Structural Analysis of Superior Bioactive Apatite Compounds by XAFS Spectroscopy

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Several types of hydroxyapatite (HAp) compounds have been applied widely for biomaterials, adsorbents, *etc.* For a function of HAp materials, ion-exchange sites in both cation (Ca^{2+}) and anion (X^-) ones in HAp relate to several unique properties in biomaterial viewpoint. The relation between the effect of substitution to several transition metal ions (such as Fe^{2+} or Zn^{2+}) and functionalized bioactivity should be clarified. It is likely that environmental structure of Ca^{2+} ions plays a key role for the functionalized property. In this study, Ca K-edge XAFS was applied to characterize the local structure of Ca ions.

Ca K-edge XAFS spectra were measured at BL01B1 of SPring-8 using 9.0 mrad mirror and Si(111) double-crystal monochromator. Each sample was molded into a disk pellet (8mmϕ) with less than 0.6 mm thickness, and measured at room temperature in a transmission mode.

Fig. 1 shows the XANES spectra of HAp samples. Typical HAp ($Ca_{10}(PO_4)_6(OH)_2$) has a hexagonal structure with sixth- and ninth-coordinated local structure. Because of these structural complexity, XANES spectrum of HAp is quite different from those of CaO or $CaH_2(PO_4)_2$. In the case of Zn-substituted HAp samples ((a)-(c)), intensity of prominent resonance peak at 4048 eV shows a slight difference according to calcined temperature; order of the intensity is (b)>(c)>(a). The XANES spectrum of (b) is similar to that of HAp. Thus, structural change around Ca ions is brought about during the calcination up to 1200°C. FT-EXAFS of these samples are shown in Fig. 2. The FT profile of (b) and (c) shows a similar feature to that of HAp. These results suggest a formation of Zn-substituted HAp, and local structure of Ca ions is slightly different between HAp and Zn-HAp. FT-EXAFS of (c) shows a lower intensity of Ca-O shell at 2.0 Å than that of HAp, indicating existence of precursor species without HAp structure. These information could not obtained by XRD, and thus, slight difference of environmental structure around Ca ions should reflect the results of XANES and FT-EXAFS.

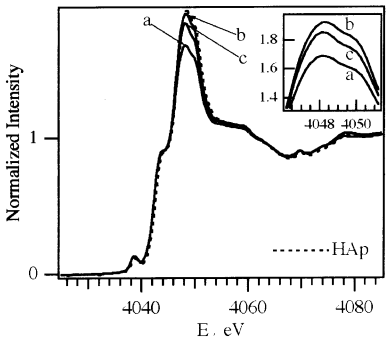

Fig. 1 Ca K-edge XANES of Zn-substituted HAp (Zn-HAp) calcined at 1000 (a), 1100 (b), and 1200°C (c).

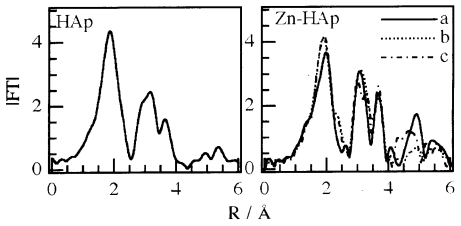

Fig. 2 FT-EXAFS of Zn-substituted HAp calcined at 1000 (a), 1100 (b), and 1200°C (c).

Fluorescence XAFS study on deca-nm insulator thin film obtained by cluster ion beam techniques

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The thin films metal oxides, for example HfO_2 and Ta_2O_5 will be widely used for semiconductor devices and multi-layer thin film for optical devices, respectively. The improvement of the semiconductor devices requires down sizing of gate insulator films thickness to deca-nm, i.e. use of deca-nm metal oxide thin films with high dielectric constant such as HfO_2, ZrO_2 and La_2O_3 instead of SiO_2 film. While it is necessary for the improvement of the optical properties to control accurately the refractive index and the optical transparency of the Ta_2O_5 layer, i.e. high stoichiometry and so-called 'amorphous' structure. The glancing angle fluorescence XAFS analysis is one of suitable tools to analyses the structure of these thin films at the atomic level instead of the thin film X-ray diffraction. In this study we measured the XAFS of HfO_2 and Ta_2O_5 thin films, which were obtained by the oxygen gas cluster ion beam assisted deposition technique. The measurements were made with a 19-segmented Ge solid state detector for Hf L_3 edge of HfO_2 films and an electron yield conversion method by He flow gas counter for Ta L_3 edge of Ta_2O_5 films, respectively.

Fig. 1 shows the comparison of the Ta L_3-EXAFS oscillations under the different deposition conditions. The significant loss of long-range-order in high k region is observed for the films deposited with assistance of 3kV and 11kV accelerated oxygen gas cluster ion beam. This suggests the amorphous-like structure of the Ta oxide films. Now the analysis of the Hf L_3-XAFS of 120- 50 nm HfO_2 films is in progress.

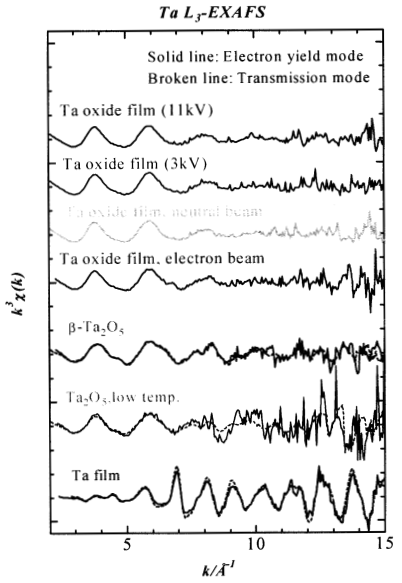

Fig. 1. Ta L_3-EXAFS of Ta oxide thin films, which were fabricated by the cluster ion beam technology (3kV and 11kV) and the other deposition techniques together with those of Ta metal, low temperature Ta_2O_5 and β-Ta_2O_5.