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Description	

OPTICAL SECOND HARMONIC SPECTROSCOPY OF RUTILE TiO_2 (110) IN AIR

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We have measured the reflected optical second harmonic (SH) intensity from rutile $TiO_2(110)$ as a function of the fundamental photon energy. A sharp rise in the SH intensity was observed above $2\hbar\omega=3.4$eV. The sum frequency intensity also shows a rise at $\hbar\omega_1+\hbar\omega_2\sim3.4$eV. Thus the observed sharp rise of the SH intensity is due to a resonance with an electronic excitation at 3.4eV. This energy is different from the two-photon resonance energy $2\hbar\omega = 3.02$eV of the bulk band gap of TiO_2. Hence the origin of this resonance is attributed to surface electronic states. We have also found that the SH intensity pattern as a function of the azimuthal angle changes drastically when the fundamental photon energy is scanned across this onset energy. We suggest that this is due to the variation of the shape of the wavefunction of the excited electronic states at this energy.

Keywords: Second harmonic generation, Titanium oxide, Sum frequency generation, Surface electronic phenomena
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Recently optical second harmonic generation (SHG) has come to be recognized as a powerful tool for surface analysis [1]. The spectroscopy using the SHG phenomenon [2] can be applied to the investigation of all surfaces or interfaces accessible by light. On the other hand the photoemission spectroscopy (PES), a very popular tool for spectroscopic surface analysis, cannot be applied to surfaces of materials in low vacuum, surfaces of insulators, or interfaces of materials. Thus we find it worth while to examine whether the optical second harmonic spectroscopy can serve as an auxiliary method of PES for analyzing such surfaces and interfaces.

As one of such applications, we have studied the changes of the surface electronic states involved in the elementary processes of the photo-catalytic reactions on the TiO_2 surface. Titanium dioxide TiO_2 is a well-known photo-catalyst for water decomposition[3]. The characterization of its surface electronic states is especially important in understanding its photo-catalytic function, but has not yet been achieved to a sufficient degree [4][5]. Hence as a first step toward developing the SH spectroscopy for this class of sample systems, we have measured the SH spectrum from rutile $TiO_2(110)$ in air. On $TiO_2(110)$ in air H_2O molecules are adsorbed [6] to form a $TiO_2(110)/H_2O$ interface. This interface is present in the catalytic reaction of water decomposition by TiO_2.

Schultz et al was the first to observe SHG from TiO_2 [7] using a light source with a fixed photon energy at $\hbar\omega$=2.33eV. They observed changes of the SH intensity when the surface is illuminated with ultraviolet light, and have shown that the SH intensity is correlated with the XPS signal of Ti^{3+} defects on the surface. Recently we have demonstrated that the SH intensity from TiO_2(110) in air at $\hbar\omega$=2.33eV shows symmetric patterns as a function of the azimuthal angle and have determined the surface nonlinear susceptibility[8]. We have shown that a large nonlinear polarization is induced along the [001] direction on this surface. However, these results using a light source of fixed photon energy do not give us any information on the surface or interface electronic states. We believe that a spectroscopic study of SHG from the TiO_2 surface is desirable.

In this paper we will show that the energy of the excitation between surface electronic states of TiO_2(110) in air is clearly obtained by optical second harmonic spectroscopy. We will also show that the SH intensity pattern as a function of the azimuthal angle changes when the incident photon energy is varied in this energy range.

The experimental setup for SHG measurement has been described elsewhere [9]. The light source of the fundamental frequency was an optical parametric oscillator (OPO) driven by a frequency-tripled Q-switched Nd^{3+}:YAG laser. We used GaAs(001) as a reference sample to calibrate the signal intensity [10]. All experiments were performed in air at room temperature. In sum frequency generation (SFG) experiments, a light beam from the OPO and a beam of wavelength 532nm from the frequency-doubled Q-switched Nd^{3+}:YAG laser were used. The preparation of the TiO_2(110) crystal faces was described in our previous paper [8].

In Fig. 1 we show the reflected optical second harmonic intensity from rutile TiO_2 (110) in air as a function of the fundamental photon energy $\hbar\omega$. The polarization configuration is *p*-in/*p*-out and the plane of incidence is parallel to the [001] direction. Above $\hbar\omega = 1.7eV$ we see a sharp increase in the SH intensity.

To determine whether the sharp increase in the SH intensity is due to a one-photon resonance or a two-photon resonance with some electronic level, we have measured the reflected optical sum frequency (SF) intensity from TiO_2 (110). The two incident beams were *p*-polarized and the *p*-polarized SF intensity was measured. In Fig. 2 we show the sum frequency intensity from TiO_2(110) in air as a function of the sum of the photon energies of the two incident laser beams $\hbar\omega_1+\hbar\omega_2$. Here the photon energy $\hbar\omega_1$ was fixed at 2.33eV and the photonenergy $\hbar\omega_2$ was varied. We see that the SF intensity increases when the sum of the photon energies of the two incident laser beams exceeds $\hbar\omega_1+\hbar\omega_2 \sim 3.4eV$. This energy is identical to twice the fundamental energy at the onset of the resonance in SHG in Fig. 1. Thus we conclude that the sharp increase of SH intensity observed in Fig. 1 is due to a two-photon resonance; i. e. a resonance of the second harmonic wave with an electronic transition.

The absorption due to the bulk band gap of TiO_2 begins at 3.02eV[11] at room temperature for the electric field parallel to the [001] axis. Because there is no structure in the joint density of states at 3.4eV in the bulk band of TiO_2[12], the bulk bands cannot produce a structure at 3.4eV in the SH intensity. Thus a probable origin of the observed onset is resonance with surface electronic states.

In our previous work we have analyzed the patterns of SH intensity from rutile $TiO_2(110)$ in air as a function of the azimuthal angle at the photon energy of $2\hbar\omega$=4.66eV, i. e. at the energy a little higher than those treated in the present study. We have shown that the SH intensity is dominated by surface nonlinearity[8]. Thus we conclude that the observed resonance in SHG shown in Figs. 1 and 2 also originate from surface electronic transitions.

The calculation of surface band gap energies of TiO_2 have been performed by several authors [5][13]. According to Tsukada et al the minimum surface band gap energy is smaller than that of the bulk [5]. When H_2O molecules are adsorbed on it, the surface band gap energy increases [13]. These results are consistent with our present interpretation.

Here we note that the surface electronic excitation found in this study is observed only in a particular polarization configuration. We have performed our experiment in a *p*-in/*p*-out polarization configuration with the plane of incidence parallel to the [001] direction. According to Kobayashi et al [8] the surface nonlinear susceptibility element $\chi^{(2)}_{S113}$ contributes dominantly to the SH intensity in this configuration. Here, the suffices 1 and 3 denote [001] and $[\bar{1}\bar{1}0]$ directions on the (110) surface, respectively. Thus the relevant surface electronic excitation is that involved in a particular nonlinear optical process. Hence, if we change the polarization combination and the azimuthal angle, we should observe the SH intensity due to different optical transitions. This means that the SH intensity patterns as a function of the azimuthal angle will change, if we change the incident photon energy. In order to check whether or not this is the case, we have measured the SH intensity patterns at different incident photon energies.

Fig. 3(a) and (b) show the azimuthal angle dependence of the SH intensity at fundamental photon energies $\hbar\omega$=1.68eV and $\hbar\omega$=1.82eV in *p*-in/*p*-out polarization configuration, respectively. These photon energies correspond to the energies indicated by the arrows in Fig. 1. In Fig. 3(c) we show a similar plot at the fundamental photon energy $\hbar\omega$=2.33eV obtained in our previous work[8]. We see that angular patterns drastically change with the incident photon energy. In Fig. 3(a), the pattern appears to have a four-fold symmetry. The patterns in Fig. 3(b) and (c) have a two-fold symmetry and their shapes are similar. A full analysis of these patterns is left for a future study, because for that purpose we also need the SH intensity patterns for other polarization combinations, and for another crystal face (001). The SH intensity pattern as a function of the azimuthal angle results from the fact that the surface is two-fold symmetric(2m) and the surface symmetry is that of the surface electronic structure. The relative strength of the SH signal along [001] and $[1\bar{1}0]$ will depend on how close the SH frequency is to their respective resonances. In the following, we will give a tentative and qualitative interpretation of the observed variation of the patterns.

If the electrons are delocalized along one direction and an electric field of the light is applied parallel to that direction, the optical response is generally strong. Thus the SH intensity patterns as a function of the azimuthal angle reflect the shapes of the electronic wavefunctions on that surface. Based on this reasoning we can infer that the variation of the SH intensity patterns observed in Fig. 3 reflects the variation of the shape of the excited state wavefunctions as a function of the energy. The strong SH response at $\phi=90^\circ$ and 270° for $\hbar\omega=1.82$eV and 2.33eV in Fig. 3(b) and (c) is likely due to a resonance with the electronic states in the bridging oxygen at the TiO_2(110)/H_2O interface[14]. At this interface the Ti atoms and the bridging oxygen on them form Ti-O-Ti-O- zigzag chains along the [001] direction [15]. Along these chains the electrons are delocalized to some extent, and the SH light is generated more efficiently when the incident light is polarized parallel to the chain than perpendicular to it.

On the other hand the pattern in Fig. 3(a) indicates that the electrons excited by photons at $2\hbar\omega \sim 3.4$eV are delocalized not only along the [001] direction but also along the $[1\bar{1}0]$ direction. This may be because the photon energy of the incident light is nearly equal to the onset energy of the resonance, and the electronic states localized in the Ti-O-Ti-O- chain is not effectively excited. The observed four-fold pattern of the SH intensity may reflect the shape of the electronic wavefunction located a little deeper than the Ti-O-Ti-O- chain at the surface. A detailed analysis will require more experimental data and theoretical work.

In conclusion we have observed a sharp rise of the SH intensity from rutile TiO_2 (110) above $2\hbar\omega=3.4$eV for the *p*-in/*p*-out polarization configuration and with the plane of incidence parallel to the [001] direction. We have concluded that the observed sharp rise of SH intensity is due to a two-photon resonance with an electronic excitation at 3.4eV between surface states.

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Figure Captions

Fig. 1 The reflected optical second harmonic (SH) intensity from rutile TiO_2 (110) as a function of the fundamental photon energy $\hbar\omega$ in air. The polarization configuration is *p*-in/*p*-out and the plane of incidence is parallel to the [001] direction. The solid curve is a guide to the eye. The arrows indicate the energies at which the angular patterns of Fig. 3(a) and (b) were measured.

Fig. 2 The sum frequency intensity from rutile TiO_2 (110) using two light beams. One is a laser beam with fixed photon energy $\hbar\omega_1$=2.33eV and the other is a laser beam with varied photon energy $\hbar\omega_2$. Both of the incident beams are *p*-polarized and the *p*-polarized SF intensity was measured. The solid curve is a guide to the eye.

Fig. 3 The azimuthal angle dependence of the SH intensity from rutile TiO_2 (110) at fundamental photon energies 1.68eV(a), 1.82eV(b), and 2.33eV(c) in the *p*-in/*p*-out polarization configuration. The zero degree corresponds to the sample angle when the plane of incidence contains the $[1\bar{1}0]$ direction of the sample.

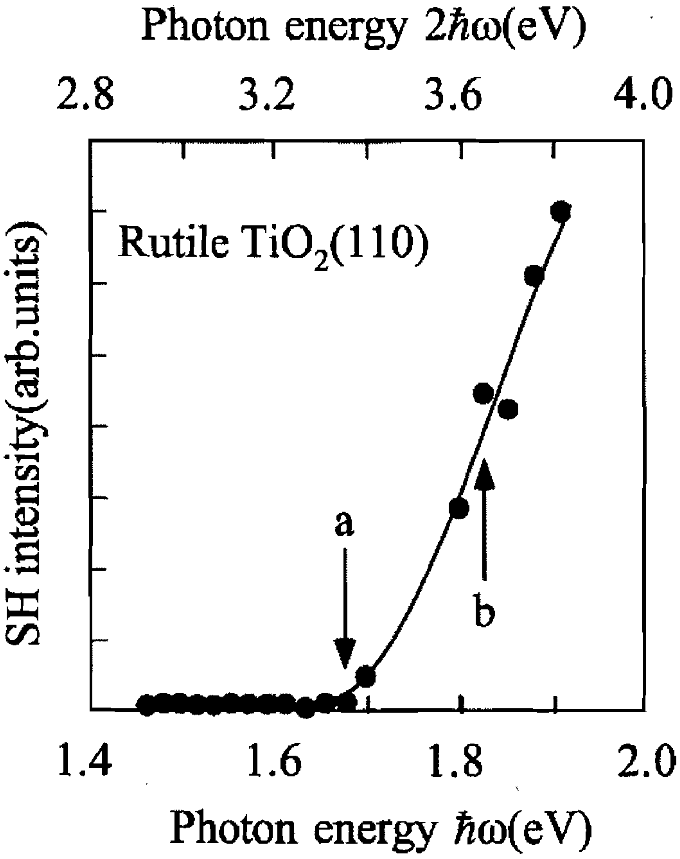

Figure 1 Kobayashi et al

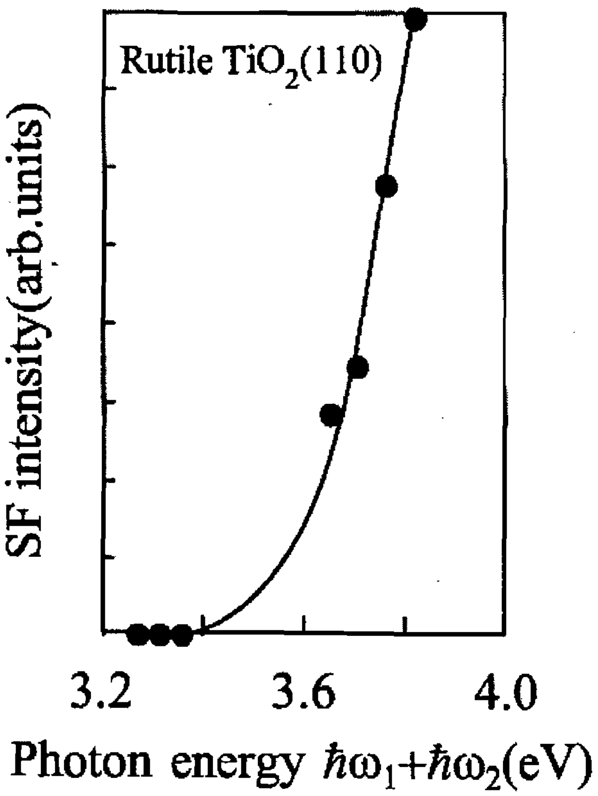

Figure 2 Kobayashi et al

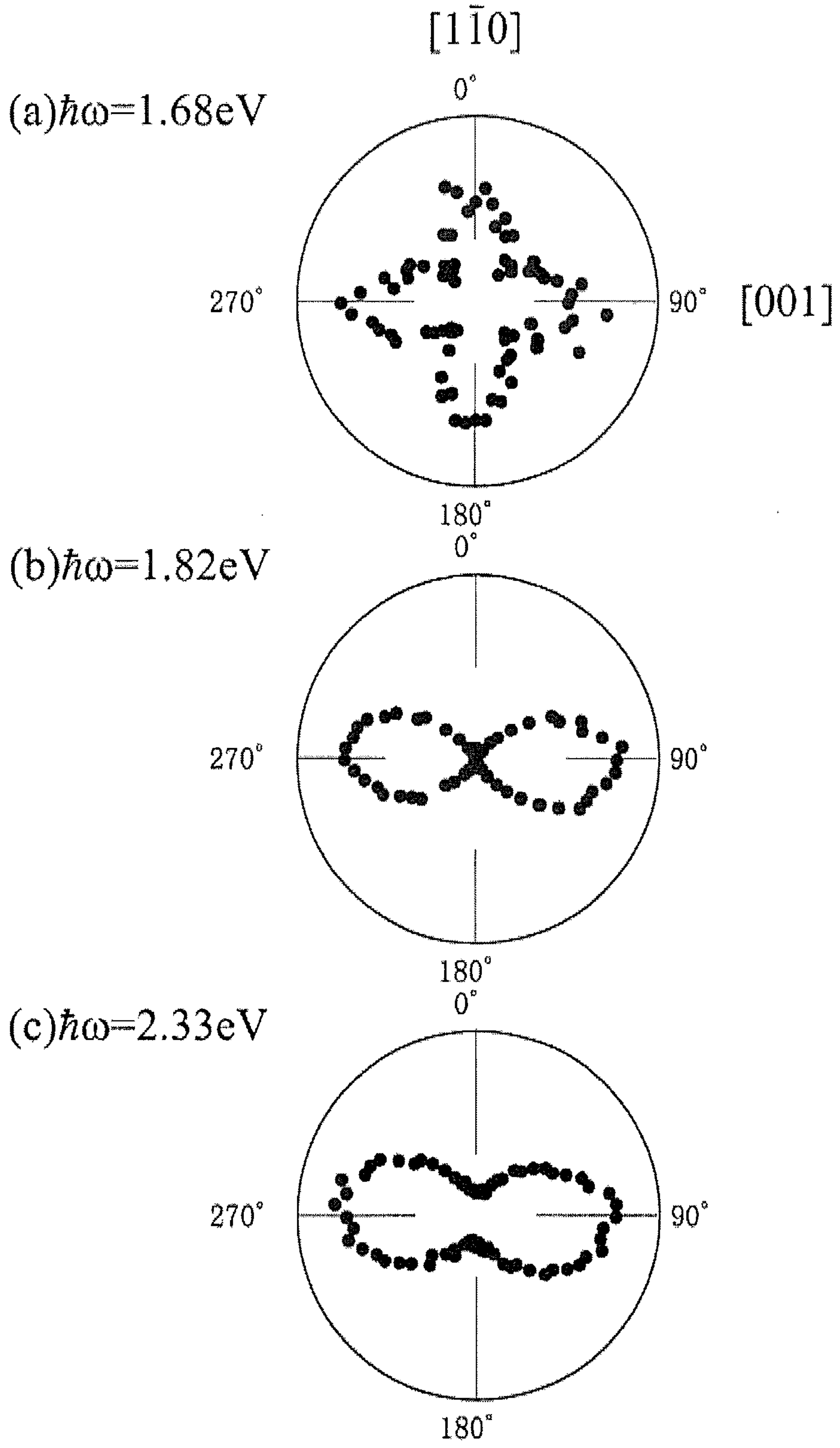

Figure 3 Kobayashi et al