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Experimental and theoretical studies on X-ray induced secondary electron yields in Ti and TiO_2

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Abstract

Generation of X-ray induced secondary electrons in Ti and TiO_2 was studied from both experimental and theoretical approaches, using X-ray photoelectron spectroscopy (XPS) attached to a synchrotron radiation facility and Monte Carlo simulation, respectively.

The experiment revealed that the yields of secondary electrons induced by X-rays (electrons/photon) at photon energies to 4950 and 5000 eV for Ti and TiO_2 are $\delta_{\mathrm{Ti}}(4950\,\mathrm{eV}) = 0.002$ and $\delta_{\mathrm{Ti}}(5000\,\mathrm{eV}) = 0.014$ while those for TiO_2 are $\delta_{\mathrm{TiO_2}}(4950\,\mathrm{eV}) = 0.003$ and $\delta_{\mathrm{TiO_2}}(5000\,\mathrm{eV}) = 0.018$.

A novel approach to obtain the escape depth of secondary electrons has been proposed and applied to Ti and TiO_2. The approach agreed very well with the experimental data reported so far. The Monte Carlo simulation predicted; $\delta^*_{\mathrm{Ti}}(4950\,\mathrm{eV}) = 0.002$ and $\delta^*_{\mathrm{Ti}}(5000\,\mathrm{eV}) = 0.011$ while $\delta^*_{\mathrm{TiO_2}}(4950\,\mathrm{eV}) = 0.003$ and $\delta^*_{\mathrm{TiO_2}}(5000\,\mathrm{eV}) = 0.015$.

An experimental examination on the contribution of X-ray induced secondary electrons to photocatalysis in TiO_2 has also been proposed.

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1. Introduction

Recently Okada et al. [1] reported that X-ray irradiation on a TiO_2-coated surface induces surface excitation, leading to a photocatalysis reaction on the TiO_2 as does ultraviolet light at energies over 3.2 eV. Since this result suggests the possibility that X-ray induced secondary electrons (XSE) are closely related to the photocatalysis reaction in TiO_2, their paper has attracted renewed attention to XSE. However, to our knowledge, there has been little basic study on XSE, although XSE has been used as a powerful signal in X-ray photoemission microscopy (XPEEM) [2].

As far as secondary electrons (SE), which are generated by a primary electron beam, are concerned, systematic studies have been performed extensively, shedding intimate insight into the mechanism of SE generation. In the generation of XSE, the photoelectrons and Auger electrons associated with photoionization are considered primary projectiles that generate XSE just as primary electrons generate SE. Since the generation of photoelectrons induced by X-ray irradiation is well understood [3], XSE generation can be described theoretically by calculating the energy loss processes of the primary projectiles (X-ray induced photoelectrons and Auger electrons) as with the conventional theory of SE generation [4–6].

In view of the basic investigation of SE and XSE generations in metal oxide, TiO_2 has long been regarded as one of the most appropriate materials because it is not insulative and free from charging from irradiation of primary electrons and/or X-rays. Furthermore, according to Okada et al., it is quite easy to get a clean TiO_2 surface by simply irradiating the surface with X-rays.

Therefore, the primary purpose of the present work is to examine whether XSE is closely correlated to the photocatalysis reaction in TiO_2 under X-ray irradiation. For this, we

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first have been involved in both experimental and theoretical studies of the generation of XSE at photon energies of 4950 and 5000 eV, just below and above the K-absorption edge of Ti, 4965 eV. Concerning the XSE yields for X-rays at photon energies above and below X-ray absorption edge, we have already reported [7] in a previous paper that the yield of XSE beyond the Ag L-absorption edge is nearly five times greater than that below the L-absorption edge. Hence, if XSE is closely correlated to the photocatalysis reaction in TiO_2, the reaction should be different for X-rays at energies on both sides of the Ti–K absorption edge.

This paper reports both the experimental and theoretical studies on XSE generated in Ti and TiO_2 to elucidate the mechanism of the XSE generation. The experiment was performed by X-ray photoelectron spectroscopy (XPS) attached to the synchrotron radiation (SR) facility (SR-XPS) [8] in the SPring-8. To describe the experiment we also performed Monte Carlo (MC) simulation based on the uses of the screened Rutherford scattering formula and Bethe's stopping power equation, combined with a photoelectron generation model [3]. Both the experimental and theoretical results have agreed very well with each other, demonstrating the significant contribution of photoionization in the K-shell to the generation of XSE.

On the possibility of the contribution of XSE to the photocatalysis on TiO_2, we have proposed quantitative measurements of contaminant growths on a TiO_2 surface under X-ray irradiation at energies of 4950 and 5000 eV by SR-XPS, shedding an intimate insight into the photocatalysis reaction in TiO_2.

2. Theoretical

2.1. Model

Fig. 1 shows the schematic diagram of the simulation model. Photons of specific energy irradiate a specimen surface, penetrating into the specimen by causing photoionization along a straight path. This photoionization generates not only photoelectrons but also Auger electrons through the relaxation process of photoionization. The probability of the generation of Auger electrons in layer Δz at depth z_i is given by

$$p(z_i) = (1-\omega)\left(\frac{r-1}{r}\right)\mu\frac{\Delta z}{\cos\theta}\,\mathrm{e}^{-(\mu z/\cos\theta)} \tag{1}$$

where ω, r, and μ are fluorescent yield, jumping ratio, and absorption coefficient for the relevant X-rays, respectively.

The generation of photoelectrons by X-rays is described by Reilman et al. [9] as

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{1}{4\pi}\left[1+\frac{\beta}{2}\left(\frac{3}{2}\sin^2\phi-1\right)\right] \tag{2}$$

where ϕ is emission angle against incident X-rays and β is an asymmetric parameter. The Auger electrons are assumed to be generated homogeneously in an emission angle. These photo and Auger electrons then penetrate through the specimen undergoing elastic and inelastic scattering processes, inducing the generation of secondary electrons called ''X-ray induced secondary electrons''. The simulation of the scattering processes of the photoelectrons and Auger electrons is, therefore, nothing but those processes that a primary electron of keV undergoes in the same specimen, which is described by conventional MC simulation [10] with considerable success. In order to extend the applicability of Bethe's stopping power equation below the keV region, Joy's modification for mean ionization energy has been used [11].

In the simulation model, we have also presumed that a part of the loss-energy dissipated by the Auger electrons and photoelectrons through inelastic scattering processes contributed to the generation of secondary electrons as was the case in the theoretical treatments extended by Baroody [4] and Dekker

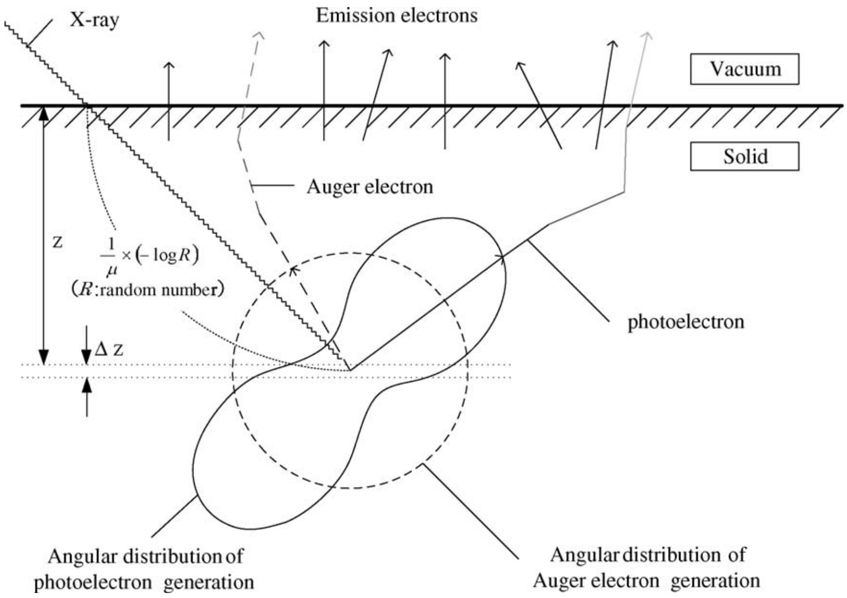

Fig. 1. Schematic illustration of MC simulation model for the generation of X-ray induced secondary electrons.