Title	Au/ステップ状TiO2(320)接合界面のSHGによる研究
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Citation	
Issue Date	2018-03
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/15334
Rights	
Description	Supervisor:水谷　五郎，マテリアルサイエンス研究科，博士

Optical second harmonic generation of the Au/stepped TiO_2 (320) interface

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Abstract

In the catalytic field, the Au/TiO_2 plays an important role due to an extraordinary high activity for low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of unsaturated hydrocarbons, and reduction of nitrogen oxides and so on. Studying the electronic states of the Au/TiO_2 interface is vital to explore the catalytic mechanism. Many researchers already studied the electronic structure of the Au/TiO_2 (110) interface by several microscopic or optical technique such as scanning tunnelling microscope (STM), transmission electron microscope (TEM), UV-Vis spectroscopy, and so on . However, the observation of the electronic states of the Au/TiO_2 interface and stepped and flat TiO_2 surface by second harmonic generation (SHG) method is very limited. For this reason, I intended to observe the electronic states of the Au/stepped TiO_2 interface using SHG method. SHG is a well-established surface-specific probe of centrosymmetric media. In the dipole approximation, SHG is forbidden in the bulk of a medium having inversion symmetry, while it is allowed at the surface where inversion symmetry is broken. Because of the symmetry selection property, the SHG method can be one of the ideal methods to measure the contribution of the step structure, while other surface tools such as XPS, TEM, STM, UV-Vis spectroscopy and microscopy technique cannot do because the number of steps are normally lower than the terrace atoms. In this research, stepped bare TiO_2 (320) single crystal surface was used as a substrate and Au thin film with the thickness of 2 nm was deposited on the

surface in a UHV chamber at a pressure of $2x10^{-7}$ Torr. This Au/TiO_2 (320) interface may act as an active sites for showing the catalytic behaviour. As it is well known, surface defects such as steps and kinks play an important role in generating active sites for catalytic reactions, so it is vital to study the structure and the electronic states of such surface defects. Thus, it would be very informative to analyse the SHG response from the interface of TiO_2 stepped surface decorated by Au. Au/TiO_2 steps should generate an SHG signal due to broken symmetry at the interface.

The SHG response from the Au/TiO_2 (320) interface and bare TiO_2 (320) surface was investigated with the incident photon energies of 1.17 eV and 2.33 eV generated by using a pulsed Nd^{3+}**:**YAG laser. The isotropic response was found from both samples at the incident photon energy of 1.17 eV. In contrast, we observed the anisotropic response from both Au /TiO_2 (320) and bare TiO_2 (320) at the incident photon energy of 2.33 eV. From the Au/TiO_2 (320) sample, an anisotropic structure was observed to the $[\bar{2}30]$ direction for Pin/Pout polarization combination. Here, the Pin denotes the input polarization mode of the incident light and Pout corresponds to the output polarization mode of the SHG light. From the experimental data, I theoretically decomposed the nonlinear susceptibility elements ($\chi_{ijk}^{(2)}$). Here, i, j and k denote the axis direction of the sample coordinate. I found that there were two groups of the nonlinear susceptibility elements corresponding to step and terrace contribution. More precisely, I have calculated SHG intensity patterns for Au/TiO_2 (320) and bare TiO_2 (320) based on the terrace and step contributions fitted to the experimental results with photon excitation energies of 2.33 eV. The anisotropic responses were observed due to the contributions of both the step and terrace groups of nonlinear susceptibility elements. From the calculated results of the step and terrace groups of $\chi_{ijk}^{(2)}$ elements, it was found that the step contribution of the Au/TiO_2 (320) is different from that of the bare TiO_2 (320) sample for the

Pin/Pout polarization combination. In order to discuss the possible reasons for this difference, I considered the four possible mechanism candidates as an origin of the signal enhancement from the Au/TiO_2 (320) interface. This four candidates are (a) Enhancement of the incident electric field by surface defects (b) Electronic resonance of Au/TiO_2 interface step (c) Surface plasmon effect on SHG enhancement (d) Fresnel factor effect on SHG enhancement.

I found that Au deposited TiO_2 (320) surface contains island structure by the observation of AFM and SEM with EDX and these islands might act as "hot spot" and make the SHG intensity stronger. However, this effect should have an isotropic nature with respect to the rotation of the sample around its normal because these islands are randomly distributed. The effect would be similar if I consider the enhancement occurring due to the random steps on the surface. This is not the case when I see the SHG pattern for Pin/Pout polarization combination. So, this candidate should be eliminated.

An electronic resonance may occur at the step region of the Au/TiO_2 interface and it is the most possible candidate for the enhancement of the SHG signal considering this case. In this study I observed the enhanced SHG signal correlated with the existence of the Au/TiO_2 (320) interface steps. Hence this interface step electronic state is a credibe candidate of the origin of the enhanced signal.

In the case of a thin gold film deposited on pre-patterned TiO_2 substrate, local field enhancement may result from the surface plasmon resonance (SPR). I measured the linear optical reflectivity in order to confirm whether there is any influence of surface plasmon resonance and Fresnel factor for the enhancement of the anisotropic SHG signal obtained from the Au/TiO_2 (320) interface. From the reflectivity data of the Au/TiO_2 (320) interface, it was

observed that, the reflectivity for P- and S- polarized light are almost the same at the azimuthal angle, $\varphi = 0^{O}$ and 180°. This result indicates that the linear optical process at frequency ω occurs almost in the same way at $\varphi = 0^{O}$ and 180° and it means that even if the SPR occurred, there is no effect on the enhanced SHG signal due to the different response from the $\varphi = 0^{O}$ and 180°. This discussion is also true for the Fresnel factors. Therefore, there is no influence of Fresnel factors on the enhancement of SHG signal.

From the above discussion of four candidates, it seems that electronic resonance at the Au/TiO_2 (320) interface step is feasibly responsible for the enhancement of the SHG. The other three mechanism candidates can be eliminated due to their less feasibility.

Keywords: Second harmonic generation (SHG); Photocatalyst; Au/TiO_2 (320) interface; Electronic states; Nonlinear susceptibility elements.