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Synthesis of hafnium oxide thin films with ion beam assisted deposition

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Abstract

Hafnium oxide thin films were prepared using a high-energy ion beam assisted deposition (IBAD) system. We used oxygen ions accelerated 1-20keV, a much higher energy regime than in other IBAD works. The transport ratio (TR), defined as the ratio between the hafnium arrival rate and the oxygen ion dose, was varied in the range of 0.5-10. The substrate was not heated during deposition. The structures and properties of the films were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Knoop microhardness.

Films with tetragonal and cubic structures, or mixtures of these with the monoclinic phase were obtained. The chemical composition of the films was oxygen deficient, with very small x values in HfOx compared to the normal stoichiometry of HfO_2. In particular, x in tetragonal films was very low ($x < 1.5$). The hardness of the films increased with increasing the TR and ion beam energy, reaching a maximum of 25 GPa at TR = 10 and ion beam energy = 20 keV. From the Knoop hardness results, the films with tetragonal structure had very dense columnar structure and very smooth surface and were harder than films with cubic and monoclinic phases. The latter showed smaller and more irregular grains with large pores and much rougher surface.

It was also found that the preferred orientation of cubic films could be controlled by substrate rotation.

KEY WORDS: (IBARD) (HfO_2) (Hardness) (XRD)

1. Introduction

Hafnium oxide and its phase modifications under high-pressure conditions have been the topic of numerous studies[1-4]. At room temperature the equilibrium phase of HfO_2 is a monoclinic structure (baddeleyte-type structure), which has the lowest free energy of formation and the largest volume. This structure varies with pressure and temperature. At about 1300 K, stoichiometric HfO_2 transforms to a tetragonal structure and at about 2700 K to a cubic structure, identified by X-ray diffraction measurements at high temperature performed by Boganov et al[5] in 1965 to be of CaF_2-type. J. M. Leger et al[6] reported the phase transformation of HfO_2 in the pressure range between 8 GPa and 30 GPa at about 1273 K. They found transformation to orthorhombic structure (cotunnite-type structure) at pressures greater than 10 GPa. These phases are reported as bulk type structures.

There is a considerable interest in the high-pressure phases of metal oxide. These phases typically exhibit very high bulk moduli and thus are candidates for hard materials[4, 7]. In particular, oxides with CaF_2 type structure are predicted to have high bulk modulus. Table 1 shows the bulk modulus of HfO_2 from calculation with several crystal systems. HfO_2 is predicted to have comparatively high hardness, especially, in the orthorhombic and cubic forms.

HfO_2 is also an attractive candidate material for optical coatings. It presents a relatively high laser damage threshold due to its high melting point, thermal and chemical stability [9,10] and its large transparent range from the IR to the UV (0.22-12 μm), with a relatively high refractive index[10], and is also relatively easy to obtain by evaporation.

Among the various attempts to obtain high quality optical films, ion beam assisted deposition (IBAD) has also been used in a number of studies[11-15], with various ion sources, sometimes using ionic species other than oxygen. But these phases are amorphous or low quality crystalline monoclinic.

In this paper we investigate HfO_2 as a candidate hard material. We attempted to prepare thin films using ion beam assisted deposition, and we also investigated the phase relationship of HfO_2 related to ion energy and transport ratio.

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2. Experimental

Table 1 The bulk modulus of each

Material	B_{theory} (GPa)	B_{exp} (GPa)
Diamond[8]	452	443
RuO_2[11]	343	399
HfO_2[4]		
Baddeleyite(Mono.)	251	---
Fluorite(Cubic)	280	---
Cotunnite(Orth.)	306	---

We used an IBAD system to prepare the HfO_2 thin films. The basic details of the ion source have been described elsewhere[16, 17]. The films were obtained on Si(100) wafers by depositing Hf vapor under simultaneous bombardment with oxygen ions. The incidence angle of the oxygen ion beam was normal to the substrate and hafnium vapor reach the substrate at an angle of approximately 45 degree from normal. The purity of the hafnium target was 98% with the major impurity Zr. Ion current density was in the range of 25 – 50 $\mu A/cm^2$, acceleration energy could be varied between 1- 20 keV. The working pressure was about 1×10^{-4} torr, and we varied the transport ratio, which is the ratio between the arrival rates of Hafnium/Oxygen, in range of 0.5 to 10.

The structure was analyzed by X-ray diffraction (XRD). The data was collected using Cu radiation in a Rigaku Miniflex apparatus at 30 kV-15 mA, with a Ni filter. The chemical composition was measured using X-ray photoelectron spectroscopy (XPS). Microstructures were obtained (courtesy of Kanagawa High-Technology Foundation (KTF)) using a field emission scanning electron microscope (FE-SEM) capable of ultra high magnification (up to $\times 10^5$).

The hardness was measured using a low load Shimazu Knoop microhardness tester at a load of 1g (0.01N)

3. Results and discussion

Figure 1 and 2 show the XRD patterns of the deposited thin films, with variation in TR at fixed ion beam energy of 20 keV and variation with ion beam energy at a fixed transport ratio of 5, respectively. The two phases appear in these figures. In Fig. 1, small peaks of the patterns fit the monoclinic phase, that fit 06-0318 card from JCPDS data base, but the other phase could not fit any of the JCPDS cards for HfO_2. This phase appears gradually with increasing the transport ratio. At 20 keV, TR = 5, it appears as only one phase.

In Fig. 2, the patterns obtained at less than IE = 20keV

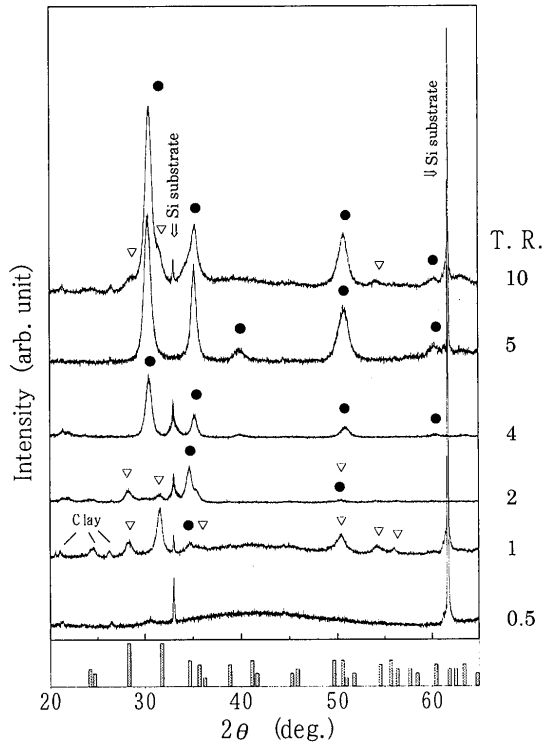

Fig. 1 XRD spectra of films deposited with ion energy 20 keV at varying TR values. ● : Tetragonal; ▽: Monoclinic; ◎: Cubic.

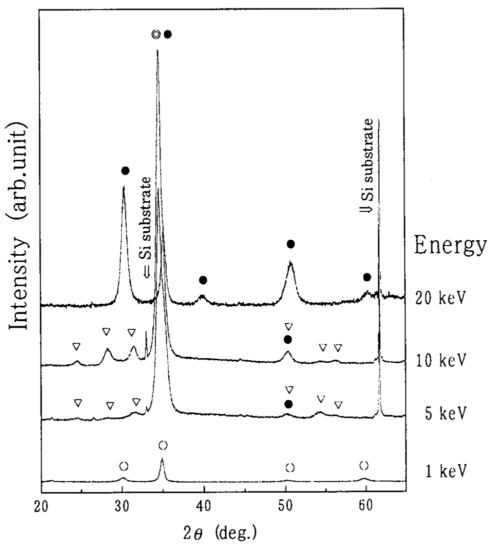

Fig. 2 XRD spectra of films deposited at a TR value of 5, with varying energy. ● : Tetragonal; ▽: Monoclinic; ◎: Cubic.

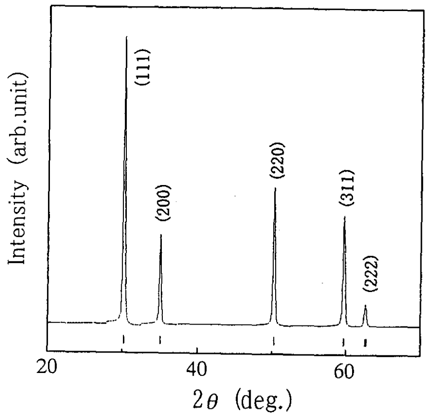

Fig. 3 Simulated pattern of a purely cubic structure ($a = 0.5056$ nm).

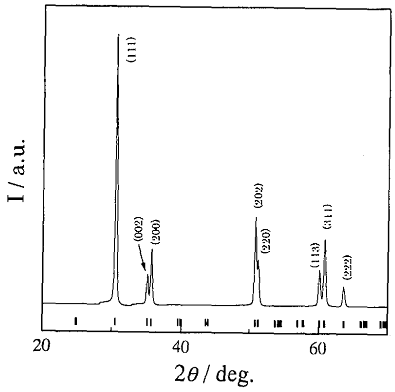

Fig.4 Simulated pattern of a purely tetragonal structure (a = 0.5055; c = 0.5111 nm).

contain the monoclinic phase. The strong peak of 35° always appears. These peaks increase with increasing the ion beam energy.

The film prepared at 20keV and TR = 5 presents three strong peaks with additional small peaks. This seems to be single phase. The JCPDS database has 11 cards of HfO_2; in monoclinic, orthorhombic and (high temperature) tetragonal structures. This spectrum cannot fit any of the existing JCPDS cards. Fig.3 shows the simulated XRD pattern of cubic structure, quoted from Pearson's handbook[18], based on a report from 1930. This space group is $Pm\bar{3}m$ and all atoms are positioned at coordinates ; Hf (0,0,0) and O (1/2,1/2,1/2). The spectrum of the film prepared at 20keV and T.R = 5 is almost the same as this simulated pattern. However, the weak peak at 40° does not fit this simulated pattern. Fig.4 presents the simulated pattern of a tetragonal structure with space group *P4/mmm*, which is a subgroup of $Pm\bar{3}m$. This pattern has a peak at 40° , and the other peaks can be separated from the broad peaks of the pattern of the film obtained at T.R. 5 and 20 keV. The peaks at 40 and 55 degrees of the XRD pattern of the latter sample are broader than those at 30 and 35 degrees. The full width at half maximum (FWHM) of the latter two peaks is 0.32, whereas that of the former two is 0.52. After deconvolution (using the Gaussian equation), it was determined that the peaks at 40 and 55 degrees indicate that the phase is tetragonal rather than cubic, and that the cell parameters are a = 0.5055 and c = 0.5111 nm. These values are very close with a/c ratio of 0.989, and this suggests that this tetragonal structure is a slightly distorted from the CaF_2 cubic structure.

The films prepared at 1 keV and TR = 5 also indicate a cubic structure and have (200) preferred orientations. This preferred orientation always appeared in the films prepared at other conditions. This spectrum does not have the additional peak at 40° and also the peak locations fit the simulated pattern of the randomly oriented cubic structure. The intensities of all peaks are very weak and broad. In this spectrum, it seems that all peaks have the same FWHM. Thus it can be said that this film has cubic

Table 2 XPS analysis results of composition of the samples.

Ion energy keV	T.R.	Chemical ratio, x (O / Hf) XPS (surface)
20	0.5	1.71
20	1	1.55
20	5	1.30
20	10	1.47
1	5	1.74
5	5	1.72
10	5	1.52

rather than tetragonal structure.

Table 2 shows the film composition results obtain in XPS analysis. All the films were oxygen deficient. It is interesting to note that despite the relatively significant variations in TR, the stoichiometry was almost identical at around $x = 1.6$. These values are very small compared to normal stoichiometry of HfO_2. The light atoms are apparently sputtered away by ion beam bombardment. In ref. 15), non-stoichiometry of HfO_x films was also reported. These films also have very low oxygen content, between 1.2-1.8. From our results, it appears that the tetragonal structure needs the oxygen vacancies combined with high-energy ion beam. The structure of tetragonal is distorted form that of cubic, and with lower oxygen content Tetragonal films have O contents below $x = 1.5$.

Fig.5 shows XRD pattern of HfO_2 thin film, which have cubic structure with preferred orientation. This XRD patterns look like that of film prepared at 20 keV and TR = 5. The difference between former and the latter films is only substrate rotation speed during deposition. The preferred orientation peak becomes stronger with increasing rotation speed. Thus we can conclude that the preferred orientation is controlled by rotation speed.

Fig.6 shows the Knoop hardness data, as a function of

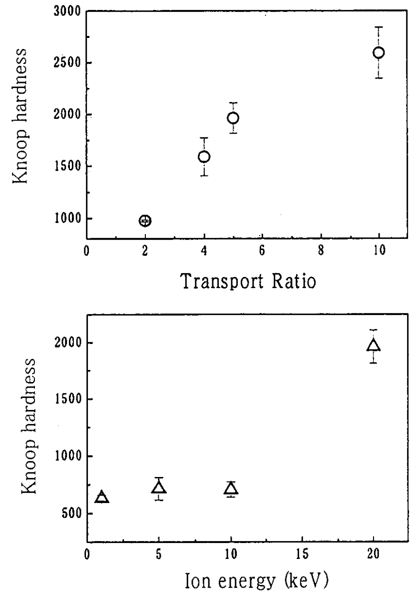

Fig.6 Knop hardness data for the films in Fig. 1 ; a) with varying TR at 20 keV; b) with varying ion energy at a TR value of 5.

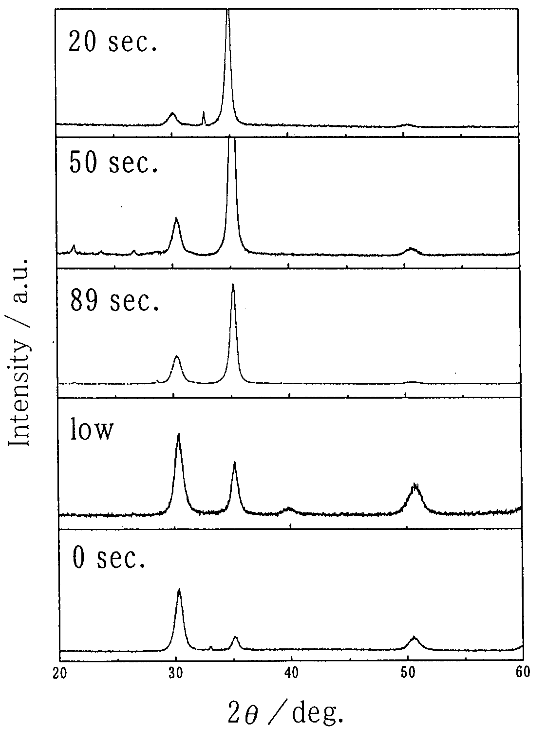

Fig.5 XRD spectra of films deposited with ion energy 20 keV at varying TR values, related to rotation speed.

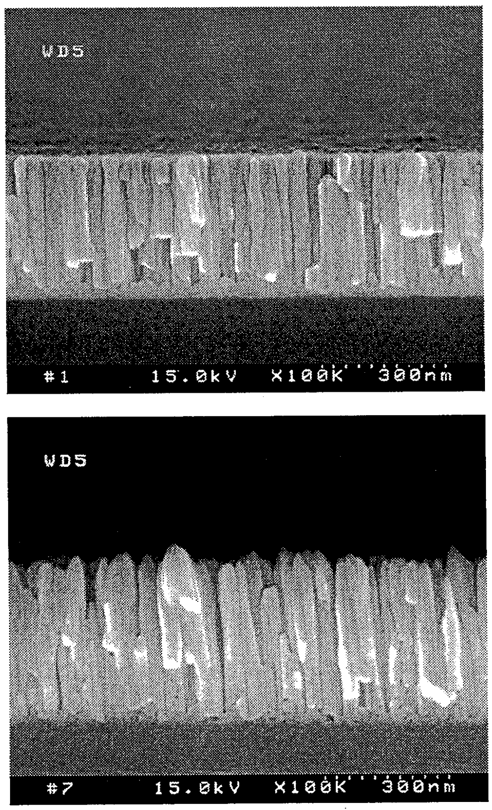

Fig. 7 FE-SEM micrographs of the films with tetragonal structure (top) and mainly monoclinic phase (bottom).

TR and ion beam energy. The films with a tetragonal structure present a higher hardness than either those with monoclinic or cubic structure, and the latter structure also presents the lowest hardness. Hardness increases with TR values and ion energy, reaching a maximum of 25 GPa at TR = 10. The hardness is not determined solely by the structure, it is also correlated to the microstructure.

Fig.7 shows FE-SEM micrographs of films with tetragonal and monoclinic structure, which have high and low hardness, respectively. Both samples present a columnar structure, but the grains and their spacing are different. The upper micrograph shows a very dense columnar structure and a smooth surface, whereas the mainly monoclinic sample shows smaller and more irregular grains with large pores and much rougher surface. These structural features correlate well with the relatively high and low hardness of the tetragonal and monoclinic samples respectively.

4. Conclusion

(1) HfO_{2-x} films were obtained using an IBAD system with high ion energy. Films of tetragonal and cubic structure or of mixtures of these with the monoclinic phase were obtained.

(2) The films were oxygen deficient.

(3) Films obtained at 20keV and above TR5 had high hardness, which is attributed to the dense columnar microstructure.

(4) The preferred orientation peak becomes stronger with increasing rotation speed. The preferred orientation of cubic phases could be controlled by the substrate rotation speed.

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