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Optical second harmonic generation from the anatase TiO₂ (101) face

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Abstract

We have observed optical second harmonic generation (SHG) from the (101) face of anatase TiO₂. The SH intensity from the TiO₂ (101) face in air as a function of the sample rotation angle around the surface normal gives asymmetric patterns for all combinations of input and output polarizations. A theoretical analysis has shown that the observed optical nonlinearity originates mainly from the surface rather than from the bulk.

Keywords : surface optical second harmonic generation, anatase TiO₂ (101), photocatalyst

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Introduction

Titanium dioxide (TiO_2) used in combination with a counter electrode of platinum decomposes water into hydrogen and oxygen under UV light illumination. The photo-catalytic activity of this material has been a subject of strong interest, because of its potential use in solar energy conversion [1]. The basic mechanism of its catalytic reaction has also attracted interest, and a great deal of efforts have been made for its elucidation [2].

The optical second harmonic spectroscopy can be applied to the investigation of the interface electronic states of working catalysts in reactive gases, because this technique does not require vacuum. Several experiments have been performed on rutile TiO_2 (110) [3, 4, 5]. It has been pointed out that the SH intensity pattern as a function of the sample rotation angle reflects the microscopic structure of the surface of TiO_2 [4] and that the SH intensity as a function of the photon energy gives information on the surface band gap [5].

The photo-catalytic activity of anatase TiO_2 [6] is several times higher than that of rutile TiO_2 [7]. Thus it is even more interesting to investigate this surface than that of rutile TiO_2 . However, single crystals of anatase TiO_2 are difficult to obtain, and little is known about its surface. No previous observation of SHG on this surface has been reported.

The goal of our study is to elucidate the mechanism of the catalytic reaction on the anatase TiO_2 surface by observing the surface electronic states in their working state. We also wish to clarify the origin of the difference in the catalytic activity between anatase and rutile. As a first step toward this goal we have measured SHG from its (101) face in air. The SH intensity patterns as a function of the sample rotation angle were asymmetric and reflected the microscopic structure of the (101) face. By a theoretical analysis we have found that the optical nonlinearity of surface is more dominant than that of the bulk.

Experiment

The sample of anatase TiO_2 (101) was grown by a chemical vapor transport reaction method reported by Berger et al [8]. Its size was about $2 \times 2 \times 3 \text{ mm}^3$ and the shape of the as-grown (101) face was trapezoidal. After growth it was annealed at 800°C for 110 hours in oxygen atmosphere to remove the bulk oxygen vacancies. During annealing the surface was found to be covered by a SiO_2 layer by an ESCA analysis. This SiO_2 layer must have come from the quartz glass tube used for annealing. This layer was removed by etching with 5 N NaOH. The crystallographic orientation of the sample face was checked by an X-ray diffraction measurement. For comparison, we have also observed SHG from the (001) face of anatase TiO_2 . The sample preparation method was exactly the same as that for the (101) face.

The experimental setup for the SHG measurements was described elsewhere [9]. The wavelength of the incident light pulses was 532 nm, and the pulse energy was set at 0.2 mJ per pulse. The incident and the observed angles were both 45° with respect to the surface normal. All experiments were performed in air at room temperature.

Results and discussion

Figure 1 shows the SH intensity from the chemically etched (101) face of anatase TiO_2 as a function of the sample rotation angle ϕ . ϕ is defined as the angle between the incident plane and the $[\bar{1}01]$ direction on the (101) face. The SH intensity is plotted in the radial direction. The SH intensity gives asymmetric patterns as a function of the sample rotation angle for all combinations of input and output polarizations. The intensity patterns were quite different from those observed before chemical etching [10]. Since this change of

the SH intensity pattern is caused by removal of the SiO₂ layer by chemical etching, we conclude that the observed SHG from the anatase TiO₂ (101) face is sensitive to its surface conditions. The SH intensity from the (001) face was very weak (not shown). In P-in/P-out polarization configuration it was 8% of that from the (101) face. In other polarization configurations, it was less than 0.5% of that from the (101) face in the P-in/P-out polarization configuration.

In order to find the origin of the observed SHG, we have carried out a theoretical analysis of the SH intensity patterns from the (101) face of anatase TiO₂. The theoretical analysis is based on the work by Kobayashi et al [4]. We have taken into account the fact that the medium is birefringent and that the c-axis of the crystal is tilted by 21.7° from the surface plane. We have considered the surface dipole polarization and the bulk electric quadrupole polarization as nonlinear radiation sources [11]. The second order bulk nonlinear dipole polarization is not induced because the bulk crystal structure has an inversion symmetry [12]. The surface nonlinear susceptibility $\chi_{sijk}^{(2)}$ was defined after Guyot-Sionnest et al [9, 13]. Under the surface symmetry C_{1v} of anatase TiO₂ (101) [14], the number of independent surface nonlinear susceptibility elements are ten as shown in Fig. 2. The numbers 1, 2 and 3 in the suffices of $\chi_{sijk}^{(2)}$ correspond to the $[\bar{1}01]$, $[010]$ and $[\bar{1}0\bar{1}]$ directions, respectively. On the (101) surface of anatase TiO₂, the atomic structure does not have mirror planes perpendicular to the $[\bar{1}01]$ and $[101]$ directions [14]. Thus the suffices of nonzero $\chi_{sijk}^{(2)}$ elements must contain odd numbers of 1 and 3's (Fig. 2). The number of independent bulk quadrupolar nonlinear susceptibility elements Γ_{ijkl} are eleven under the bulk crystal symmetry D_{4h} (Fig. 2) [13]. The subscripts x, y and z refer to the crystal axes.

Figure 2 shows the calculated SH intensity patterns and the peak intensity from the anatase TiO₂ (101) and (001) faces when one of the eleven Γ_{ijkl} and ten $\chi_{sijk}^{(2)}$ elements is set

equal to a certain common value and the other elements are all set equal to zero. We used linear dielectric constants of anatase TiO_2 $\epsilon_{//}(2.33 \text{ eV})=6.413$ and $\epsilon_{//}(4.66 \text{ eV})=1.299+i4.645$ for the electric fields parallel to the [001] axis, and $\epsilon_{\perp}(2.33 \text{ eV})=6.822$ and $\epsilon_{\perp}(4.66 \text{ eV})=4.795+i11.212$ for the electric fields perpendicular to the [001] axis [15, 16].

The calculated patterns were fitted to the experimental data by varying $\chi_{sijk}^{(2)}$'s and Γ_{ijkl} 's in the complex plane, using an automatic algorithm that minimizes the sum of the squares of deviations. From the result that the observed SH intensity from the (001) face in S-in/P-out polarization configuration was very weak and from the calculated results shown in the last column of Fig. 2, we have set Γ_{xxxx} , Γ_{xxyy} , Γ_{xyxy} , Γ_{xyyx} , and Γ_{zyzy} equal to zero. The best-fit result is shown by the thin solid curves in Fig. 1. The ratios of the best-fit susceptibility elements are:

$$\begin{aligned} \chi_{s212}^{(2)} : \chi_{s122}^{(2)} : \chi_{s111}^{(2)} : \chi_{s113}^{(2)} : \chi_{s223}^{(2)} \\ = (36-65i) : (-53+2i) : (25-11i) : (-24+4i) : (22-7i). \end{aligned} \quad (1)$$

The contributions from other elements are small.

In order to find out whether the observed SHG comes from the surface or from the bulk, we have separated the calculated SH intensity patterns into the surface and the bulk contributions as shown in Fig. 3. For P-in/P-out polarization configuration, the contribution of the surface is about ten times larger than that of the bulk. For P-in/S-out polarization configuration, the contribution of the bulk is negligible. Thus we conclude that the observed optical nonlinearity of the chemically etched anatase TiO_2 (101) face originate mainly from the surface.

Conclusion

We have observed SHG from the anatase TiO_2 single crystal faces. The SH

intensity patterns as a function of the sample rotation angle and as a function of the input and output polarizations were analyzed successfully by a phenomenological electromagnetic theory. The result of the analysis has shown that the origin of the observed SHG mainly arises from the surface. We have obtained the ratio of the nonlinear susceptibility elements responsible for the observed SHG.

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Figure captions

Fig. 1 SH intensity patterns from the (101) face of anatase TiO_2 (dots) as a function of the sample rotation angle. Solid curves represent a theoretical calculation. The fundamental photon energy is 2.33 eV.

Fig. 2 SH intensity patterns obtained by theoretical calculation when one of the surface or bulk nonlinear susceptibility elements $\chi_{sijk}^{(2)}$'s or Γ_{ijkl} 's is set equal to a certain common value and all the other elements are set equal to zero. The SH intensity is normalized by the maximum intensity in each pattern and the maximum intensity is written next to each pattern. The intensities are in arbitrary, but common units.

Fig. 3 Decomposition of the SH intensity patterns in Fig. 1 (a) and (b) into surface (empty circle) and bulk (filled circle) components by a theoretical calculation.

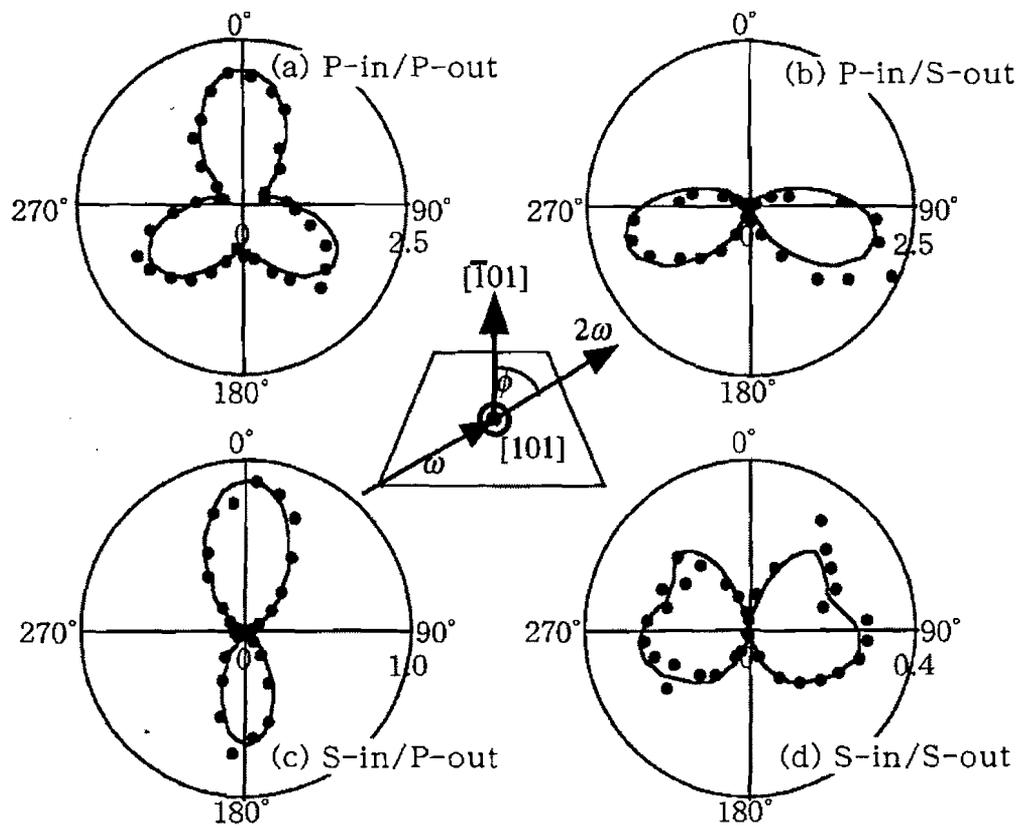


Figure 1 Nakamura et al

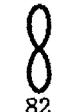
| | (101) surface | | | (101) bulk | | (001) bulk |
|---------------------|--|---|-----------------|---|---|---|
| | P-in/ P-out | P-in/ S-out | | P-in/ P-out | P-in/ S-out | S-in/ P-out |
| $\chi_{s111}^{(a)}$ |  82 |  9 | Γ_{xxxx} |  0.18 |  0.03 |  0.03 |
| $\chi_{s122}^{(a)}$ |  13 |  60 | Γ_{xxyy} |  0.19 |  0.08 |  0.03 |
| $\chi_{s133}^{(a)}$ |  1341 |  817 | Γ_{xyxy} |  0.12 |  0.10 |  0.11 |
| $\chi_{s212}^{(a)}$ |  6 |  5 | Γ_{xyyx} |  0.20 |  0.08 |  0.03 |
| $\chi_{s313}^{(a)}$ |  4063 |  401 | Γ_{yyzz} |  0.05 |  0.04 | 0 |
| $\chi_{s113}^{(a)}$ |  331 |  59 | Γ_{zyyz} |  0.56 |  0.02 | 0 |
| $\chi_{s223}^{(a)}$ |  156 |  30 | Γ_{yzyz} |  0.05 |  0.04 | 0 |
| $\chi_{s311}^{(a)}$ |  1369 |  65 | Γ_{zyyz} |  1.30 |  0.09 | 0 |
| $\chi_{s322}^{(a)}$ |  445 |  389 | Γ_{zyzy} |  0.72 |  0.96 |  0.37 |
| $\chi_{s333}^{(a)}$ |  13101 |  5240 | Γ_{zzyy} |  1.30 |  0.09 | 0 |
| | | | Γ_{zzzz} |  1.47 |  0.11 | 0 |

Figure 2 Nakamura et al

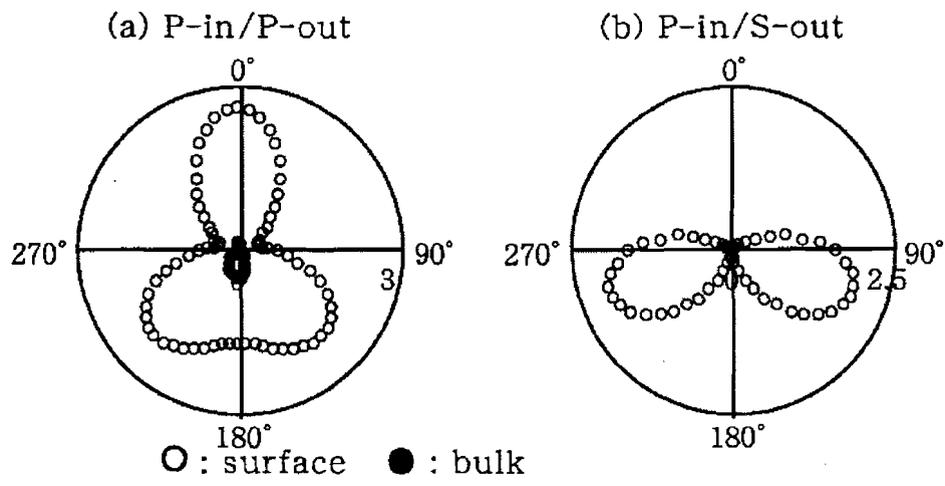


Figure 3 Nakamura et al