Optical Second Harmonic Generation as a Probe of Electrostatic Fields and Flatband Potential at Single-Crystal TiO₂ Electrodes

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The surface-sensitive technique of optical second harmonic generation (SHG) is applied to the measurement of dc electrostatic fields and the flatband potential at the TiO_2 semiconductor electrode–electrolyte interface. A large SHG response is observed from n-type single-crystal $TiO_2(001)$ electrodes at potentials for which a depletion layer exists at the surface. This response is attributed to the electric field-induced SHG from the polarized TiO_2 lattice in the space charge layer at the semiconductor surface. The SHG from the interface varies linearly with the applied potential and reaches a minimum at the flatband potential of the electrode. The potential at which this minimum occurs shifts with pH at the expected rate of 60 mV/pH unit. A simple model of the electrostatic fields as a function of the band bending at the interface can be used to explain the observed dependence of the SHG on applied potential. These experiments suggest that SHG can be used as a local, time-resolved spectroscopic measurement of the electrostatic fields and surface charge density at single-crystal TiO_2 electrodes.

Introduction

Since the photoelectrochemical splitting of water at a TiO₂ electrode 20 years ago,[1] researchers have studied this semiconductor–electrolyte interface with the hope of using it as a means of converting optical energy into chemical or electrical energy.[2] More recently, TiO₂ has been investigated as a possible photocatalyst for a variety of organic and inorganic oxidation–reduction reactions.[3] Both of these practical reasons, as well as a general interest in fundamental studies of semiconductor electrodes, have resulted in an extensive amount of characterization work on polycrystalline and single-crystal TiO₂ electrodes in both aqueous and nonaqueous environments.[4] Electrochemical characterization of these interfaces is typically performed with a combination of ac impedance and photocurrent measurements.[4–6] However, complications in the analysis of these experiments make it difficult to extract consistent and meaningful parameters from the electrochemical data.[4] To avoid these problems, a number of *in situ* optical techniques such as absorption, luminescence, electroreflectance, and transient grating measurements have been applied to help characterize these electrodes.[5,7–11] Most recently, STM measurements have also been used in an attempt to characterize TiO₂ electrochemical surfaces.[12,13]

One technique that has been applied quite successfully to both solid–liquid[14–16] and liquid–liquid electrochemical[17] interfaces is the nonlinear optical process of second harmonic generation (SHG). SHG is a surface-sensitive and surface-selective method that can be used to supply information on molecular adsorption and orientation, single-crystal electrode surface symmetry, interfacial electrostatic fields, and time-resolved measurements of chemical reactions at surfaces.[18–22] In this paper, SHG is applied to the measurement of dc electrostatic fields and the flatband potential at the TiO₂ electrode–electrolyte interface. The SHG response from these electrodes is attributed to the electric field-induced SHG from the polarized TiO₂ lattice at the semiconductor surface. A simple model of the electrostatic fields as a function of the band bending at the interface is used to relate the SHG to the applied potential. In addition, the polarization dependence and rotational anisotropy of the SHG from the single-

crystal surface are used to determine the average surface symmetry of the electrode.

Experimental Considerations

Pieces (10 × 10 × 1 mm) of epilayer-polished, single-crystal rutile TiO₂(001) were obtained from Commercial Crystal Labs and heated in a H₂/N₂ mixture to 590–650 °C in order to produce n-type electrodes with donor densities between 10^{16} and 10^{18} cm⁻³ as determined from a Mott–Schottky analysis of electrochemical ac impedance measurements. The electrochemical measurements were controlled with a Princeton Applied Research 173/175 potentiostat in a three-electrode Teflon cell using a Pt counter electrode and a NaCl-saturated calomel reference electrode (SSCE). All potentials are reported versus SSCE. Solutions were prepared from Millipore-filtered water and contained 0.3 M NaClO₄ (Aldrich) as the supporting electrolyte along with 10 mM Na₂HPO₄ (Fluka). The pH of the electrolyte solutions was controlled by adjusting the phosphate buffer with HClO₄ (GFS Chemicals). In some cases, the TiO₂ electrodes were lightly etched prior to use by boiling for approximately 15 min first in concentrated HCl and then in 2:1 (v/v) H₂SO₄:H₂O.[4]

SHG experiments were performed with 604-nm light from a picosecond cavity-dumped dye laser that was synchronously pumped with the doubled output of a mode-locked Nd:YAG laser (Coherent Antares/Model 702, 4-MHz repetition rate, 50 nJ/pulse, 3-ps pulse width) at an angle of incidence of 60° from the surface normal. Typical peak power densities on the surface were approximately 100 MW cm⁻². At the power densities used in these experiments, the amount of 302-nm light generated at the electrode surface (<0.007 photon/pulse) was insufficient to create an observable photocurrent. The SHG from the interface at 302 nm was separated from the reflected fundamental light with filters and a 0.175-m monochromator and then detected with a cooled photomultiplier tube and gated photon-counting electronics. A more detailed description of the SHG experimental apparatus has been given previously.[23]

The polarization of the fundamental and second harmonic beams was set to either p-polarized (parallel to the plane of incidence) or s-polarized (perpendicular to the plane of incidence) light. The polarization dependence of the surface SHG signal depends upon the magnitudes and phases of the active tensor

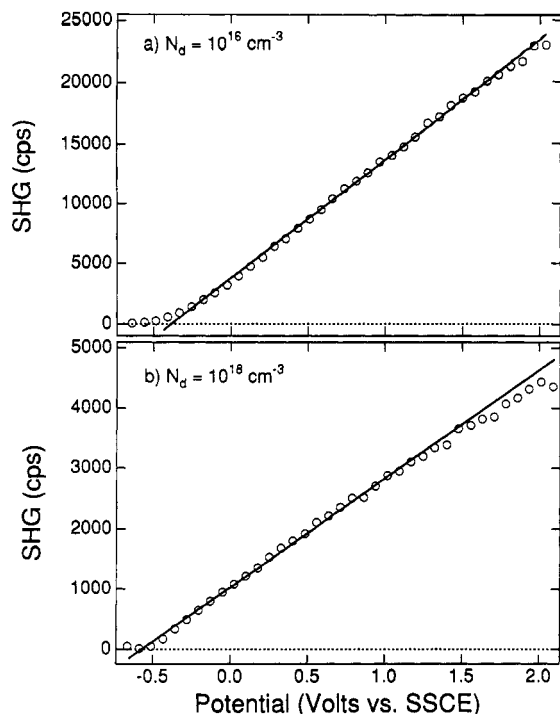† University of Wisconsin—Madison.
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Figure 1. Potential-dependent SHG signal at 302 nm from n-TiO$_2$ electrodes. The doping levels in these two experiments are (a) N_d = 10^{16} cm^{-3} and (b) N_d = 10^{18} cm^{-3}. In both experiments the supporting electrolyte is 0.3 M NaClO$_4$ + 10 mM Na$_2$HPO$_4$, with the pH of the phosphate buffer set to 2.3 for (a) and 2.7 for (b). In these SHG experiments the fundamental light at 604 nm is p-polarized, and the second harmonic beam generated at the interface is s-polarized. SHG measurements utilizing other polarization combinations exhibited a very similar potential dependence.

elements of the surface nonlinear susceptibility. These active tensor elements are in turn determined by the average surface symmetry of the single-crystal electrode. By using different polarization combinations, the active tensor elements can be measured with either SHG rotational anisotropy or normal incidence polarization anisotropy measurements; these experiments can therefore be used to determine the average surface symmetry.[14-16,19,22] For example, the unreconstructed TiO$_2$(001) surface has an average surface symmetry of C_{2v} for a single domain and an average surface symmetry of C_{4v} if there are equal amounts of the two possible domains present on the surface. For the TiO$_2$ surfaces reported here, we observed a surface SHG response from the combination of p-polarized fundamental and s-polarized second harmonic light that displayed a 2-fold rotational anisotropy. The observation of this SHG signal requires that the average surface symmetry for these electrodes be no greater than C_2.[24] A more complete description of the rotational anisotropy measurements will be presented in a subsequent paper.

Results and Discussion

The potential dependence of the surface SHG at 302 nm generated at the TiO$_2$–electrolyte interface is plotted for two different electrodes in Figure 1. The electrodes for Figure 1 had doping densities of approximately (a) 10^{16} cm^{-3} and (b) 10^{18} cm^{-3}. These electrodes were in contact with 0.3 M sodium perchlorate aqueous electrolyte solutions that were buffered to a pH of 2.3 and 2.7, respectively. The SHG from these electrodes at the most positive potentials was approximately 500 times larger than that observed from the same TiO$_2$ surfaces in air and did not vary with supporting electrolyte or phosphate buffer concentrations. However, as seen in Figure 1, the SHG from the more highly doped sample was approximately 5 times less than that from the sample with the lower doping density.

The SHG from the interface varied linearly with applied potential in both cases and reached a minimum at a potential of

−0.60 and −0.46 V, respectively. These values agree approximately with the expected values of the flatband potential (V_{fb}) for TiO$_2$ electrodes at this pH as determined from both electrochemical and optical measurements.[4] Only a small amount of surface SHG was observed negative of the flatband potential (the "accumulation region") where there is a surplus of electrons at the semiconductor interface. The fact that a large SHG signal is only observed at potentials positive of V_{fb}, where there is a depletion of free electrons at the interface (the "depletion region"), implies that the electrons are not the source of the surface second harmonic response. Instead, the electrostatic fields associated with the space charge layer created at the interface in the depletion region must be polarizing the TiO$_2$ lattice and inducing a large SHG response. This phenomenon is known as electric field-induced second harmonic generation (EFISH).

The lack of EFISH in the accumulation region can be attributed to the combination of two effects. First, at these potentials substantial cathodic currents are observed. These currents reduce the surface concentration of free electrons, thereby diminishing the interfacial electric fields. Second, in the accumulation region the majority carriers reside primarily at the surface (causing the semiconductor to become metallic[4]), and subsequently the potential drop in this region occurs over only a few angstroms.[25] Therefore, the interfacial electric fields do not polarize a substantial amount of the TiO$_2$ lattice, and a large EFISH response is not observed.

SHG in the presence of externally applied electrostatic fields has been observed previously in bulk centrosymmetric media[26] and at interfaces.[27-30] The SHG intensity $I(2\omega)$ depends upon the square of the second-order surface nonlinear polarization $\mathbf{P}^{(2)}(2\omega)$:[27,29]

$$\mathbf{P}^{(2)}(2\omega) = [\chi^{(2)} + \chi^{(3)}:\mathbf{E}_{dc}]:\mathbf{E}(\omega):\mathbf{E}(\omega) \qquad (1)$$

where $\chi^{(2)}$ is the second-order nonlinear susceptibility of the surface in the absence of electrostatic fields and $\chi^{(3)}$ is the third-order nonlinear susceptibility that relates the three input electric fields, two at frequency ω and one at zero (dc) frequency, to the surface nonlinear polarization at frequency 2ω. The product of $\chi^{(3)}$ and $\mathbf{E}_{dc}$ can be thought of as creating an effective $\chi^{(2)}$ for centrosymmetric media.[31] In cases where the dc electric fields exist over an extended distance, eq 1 must be integrated over the entire interfacial region.[27] For the TiO$_2$–electrolyte interface, our SHG measurements indicate that in the depletion region the $\chi^{(3)}:\mathbf{E}_{dc}$ term is much larger than the $\chi^{(2)}$ from the surface. In this case, eq 1 predicts that the intensity of the SHG from an interface should vary as the square of the dc electric fields.

The magnitude of $\mathbf{E}_{dc}$ at a TiO$_2$–electrolyte interface in the depletion region will vary with the amount of excess charge density at the TiO$_2$ surface. Using the Mott–Schottky approximation,[25,32,33] the total amount of charge density q_{sc} in the space charge layer will be related to the band bending at the interface ΔV_{sc} and the doping density N_d by eq 2:

$$q_{sc} = (2\epsilon\epsilon_0 eN_d)^{1/2}\Delta V_{sc}^{1/2} \qquad (2)$$

where ΔV_{sc} is the difference between the applied potential and the flatband potential, ϵ is the dielectric constant of TiO$_2$ (perpendicular to the c axis), and all other symbols have their usual meaning. At the flatband potential there is no band bending at the interface (ΔV_{sc} = 0), no space charge layer (q_{sc} ≈ 0), no electrostatic fields ($\mathbf{E}_{dc}$ = 0), and thus from eq 1 a minimum value in SHG from the interface. Therefore, the potential at which the SHG reaches a minimum can be used as a measure of the flatband potential for the TiO$_2$ electrode. Note that (i) this observation does not require either an elaborate analysis of the experimental data as required in ac impedance measurements or the creation of charge carriers during the course of the experiment as required in photocurrent measurements; (ii) this observation is a local measurement of a flatband potential (the
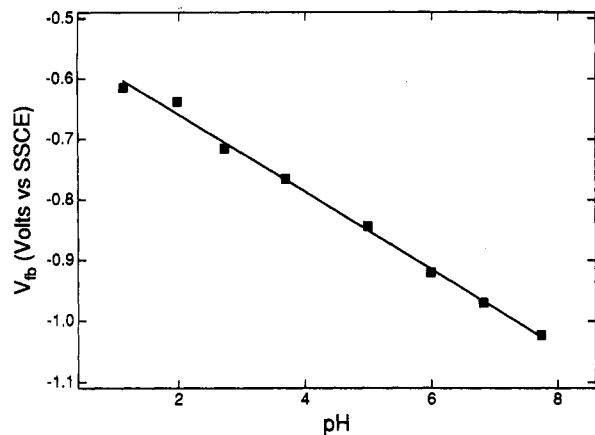
Figure 2. pH dependence of the flatband potential for a TiO_2 electrode as determined from the minimum in the potential-dependent SHG signal. $N_d = 10^{16}$ cm^{-3}. The flatband potential for these electrodes is known to vary by approximately 60 mV/pH unit due to the deprotonation of the Ti–OH surface sites. This graph indicates a dependence of 64 ± 5 mV/pH unit. In these experiments, the electrolyte solution is 0.3 M $NaClO_4$ + 10 mM Na_2HPO_4, with the pH being adjusted by the addition of $HClO_4$. The incident fundamental and collected SHG light were both p-polarized.

spot size of the SHG experiment is typically less than 1 mm^2); and (iii) this direct measurement of the interfacial electric fields has a virtually instantaneous response time and can thus be used in pump–probe measurements of the interfacial charge density.[34] The monitoring of SHG in the depletion region to measure flatband potentials for TiO_2 electrodes can be compared to the recent measurements of Grätzel and co-workers.[8-11] In their experiments using high surface area TiO_2 colloid films in both aqueous and nonaqueous environments, the onset of optical absorption from surface electrons in the accumulation region was used to determine V_{fb}. In contrast to these absorption measurements, the SHG experiments reported here have a much higher surface sensitivity and can be used to determine V_{fb} on single-crystal TiO_2 surfaces.

To verify that the minimum in the SHG from a TiO_2–electrolyte interface can be used as a measure of the flatband potential, this intercept was obtained as a function of pH. Figure 2 plots the pH dependence of the flatband potential for a TiO_2 electrode as determined from the minimum in the surface SHG response. A change in V_{fb} of approximately 60 mV/pH unit is observed, as is expected due to the protonation of the Ti–O$^-$ sites.[35] This correct pH dependence of the optically determined V_{fb} further supports the EFISH mechanism for SHG from this semiconductor–electrolyte interface.

In addition to predicting that the minimum in the SHG signal will correspond to the flatband potential of the electrode, the Mott–Schottky approximation as implemented in eq 2 can also be used to predict the linear potential dependence of the SHG signal in the depletion region. The EFISH mechanism requires that the intensity of the SHG be proportional to the square of the electrostatic fields (E_{dc}) present in the space charge layer. However, not all of the space charge layer will contribute to the surface SHG. The second harmonic light at 302 nm generated in this experiment is well above the band gap (3.02 eV or 410 nm) for a TiO_2 electrode at all potentials and will be strongly absorbed by the semiconductor. At 302 nm the escape depth for light from the surface is approximately 20 nm,[4] and thus only the small portion of the space charge layer near the surface will contribute to the SHG intensity. (For example, at $\Delta V_{sc} = 1$ V, the space charge layer is approximately 1.4 μm for an N_d of 10^{16} cm^{-3}.) In this surface region, the dc electric fields responsible for the SHG will be directly proportional to the total charge density in the space charge layer (q_{sc}) by Gauss' law.[32,33] Equation 2 predicts that the SHG intensity $I(2\omega)$ should then depend linearly on
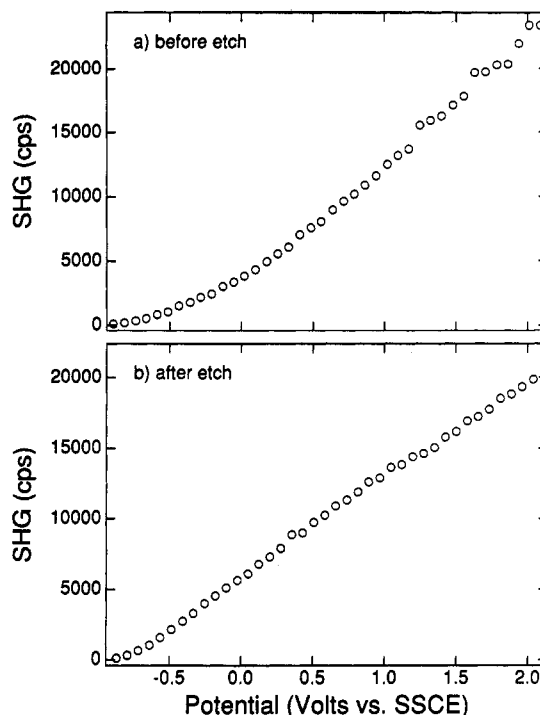

Figure 3. Effect of surface etching on the potential dependence of the SHG signal from n-TiO_2 electrodes ($N_d = 10^{16}$ cm^{-3}): (a) the potential-dependent SHG of a TiO_2 crystal immediately following the doping procedure, and (b) the same crystal following an HCl and an H_2SO_4 etch. In these experiments, the electrolyte solution is 0.3 M $NaClO_4$ + 10 mM Na_2HPO_4, with a pH of 7.1. The incident fundamental and collected SHG light were both p-polarized.

ΔV_{sc}:

$$I(2\omega) \propto |E_{dc}|^2_{x=0} \propto q_{sc}^2 \propto \Delta V_{sc} \qquad (3)$$

Equations 2 and 3 also appear to predict that $I(2\omega)$ should increase linearly with doping density N_d. However, this relationship is complicated by the fact that the penetration depths at both 604 and 302 nm will decrease with higher N_d levels. Experimentally, we observed a slight decrease (factor of 5) in $I(2\omega)$ as N_d was increased from 10^{16} to 10^{18} cm^{-3}. On the other hand, an electrode with an N_d of 10^{13} cm^{-3} exhibited a significantly smaller amount of SHG, presumably due to the lower electrostatic fields in the space charge layer. A more complete calculation of the dependence of the SHG signal on doping density requires the inclusion of all of the various optical and electrical parameters.

Although the SHG data from both of the electrodes shown in Figure 1 exhibited a linear relationship with applied potential in the depletion region, the exact functional form of the potential dependence of the SHG from the TiO_2 electrode was sensitive to the electrode surface preparation. Figure 3 plots the potential dependence of the p-polarized input/p-polarized output SHG from a TiO_2 electrode before and after lightly etching the surface. As seen in the figure, prior to the etching of the electrode the potential dependence cannot be fit by a single straight line. In contrast, the potential dependence of the etched electrode is linear and resembles the data in Figure 1. These differences with surface preparation can be attributed to the changes in electronic structure of the interface that arise from inhomogeneities on the TiO_2 surface. Similar effects upon etching have been observed in ac impedance measurements.[36] In all cases, however, the minimum in the SHG signal as a function of applied potential did not change and agreed with the expected value of the flatband potential.

Conclusions

In summary, optical second harmonic generation is demonstrated as a new *in situ* technique that directly probes the flatband

potential and electrostatic fields at TiO_2 electrodes. Through an EFISH mechanism, the surface SHG is proportional to the square of the electric fields present at the electrode surface. Thus, SHG provides an accurate measurement of the band bending of the TiO_2 semiconductor interface that is spatially and temporally resolved and is independent of any circuit model. In the future the instantaneous time response of the SHG measurements will be used to examine the time dependence of charge generation and accumulation at the TiO_2–electrolyte interface.

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