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# Influence of Ion Irradiation on Crystalline Phases of Oxide Films<sup>†</sup>

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## Abstract

### (Abstract)

*The films of four oxides of silicon, aluminum, titanium and zirconium synthesized by ion beam assisted deposition (IBAD) method and also their crystalline states were examined by XRD and XPS methods. Further, the influence of ion irradiation on the crystalline-amorphous transition was examined by ion process parameters. The change of the deposited oxide films from crystalline state to amorphous one was characterized by the coordination number of cation to oxygen in these oxides and the ionicity of cation-oxygen bond.*

KEY WORDS: (Ion Irradiation) (Amorphization) (Ion Beam Assisted Deposition) (Ionicity)

## 1. Introduction

Recent energetic processes enable us to synthesize various new materials by introducing non-equilibrium conditions. For example, new hard materials such as cubic boron nitride[1,2] and B1 type pseudobinary nitrides[3,4] have been extensively studied by using various PVD methods. In these syntheses, the importance of energetic ions has been indicated for inducing high quenching velocity[5], high compressive stress[6] and so on.

Syntheses of materials by the energetic ion processes have been widely conducted in the fields dealing with electronic devices and hard coatings. Silicides have been much favoured for applying to contact materials in semiconductor devices[7] and thermo-electric conversion elements[8]. Nitrides have been applied for diffusion barriers[9] as well as for hard coatings. On the other hand, oxide materials such as zirconia[10] have been studied for high dielectric and high reflective compound formation.

In materials synthesis based on the ion assisted processes, it is important to control the crystalline phase and, in some cases, the amorphous-crystalline transition because ion irradiation causes the formation of a metastable phase. For the metallic alloys, microalloying and amorphization induced by ion irradiation have been well investigated and various interpretations have been

proposed on the basis of collision cascade[11], thermodynamics[12], structure relaxation related to collision process[13] and so on. On the other hand, amorphization of insulating compounds induced by ion irradiation was extensively investigated from the standpoint of bond type[14]. However, the phase changes of oxide materials in the ion assisted deposition process have not been investigated systematically.

In this study, we have synthesized four kinds of oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>) using the ion beam assisted deposition (IBAD) method for the purpose of clarifying the influence of ion beam irradiation on the crystalline and/or amorphous phases of synthesized films. An attempt was made to understand the phase change of these oxides by correlating ion beam parameters with bond character of the oxide.

## 2. Experimentals

IBAD system used in this study consists of a mixing chamber, an electron beam evaporator and an ECR ion source. In the source region, oxygen ions are produced by a microwave energy of  $f=2.45$  GHz and extracted through a multi-aperture three electrode system with an energy ranging from 1 keV to 25 keV. Metal vapors deposited simultaneously during the beam injection are supplied by a 2 kW electron beam evaporator. Oxygen ion beam injection and metal vapor deposition was performed at an

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angle of 45 degrees with respect to the substrate surface.

P-type CZ (111) silicon wafers were used as substrates. Before deposition, the surface of the silicon substrates was treated with 0.1wt% HF solution and was washed with distilled water. Oxygen ion injection was performed at vacuum conditions below  $3 \times 10^{-5}$  Pa. The transport ratio of metal vapor and oxygen ion for each deposition was varied from 0.8 to 5.3, depending on the species of oxide materials. Compositions of metallic and oxygen elements were analyzed using the respective intensities obtained from X-ray photoelectron spectroscopy(XPS) after the correction of sensitivities. Phase identification was performed by XRD measurement with glancing angle method.

### 3.Results and Discussion

#### 3.1 Silicon oxide

Appearance of XRD patterns of silicon oxide films synthesized by the IBAD method is shown in Fig.1. Typical patterns for the amorphous phase were obtained in these XRD results. The refractive indices of these films were somewhat lower than that of silicon dioxide, so that the ratio of oxygen to silicon in these films is estimated to be somewhat less than 2. In other words, it is suggested that there exist some defects related with oxygen vacancies. Among the XRD patterns in Fig.1, a small peak was observed around 27 degree in the upper two patterns. The position roughly corresponds to that( $2\theta=26.6$  degree) of the most intense peak of quartz. Accordingly, the observation of the small peak around 27 degree suggests a precursory stage of the formation of crystalline silica.

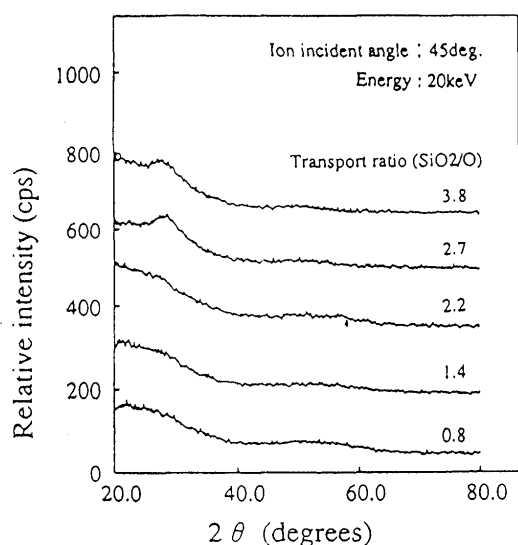


Fig.1 X-ray diffraction patterns of silicon oxide films deposited by the various transport ratios and the oxygen ion energy of 20 keV.

#### 3.2 Zirconium oxide

XRD patterns of zirconium films at various deposition conditions are shown in Fig.2. Except for the films shown in the lower two XRD patterns in this figure, almost all deposited films were identified as a tetragonal zirconia from the observation of asymmetry in the (220) peak. However, it is difficult to judge whether or not the deposited films consist completely of single tetragonal zirconia phase. Certain amounts of cubic zirconia phase may be contained in the film identified as tetragonal phase. The film deposited at the oxygen ion energy of 5 keV and the transport ratio of 5.3 shows an XRD pattern in which crystalline and amorphous phases coexist. Thus, the crystallinity of the deposited zirconia film has a tendency to increase with decreasing transport ratio and with increasing oxygen ion energy. The diagram for phase change between crystalline and amorphous states is illustrated in Fig.3 by plotting the oxygen ion energy against the ratio( $\phi_{ion}/\phi_{Zr}$ ) of the dose( $\phi_{ion}$ ;ions/cm<sup>2</sup>·sec) of oxygen ion to the dose( $\phi_{Zr}$ ;atoms/cm<sup>2</sup>·sec) of zirconium atom as the coordinates. The amorphous phase was only formed at the conditions of low oxygen ion energy and small value of  $\phi_{ion}/\phi_{Zr}$ .

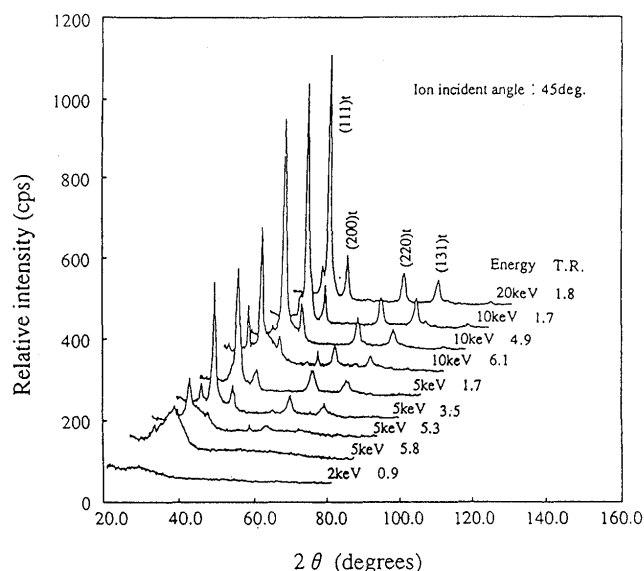


Fig.2 X-ray diffraction patterns of zirconium oxide films deposited by the various transport ratios and oxygen ion energies. The notation of t for XRD peaks means the tetragonal phase of zirconia and T.R means transport ratio.

#### 3.3 Titanium and aluminum oxides

The films of titanium and aluminum oxides synthesized by IBAD method have also been investigated in our previous works[15-19]. The diagrams for phase

change between crystalline and amorphous states in these oxide films are illustrated in Figs.4 and 5 by taking as coordinates similar parameters to those in Fig.3. Almost all aluminum oxide films were in the amorphous state while titanium oxide films showed rutile structures except for the appearance of the TiO phase in the oxygen deficient condition.

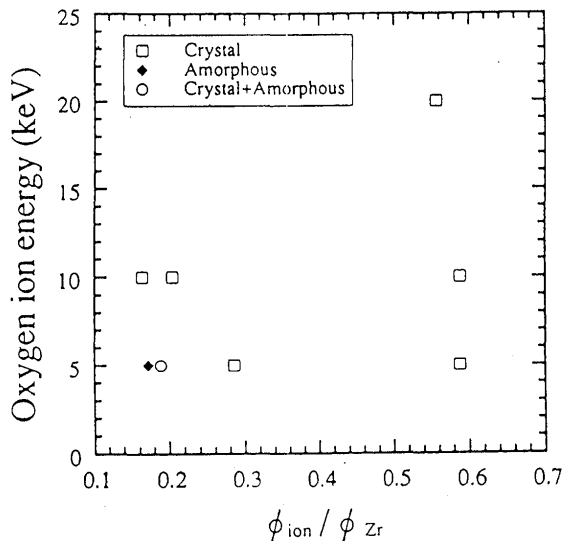


Fig. 3 The diagram for the crystalline/amorphous change in the zirconium oxide films by taking the ion energy and the dose ratio of oxygen ion to zirconium atoms as coordinates.

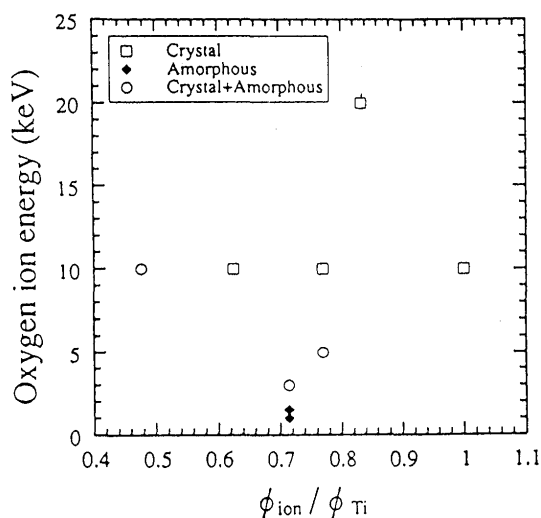


Fig. 4 The diagram for the crystalline/amorphous change in the titanium oxide films by taking the ion energy and the dose ratio of oxygen ion to titanium atoms as coordinates.

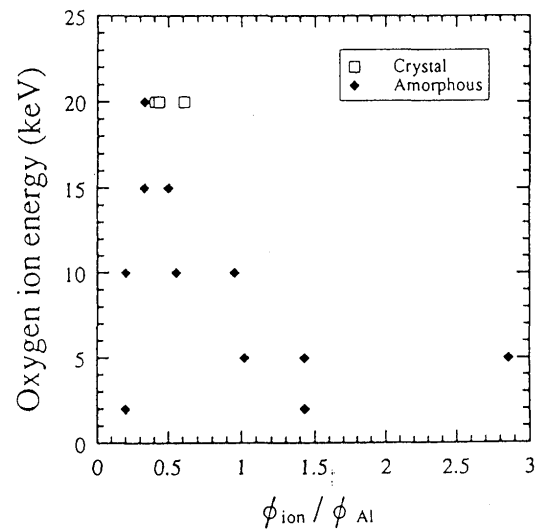
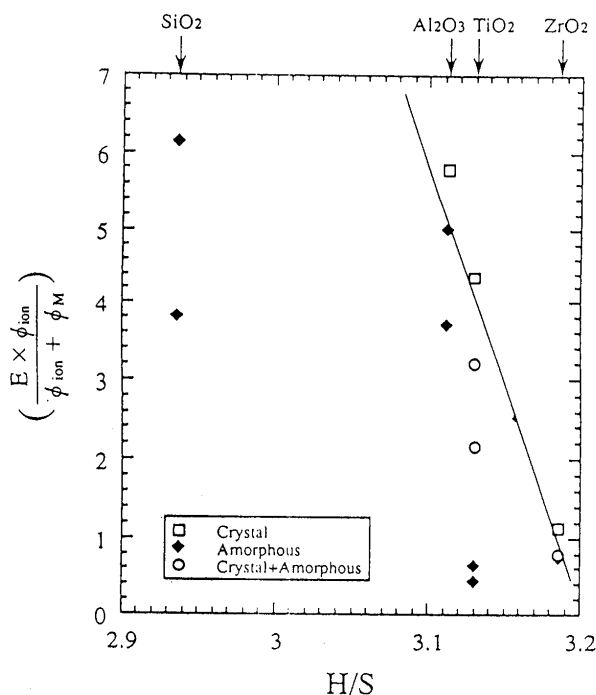


Fig. 5 The diagram for the crystalline/amorphous change in the aluminum oxide films by taking the ion energy and the dose ratio of oxygen ion to aluminum atoms as coordinates.

### 3.4 Amorphization and bond character

It has been indicated that the formation of amorphous phase in oxide system is facilitated with a decrease in the coordination number of cations in the oxides[20]. The coordination number of cation to oxygen changes from 4 for quartz, through 6 for  $\alpha$ -alumina and rutile, to 7 for monoclinic zirconia. Aluminum ion in some aluminosilicates coordinates to 4 or 5 oxygens in some aluminosilicates(for example, sillimanite and andalusite) and  $\gamma$ -alumina. Thus, the average coordination number of cation to oxygen increases in the sequence Si $\rightarrow$ Al $\rightarrow$ Ti $\rightarrow$ Zr and the amorphous phase can be easily formed in the sequence Si $\rightarrow$ Al $\rightarrow$ Ti $\rightarrow$ Zr. The prediction, based on the cation coordination, shows quite good agreement with the results observed in oxide films deposited by IBAD.

We can discuss the possibility of the formation of amorphous phases more quantitatively when the ionicity is used instead of the coordination number of the cation. Here, we use the ionicity of the metal-oxygen bond defined by band parameters, which are constructed from pseudopotential radii though a modelling of localized electron theory[21]. When the relation between the ionicity and the average ion energy per sum of oxygen ions and metallic atoms is plotted, Fig.6 is obtained. The boundary between amorphous and crystalline phases can be divided by a straight line though the slope is fairly steep. Thus the ionicity of metal-oxygen bond can indicate the possibility of the formation of amorphous phase in the formation of films by the IBAD method.



**Fig. 6** Dependence of crystalline/amorphous change in IBAD oxide films on the H/S. (H and S are the two band parameters and the H/S ratio substantially corresponds to the ionicity of metal-oxygen bond[21].)

#### 4. Summary

Crystalline states of silicon, aluminum, titanium and zirconium oxides synthesized by the ion beam assisted deposition method were investigated by the XRD method. Change from crystalline to amorphous state, induced by ion irradiation, was also examined using the ion process parameters. It was found that silicon dioxide was most easily amorphized among these four oxides while amorphization less easily occurred in zirconium dioxides, even though the ion irradiation effect is added. This suggested that phase changes of these oxides from crystalline to amorphous phases can be understood qualitatively by coordination number of cation to oxygen and quantitatively by the ionicity of the metal-oxygen bond.

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