Information observed in Ti-Lα,β and Ti-Lℓ,η emission lines of Ti and its oxides

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Abstract. Ti L-emission lines of metal-Ti and its oxides are measured by using a soft-X-ray emission spectrometer attached to a scanning electron microscope. Lα,β emissions due to electron transitions from valence 3d states to core 2p levels show a variety of intensity distributions for Ti oxides with different crystal structures reflecting different bonding states. Lℓ,η-emissions are due to transitions from 3s level to 2p levels and show simple intensity distribution. The energy shift of Lℓ,η-emission peak should reflect a relaxation energy in the final state with a hole in 3s level. The information of L-emission spectrum is discussed based on a chemical shift of photoemission experiment.

1. Introduction
Recent developments of soft-X-ray emission spectroscopy (SXES) instruments for conventional transmission electron microscope (TEM) enable us to obtain partial density of states (DOS) of valence bands (VB, bonding electron states) from identified specimen areas by transmission electron microscopy [1]. SXES method has two advantages in practical applications as follows, 1) SXES is not a surface sensitive method as photoemission spectroscopy and electron spectroscopy for chemical analysis (ESCA) and does not need ultra-high vacuum condition due to a larger absorption length of soft-X-ray photons than a few tens nm [2], and 2) the spectrum energy position is not affected by charging of specimen because of soft-X-ray emission originates from electronic transitions inside a specimen. The latest SXES spectrometer for TEM has an acceptable energy range from 50 eV to 4,000 eV by using four varied-line-spacing (VLS) gratings. It can detect from Li K-emission (55 eV) to Ta L-emission (3.8 keV) [3, 4]. Major problem of this method is extremely low emission efficiency lower than 1 % [5]. Thus, an application to electron probe microanalyzer (EPMA) as a commercial instrument has been done due to its large probe current [6]. The commercial instrument has a detectable energy range from 50 to 210 eV for first order diffracted spectrum observation. It realised a shorter detection time than one minute except a spatial resolution is lower than that of TEM. The 50 - 3,800 eV spectrometer was also applied to a conventional scanning electron microscope (SEM) for testing capabilities of the spectrometer [7].

X-rays originating from electronic transitions from valence bands to inner-shell electron levels inform us energy states of bonding electrons, L-emissions of 3d transition metal elements. Those range from 400 to 1,000 eV, are very important to assign chemical states of those elements in compounds.
Lα- and Lβ-emissions due to 3d_{5/2,3/2} → 2p_{3/2} and 3d_{3/2} → 2p_{1/2} transitions, respectively, are a suitable probe of valence states (bonding states). On the other hand, Lℓ- and Lη-emissions correspond to transitions from a shallow inner-shell level of 3s_{1/2} to 2p_{3/2} and 2p_{1/2} levels, respectively. Thus, Lℓ,η-lines can give us different information from that of Lα,β-emissions. Furthermore, the charge state is also important when discussing physical properties because of the amount of 3d electrons closely related to magnetism and conductivity of 3d transition metal compounds.

SXES analysis across a wide variety of materials can be conducted by using a SEM-SXES instrument as a tool of chemical state analysis for bulk materials. In this paper, Ti L-emission lies obtained by a SXES-SEM instrument and the information obtained are discussed not only the DOS of VB but also the chemical shift based on the discussion in photoemission spectroscopy.

2. Experimental

Present experiments were done by using an improved SEM-SXES instrument with an energy resolution of 80 meV at aluminium L-emission [8]. Figure 1 shows a photo of the SEM-SXES instrument used. For obtaining Ti L-emission, a grating of JS2000 with a groove density of 2,400 lines/mm was applied. A multichannel plate (MCP) detector was operated in photon counting mode. Then, relative intensity of emission lines is directly related to emitted number of photons. An energy resolution for Ti L-emission is estimated to be 0.2 - 0.3 eV. The energy of the spectrum was calibrated by using a fifth order curve determined by using energies of Ti-Lα- and Lℓ-lines of metal-Ti, Cu-Lα and -Lℓ and its higher-order lines of metal-Cu. Those calibration data were obtained under the same experimental set up of present investigation. The electron probe current and acquisition time are 190 nA and 20 minutes, respectively. Figure 2 shows a comparison of X-ray emission spectra of TiO_2 (rutile) obtained by a conventional energy-dispersive X-ray spectrometer (EDS) attached to a TEM (left, 0.0 - 5.5 keV) and the SEM-SXES instrument used in this experiments (right, 350 - 580 eV). An asymmetrical intensity distribution of O K-emission in EDS data is clearly resolved into three sharp peaks of O-K, Ti-Lα,β and Ti-Lℓ,η lines with the present SXES instrument. In a simple ionic model, TiO_2 is considered as Ti^{4+}O_2^- and cannot emit Lα,β-intensity because Ti^{4+} ion does not have any 3d electron. However, Lα,β-emissions are clearly seen. Thus, Ti atom in TiO_2 is not a pure Ti^{4+} ion via covalent bonding between Ti and surrounding O atoms. A broad intensity in the lower energy side of Ti-Lℓ,η peak is a plasmon satellite (ps).
3. Results and discussion

Figure 3 shows Lα,β- and Lℓ,η-emissions of metal-Ti, ε-TiO, new crystalline phase recently reported [9], and TiO2 (rutile). These spectra were obtained from those bulk specimens. Spectral intensities are normalised in each figure. Lα-peak of metal-Ti shows asymmetric intensity distribution originating from DOS of 3d electrons of VB. Those intensity profiles of ε-TiO and TiO2 (rutile) show a peak and a shoulder structures. However, those positions of peaks and shoulders are different for two crystalline materials, reflecting different bonding states. Ti atom is surrounded by six O atoms forming an octahedron in TiO2, and surrounded by trigonal prismatic (six-fold coordination) and trigonal planar (three-fold coordination) arrangements of O atoms in ε-TiO. Those characteristic intensity profiles of ε-TiO and rutile are well reproduced by theoretical calculations of Ti-3d DOS of VB [9, 10]. When discussing the relative energy positions of those spectra, chemical shifts of Ti-2p level and band gap energies of those materials should be taken into account. For the analysis, assignment of the top of VB position is important as a reference energy position. However, it is difficult to deduce it from present Lα,β-intensity distribution, because of a presence of Lβ-intensity and Lα-absorption edge exists between Lα- and Lβ-emissions. In contrast, Lℓ-emission due to transitions between inner-shell levels should show symmetric intensity distribution about the peak position. Each vertical line for Lℓ-emission peak is placed at the middle of each peak width. Compared to metal-Ti, TiO2 shows an apparent shift to higher energy side by 0.7 eV. Lℓ-peak position of ε-TiO is almost the same with metal-Ti, but seems a little shift to higher energy side by 0.1 - 0.2 eV. Those differences in Lℓ-peak position should be related to local screening energy of 3s core-hole in the final state (see following discussion).

Figure 4 shows Lα,β- and Lℓ,η-emissions of three TiO2 crystals with different crystal structures of rutile, anatase and brookite. Those spectra were obtained from those bulk specimens. Spectral intensities are normalised in each figure. Crystalline anatase and brookite of natural minerals are used in this measurement. The rutile used was an artificial gemstone. Although these crystalline materials are composed of similar TiO6 polyhedra, distortion and arrangement of TiO6 and resulting space group of the materials are different. Each Lα-peak shows a peak with a shoulder in higher energy side. However, energy separations of the two structures of the materials are different each other. From a theoretical study on the electronic structure of those three TiO2 materials, the main peak and the shoulder structures of Lα-intensity can be assigned to σ-hybrid state between Ti and O atoms and lone pair π-state, respectively [10]. Lℓ-emission peak of each TiO2 material indicated by a vertical line at the middle of the peak width is in higher energy position relative to that of metal-Ti. Rutile and anatase show almost the same energy position of Lℓ. That of brookite is a little higher energy position than those of rutile.
Figure 3. Lα,β (right) and Lℓ,η (left) mission intensity distribution of metal-Ti, ε-TiO and TiO₂ (rutile).

and anatase. It should be noticed in spectra of TiO₂ materials that Lα peaks are shifted to lower energy and Lℓ-peaks are shifted in higher energy side compared with those of metal-Ti. This suggests that chemical effects on Ti atoms appear in different ways for Lα- and Lℓ-emissions. Lβ and Lη should show similar information to those of Lα and Lℓ, respectively, but those are too weak to discuss in those spectra.

Figure 4. Lα,β (right) and Lℓ,η (left) emission intensity distribution of TiO₂ materials of rutile, anatase and brookite. Those crystalline materials are composed of similar TiO₆ polyhedra but different distortions.

For discussing chemical effects on Lα- and Lℓ-emissions, an expression on binding energy shift due to a change of chemical effects in X-ray photoelectron spectroscopy is helpful [11]. A change in binding energy referred to Fermi level ΔE_B is written as follows:

$$\Delta E^F_B = \Delta q/r - \Delta V - \Delta E_R - \Delta \phi$$
where $\Delta q/r$ represents a core-level shift due to a change of valency, a chemical effect in an initial state. $\Delta V$ is a change of solid state effects of crystal-field, density of states, bandgap and etc. This term usually works for valence states. $\Delta E_R$ is a change of relaxation effects, a final state effects with a hole. $\Delta \phi$ represents a change of work function. For the case of X-ray emission, two electron levels inside a material are involved and thus $\Delta \phi$ is zero. As L$\alpha$-emission is due to electronic transitions from valence states to core 2p$^{3/2}$ states, there remains a hole in valence states in the final state. This final state is an excited state from the ground state with a rather low energy. Then, relaxation energy due to this valence hole should be small and/or negligible. Thus, chemical effects on a change of L$\alpha$-emission energy, $\Delta E_{L\alpha}$, is written as follows:

$$\Delta E_{L\alpha} = \Delta q/r - \Delta V.$$  

As already presented in figures 3 and 4, solid state effect $\Delta V$ is dominated. The initial state effect $\Delta q/r$ is included in L$\alpha$-emission but difficult to deduce accurately from experimental data. As L$\ell$-emission due to transitions from a shallow core-state 3s$^{1/2}$ to deeper core-level 2p$^{3/2}$, $\Delta V$ term should be ignored. There remains a core-hole in 3s$^{1/2}$ state in the final state. Then, $\Delta E_R$ term should remain, core-hole effect in the final state. A theoretical study showed the valency effect $\Delta q/r$ on different core-levels, binding energy shifts, are almost uniform for all core-levels [12]. Thus, $\Delta q/r$ can be omitted and chemical effects on a change of L$\ell$ emission energy, $\Delta E_{L\ell}$, is written as follows:

$$\Delta E_{L\ell} = - \Delta E_R.$$  

This means that L$\alpha$- and L$\ell$-emissions gives different chemical information. To evaluate the discussion of $\Delta E_{L\ell}$, theoretical calculations were conducted by using WIEN2k code for metal-Ti and TiO$_2$ (rutile) with a core-hole in 3s$^{1/2}$ level, which corresponds to the final state for L$\ell$-emissions. A 3 x 3 x 3 super-cell was used in the calculation. Energy differences between 3s$^{1/2}$ and 2p$^{3/2}$ of rutile was larger than that of metal-Ti by 0.64 eV. This value is almost equal to the observed shift for higher energy side by 0.7 eV.

The above discussion on $\Delta E_{L\ell}$ for L$\ell$-emission is also applied for other emissions caused by electronic transitions between two core-levels. For example, K$\alpha$-emissions of atoms later than sodium atom in the periodic table are due to transitions between core-levels. Chemical shifts of Al-K$\alpha$ emissions of metal-Al and its compounds including an oxide were reported and discussed a relation with amounts of valence charge of the materials [13]. A more precise scheme of the discussion should be as follows that chemical shifts of K$\alpha$ are directly related to relaxation energy (core-hole effect or local screening effect), which is related to a valence charge and/or local dielectric properties of materials. Similar information on relaxation energy is also obtained by taking differences between two core-level binding energies in X-ray photoelectron spectroscopy (XPS) experiments. Relation between relative chemical shifts of 1s and 2p in XPS spectra and dielectric constants are reported for Si and its compounds [14] and Al and its compounds [15].

4. Concluding remarks

Ti-L$\alpha$$\beta$- and Ti-L$\ell$, L$\eta$-emission spectra of metal-Ti and its oxides obtained by using a SEM-SXES instrument were discussed. As L$\alpha$$\beta$-emissions caused by electron transitions from VB to core 2p levels, variety of intensity distributions were observed for Ti oxides with different crystal structures reflecting different bonding states. Thus, L$\alpha$$\beta$-emissions is useful for chemical bonding analysis. Simple intensity profiles of L$\ell$, L$\eta$-emissions due to transitions between core levels is suited for examining peak energy shifts, which indicate the relaxation energy (core-hole effect or local screening effect) in the final
state. It should be noted that integrated intensity of L_α,β should be related to the number of 3d electrons and that of L_λ,η-intensity is to the number of atoms included in the analysed volume. This information is important in microbeam analysis of materials including 3d transition metal elements.

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