b)

The XRD results for the films deposited at room temperature after Ar^+ ion bombardment at room temperature show that the films bombarded with a dose of 5×10^{15} Ar^+ ion cm^{-2} were a mixture of amorphous, a main component polycrystalline structure, as shown in Fig.2(a), the crystallized part is a Y_2O_3 hexagonal phase. The films bombarded with a dose of 2×10^{16} Ar^+ ions cm^{-2} were also a mixture of polycrystalline and amorphous structures, as shown in Fig.2(b), in this crystallized part T' phase with a high yttria content appeared in addition to the Y_2O_3 hexagonal phase. The films bombarded with a dose of 6×10^{16} Ar^+ ions cm^{-2} were still a mixture of polycrystalline and amorphous shown in Fig.2(c), in this crystallized part a new cubic phase with a little quantity of content appeared apart from those phases existed in the situation of Ar^+ ion bombardment with lower doses. With increasing Ar^+ dose from 5×10^{15} to 6×10^{16} ions cm^{-2}, the amount of the amorphous component decreased and the crystallized one increased, where the T' phase was subsequently increased, and the cubic phase began to appear, while the H phase seemed decreased.

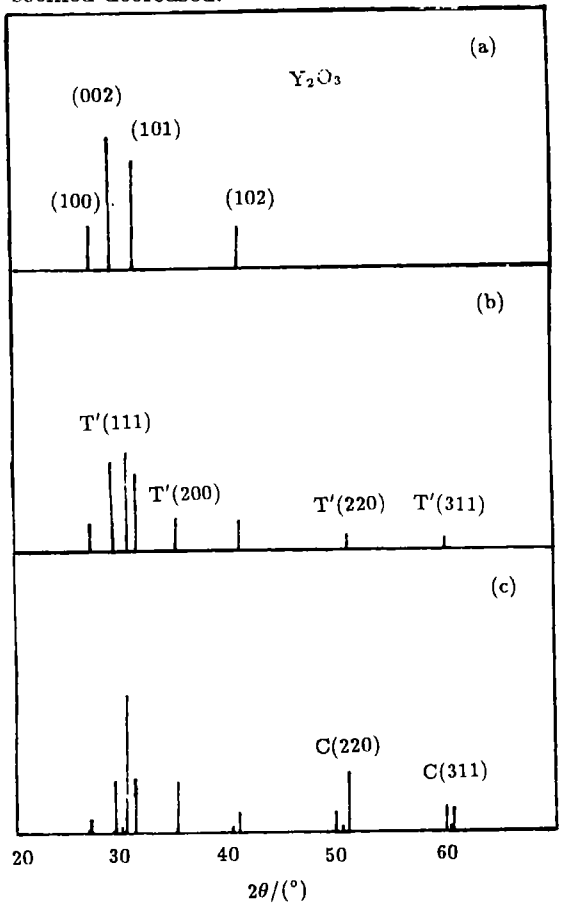

Fig.2 XRD peaks of the ZrO_2-12 wt%Y_2O_3 films deposited at 25°C after Ar^+ irradiation with a dose of (a) 5×10^{15}, (b) 2×10^{16}, (c) 6×10^{16} ion cm^{-2}

The ZrO_2-12wt%Y_2O_3 films deposited by r.f. magnetron sputtering at 400°C after Ar^+ irradiation were a mixture of polycrystalline and amorphous structures shown in Fig.3, but we found that the Y_2O_3 hexagonal phase no longer appeared. The T' phase was observed after Ar^+ irradiation with a dose of 5×10^{15} ions cm^{-2} in

addition to cubic and monolinic phase peaks shown in Fig.3(a). With increasing Ar^+ doses from 5×10^{15} to 6×10^{16} ions cm^{-2} the diffraction peaks became sharped indicating the amorphous component was quickly decreased and transformed to crystal phases, the monoclinic phase seems disappeared, the cubic phase was not changed by comparing with the intensities of their peaks before and after Ar^+ irradiation,

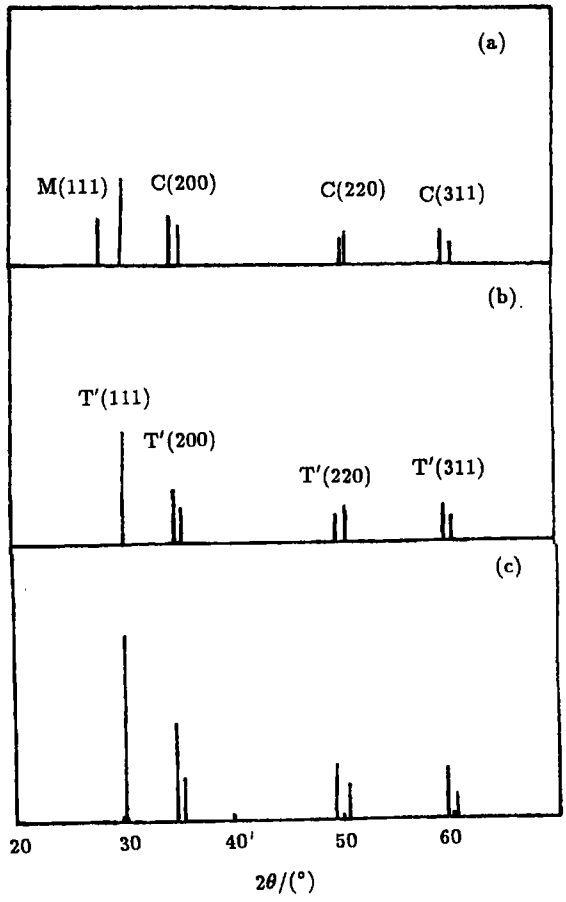

Fig.3 XRD Pekas of the ZrO_2-12 wt%Y_2O_3 films deposited at 400°C after Ar^+ irradiation with a dose of (a) 5×10^{15}, (b) 2×10^{16}, (c) 6×10^{16} ion cm^{-2}

while the T' phase was obviously increased. For clarification, the phase compositions for the r.f. magnetron sputtering deposited at room temperature or at 400°C followed by Ar^+ ion bombardment with different doses are listed in Table 1, where the phases are grossly arranged in their content order.

Table 1 Phase compositions of the Ar^+ irradiated ZrO_2-12wt% Y_2O_3 films

	Ar^+ Dose/cm^{-2}			
t/°C	0	5×10^{15}	2×10^{16}	6×10^{16}
25	a	a+H	a+T'+H	a+T'+H+C
400	C+a+M	C+T'+a+M	T'+C+a	T'+C+a

Plasma spraying of the ZrO_2-8wt%Y_2O_3 coatings with cooling rates of the order of 10^{16} °C/s[7] leading to a suppression of the decomposition of diffusion-controlled phase, hence results in a high percentage of non-transformable tetragonal phase. Borom's modification of the phase boundaries for the phase diagram of Scott[8] shown in Fig.4(a) is illustrated on Fig.4(b)[9], the single-phase tetragonal field with high yttria concentrations avoids the diffusional constraints on the conversion of either a higher temperature tetragonal or a strained cubic to a lower temperature tetragonal which are imposed by the diagram given

by Scott. It seems that the situation of the quenched-in non-transformable T' phase produced by ion irradiation coincides with that described in Fig.4(b). To make clear it represents with dot-line in Fig.4(a), where the dot -row line is in accordance to Borom boundaries shown in Fig.4(b). This means that the phase transformation happened under Ar^+ ion irradiation in such a route according to our measurement results: Amorphous(a) + M---- T'

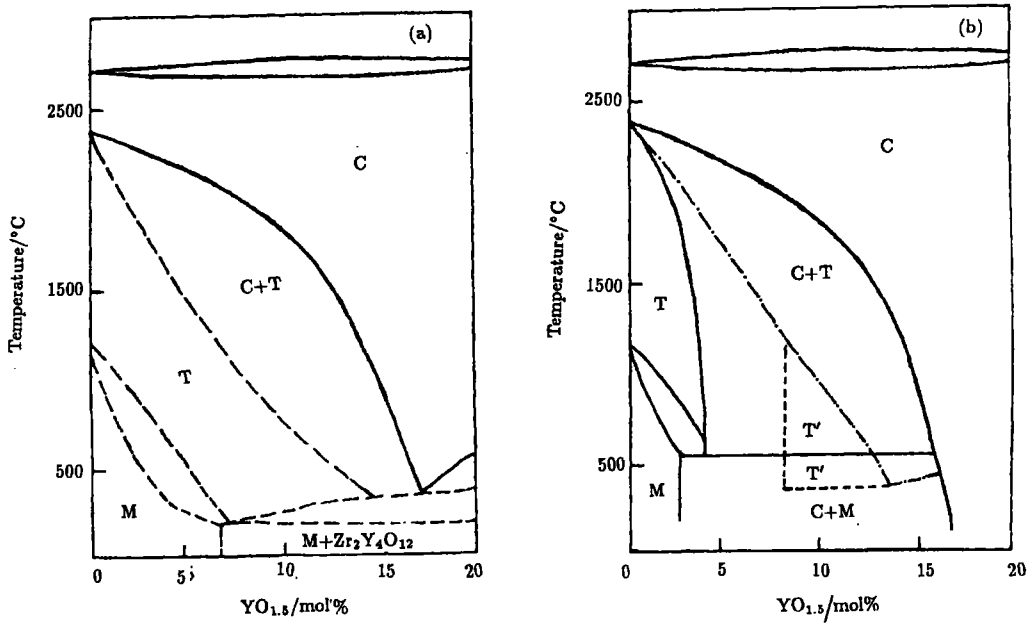

Fig.4 Phase diagram for the ZrO_2-Y_2O_3 system
(a) According to Scott[8], (b) Acorrding to Borom[9]

4 Conclusions

The following conclusions may be drawn from the results presented above.

(1) The amorphous ZrO_2-12wt% Y_2O_3 films deposited with r.f. magnetron sputtering were partially crystallized by Ar^+ irradiation with the doses of $5\times10^{15} \sim 6\times10^{16}$ ions·cm^{-2}. With the increasing of Ar^+ ion doses, the T' phase was subsequently formed and increased, after that the cubic phase also formed, while the amount of the amorphous component as well as the originally formed Y_2O_3 hexagonal one were decreased.

(2) For the partially crystallized ZrO_2-12wt% Y_2O_3 films deposited with r.f. magnetron sputtering at substrate temperature of 400°C, T' phase no Y_2O_3 hexagonal one was first formed due to Ar^+ bombardment. With increasing of Ar^+ ion doses, the amount of T' phase was increased, the amorphous was rapidly decreased, while the monoclinic phase seems disappeared.

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