

X-ray photoelectron spectra of ZrTiO₄ and HfTiO₄

大橋直樹 秋葉伸太郎¹ 井川博行* 田中順三** 鶴見敬章 福長脩

Naoki OHASHI, Shintaro AKIBA¹, Hiroyuki IKAWA*, Junzo TANAKA**,

Takaaki TSURUMI and Osamu FUKUNAGA

東京工業大学無機材料工学科 152 東京都目黒区大岡山 2-12-1

Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology,
2-12-1 O-okayama, Meguro, Tokyo 152 JAPAN.

FAX +81-3-5734-2514 e-mail : nohashi@ceram.titech.ac.jp

*神奈川工科大学応用化学科 243-02 神奈川県厚木市下荻野 1030

Department of Applied Chemistry, Kanagawa Institute of Technology,
1030 Shimo-ogino, Atsugi, Kanagawa 243-02 JAPAN.

**無機材質研究所 305 茨城県つくば市並木 1-1

National Institute for Research in Inorganic Materials,
1-1 Namiki, Tsukuba, Ibaraki 305 JAPAN.

ABSTRACT : X-ray photoelectron spectra (XPS) of ZrTiO₄ and HfTiO₄ were measured to assign unidentified satellite peaks due to O 1s and valence region reported previously. The unidentified XPS peaks were observed for samples exposed to air and their relative intensities changed systematically with composition and with the condition of post heating. However, the satellite peaks did not appear for freshly fractured or etched surfaces. It was concluded that the satellite peaks originate from carbon oxides adsorbed on the sample surface.

Key Words : ZrTiO₄, HfTiO₄, XPS, Adsorption

1 Introduction

The zirconium-tin titanate solid solution, Zr_{0.8}Sn_{0.2}TiO₄, is an important material for a ceramic dielectric resonators in microwave communication systems[1]. This material is used as a high-power filter of 800 MHz band cellular base stations due to its very high stability, high Q-value (5×10^4 at 1 GHz[2]) and low third harmonic distortion[3,4].

ZrTiO₄ has been extensively studied in the last decade and the solid solutions based on ZrTiO₄ are important in relation to order-disorder phase transformations[5-11], modulated crystal structures of cation sequence such as Zr-Zr-Ti-Ti[8,12-17], thermal expansions which are sensitive to chemical compositions[7,18-20], and dielectric properties [1-4,17,21-25]. Ikawa et al.[7] has shown a hypothesis to explain the crystallochemical and thermal properties of the ZrTiO₄ and its solid solutions; detail of

the hypothesis is written elsewhere[7,19, 21,22].

According to previously published X-ray photoelectron spectroscopy (XPS) measurements[26], there was a difference between the XPS spectra of the high and low temperature forms of ZrTiO₄ and the XPS spectra of the high temperature form could not be clearly assigned. The unassigned peaks was observed at O1s region ($E = 532\text{eV}$) and O2s region ($E = 25\text{eV}$). Those unassigned XPS peaks were expected to be helpful in refining the hypothesis of Ikawa et al.[7,19,21,22]. However, one can doubt whether the unassigned peaks correspond to the hypothesized molecular orbitals or not, since it has been indicated in the previous report[26] that C1s peak and the unassigned peak were simultaneously observed.

In the present study, the XPS spectra of ZrTiO₄ and HfTiO₄ have been reexamined under more controlled experimental condition

1 Present Address : 中部電力株式会社 447 愛知県碧南市
Chubu Denryoku Co. Ltd., 2-8-2 Kounan-cho, Hekinan-shi, Aichi 447 JAPAN.

to discuss the origin of the unassigned XPS spectra for $ZrTiO_4$ and $HfTiO_4$ reported by Ikawa et al.[26].

2 Experimentals

The source materials of $ZrTiO_4$ and $HfTiO_4$ were prepared by a co-precipitation method from a sulfate solution; the detailed preparation process has been written elsewhere[7]. The precipitated powder was heated in the air at 1300°C for 5 hours. The calcined powder was pressed into 5 mm x 40 mm rods or 10 mm x 3 mm cylindrical pellets using a cold iso-static pressing apparatus under $1.0 \times 10^3 \text{ kg/cm}^2$. The rods and pellets were heated in the air at 1600°C for 12 hours and then cooled at $10^\circ\text{C}/\text{min}$ to room temperature.

The sintered samples were post-heated to obtain high and low temperature forms of $ZrTiO_4$ and $HfTiO_4$ [8,26]. The high temperature form, hereafter abbreviated by H-form, was prepared by a two step annealing procedure. In the first step the samples were annealed at 1500°C for 5 hours and then quenched to room temperature in air; the second step consisted of a 700°C anneal for 3 days in the air followed by a furnace cooling. The annealing at 700°C was performed to re-oxidize the samples, since the quenched sample was pale purple due to reduction. The low temperature form, hereafter abbreviated by L-form, was prepared by a slow cooling procedure by post-heating at 1200°C for 5 hours in air followed by slow cooling to 1000°C at $1.2^\circ\text{C}/\text{hour}$. The nomenclature used in the previous work[26], i.e. high and low temperature forms of $HfTiO_4$, is for the convenience used here.

X-ray photoelectron spectra(XPS) for freshly fractured surfaces were measured with MICROLAB320D (VG SCIENTIFIC, UK; abbreviated by XP-V) equipped with a $MgK\alpha$ radiation source and sample fracturing device. The fracturing device was located in an ultra high vacuum (UHV) chamber which was connected with an UHV chamber for XPS analysis. Pressure in those UHV chambers was always kept at less than 1.0×10^{-9} torr.

The rod shape sample fractured with the device was transferred into analysis chamber as soon as possible. Selected area on the freshly fractured surface was exposed to incident X-ray beam during the XPS measurement.

Air exposed samples were also investigated by XPS measurements with 5500MT (ULVAC-PHY, JAPAN; abbreviated by XP-U) equipped with a monochromatic $AlK\alpha$ X-ray source and an Ar-ion-gun to etch the sample surface. The samples were scraped with silicon carbide abrasives and polished with acetone; samples were exposed to air again after the polishing. Etching was conducted using an accelerating voltage 0.5 kV and under a pressure of 6.0×10^{-5} torr.

3 Results and discussion

Figure 1 shows the O_{1s} photoelectron spectra for samples of $ZrTiO_4$ and $HfTiO_4$ exposed to air. The spectra consist of two peaks. The peaks at higher and lower binding energies (E_B) are hereafter abbreviated by $O_{1s}(I)$ and $O_{1s}(II)$ peaks, respectively. In comparison of present and previously published work[26], $O_{1s}(I)$ peak was indicated to correspond to unassigned peak in the previous paper. The relative intensity of the $O_{1s}(I)$ peak for the H-form of $ZrTiO_4$ (Fig. 1 (b)) was more intense than that for the L-form of $ZrTiO_4$ (Fig. 1 (c)). The $O_{1s}(I)$ peak was also observed for $HfTiO_4$; however, the relative intensity of the $O_{1s}(I)$ peak for both H- and L-form of $HfTiO_4$ (Fig. 1 (d) and (e), respectively) was less than that for the H-form of $ZrTiO_4$ prepared by the same procedure. The relative intensity of the $O_{1s}(I)$ peak for the H-form of $ZrTiO_4$ was most intense among all the samples in the present study. Present results for air exposed samples are qualitatively consistent to the previously published results[26]. However, relative intensities of $O_{1s}(I)$ peak in the present study is different from that reported in ref.26.

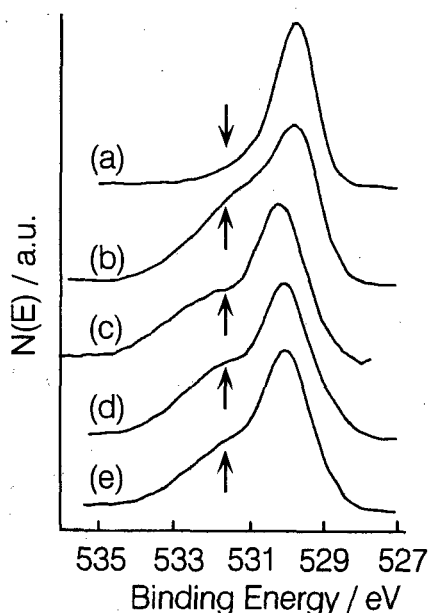


Figure 1 X-ray photoelectron spectra of O_{1s} for $ZrTiO_4$ and $HfTiO_4$ measured with XP-U, see text. (a) for the surface etched by Ar ion gun for 60 sec. and (b), (c), (d) and (e) for the surface exposed in air.

- (a) $ZrTiO_4$ high temperature form,
- (b) $ZrTiO_4$ high temperature form,
- (c) $ZrTiO_4$ low temperature form,
- (d) $HfTiO_4$ high temperature form
- (e) $HfTiO_4$ low temperature form.

A comparison of Fig. 1(a) and (b) indicates that the relative intensity of the $O_{1s}(I)$ peak compared to the $O_{1s}(II)$ peak decreases with etching time. It was also found that the relative intensity of a C_{1s} peak in the spectra decreased with etching time. This result indicated that part or all of the $O_{1s}(I)$ peak is due to carbon oxides adsorbed on the sample surface. Furthermore, the $O_{1s}(I)$ peak was not observed in XPS spectra collected from freshly fractured surfaces as shown in Fig.2. Profile of O_{1s} peaks shown in Fig.2 are seemed to be similar to each other. It is plausible that the $O_{1s}(I)$ peak is not corresponding to chemical state of bulk but due to carbon oxide adsorbed on the sample surface. It cannot be expected that analysis of the $O_{1s}(I)$ peak gives useful information about electronic state of bulk.

The intensity of the unassigned peak at $E_B=25eV$ was also found to decrease with the

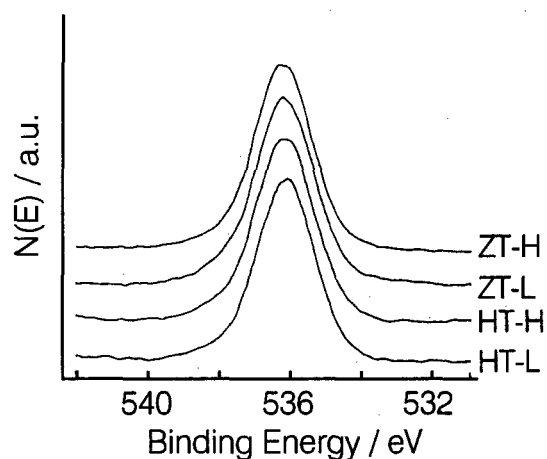


Figure 2 X-ray photoelectron spectra of O_{1s} core-level region for $ZrTiO_4$ and $HfTiO_4$ obtained from freshly fractured surface measured with XP-V, see text.

- ZT-H : $ZrTiO_4$ high temperature form;
- ZT-L : $ZrTiO_4$ low temperature form;
- HT-H : $HfTiO_4$ high temperature form;
- HT-L : $HfTiO_4$ low temperature form.

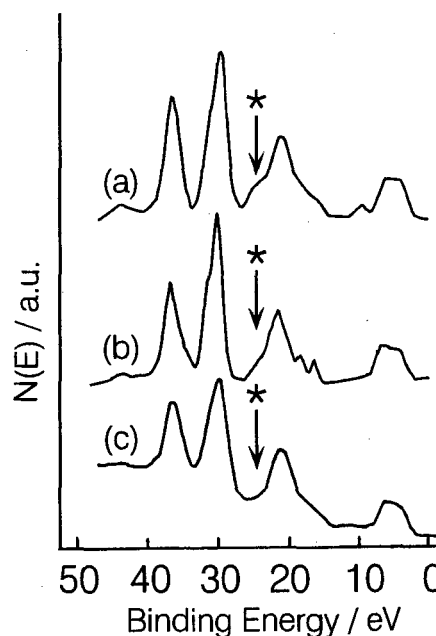


Figure 3 X-ray photoelectron spectra in valence region for $ZrTiO_4$ high temperature form. (a) exposed to air and measured with XP-U, (b) etched for 60 sec. by Ar-ion-gun and measured with XP-U and (c) freshly fractured surface measured with XP-V. Notations for XP-U and XP-V are written in text.

etching time and the peak at $E_p=25\text{eV}$ was not observed for the freshly fractured surface as shown in Fig.3. Thus, it is also indicated that the unassigned peak at 25eV originates from surface contamination, i.e. adsorption of carbon oxide.

From the result of XPS measurement under highly controlled condition, it was found that unassigned peaks shown in the previously published paper[26] were not correspond to hypothesized molecular orbital as mentioned earlier but due to carbon oxide adsorbed on air exposed surface. It is also noted that the amount of adsorbed carbon oxide was changed by the cation species, i.e. Hf or Zr, and annealing conditions. However, the reason for the difference in the surface activity of ZrTiO_4 family has been still an unsolved question.

Existence of hypothesized molecular orbital could not be detected even if the XPS measurement was carefully performed. In addition, magnetic measurement[27] for H and L-form of ZrTiO_4 and HfTiO_4 showed no significant change in paramagnetic behavior due to cation substitution and heat treatment: that result suggested that existence of hypothesized molecular orbital is undetectable by conventional magnetic measurement. Here, it must be also mentioned that no definitive result which dispute the existence of the hypothesized molecular orbital was also detected in the present study. Considering the limitation of energetic resolution of electron spectroscopy, theoretical calculation, e.g. total energy calculation and/or angular resolved UPS method for single crystal must be applied to discuss the difference in electronic structure of between ZrTiO_4 and HfTiO_4 .

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