

## Substrate Fermi level effects in photocatalysis on oxides: Properties of ultrathin TiO<sub>2</sub>/Si films

D. Kazazis,<sup>1</sup> S. Guha,<sup>2,a)</sup> N. A. Bojarczuk,<sup>2</sup> A. Zaslavsky,<sup>1</sup> and H.-C. Kim<sup>3</sup>

<sup>1</sup>Division of Engineering, Brown University, Providence, Rhode Island 02912, USA

<sup>2</sup>IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, USA

<sup>3</sup>IBM Almaden Research Center, San Jose, California 95120, USA

(Received 25 November 2008; accepted 15 July 2009; published online 11 August 2009)

Photocatalysis has widespread applications from solar cells to photolithography. We studied the photocatalytic properties of TiO<sub>2</sub> films of thicknesses down to 2 nm, grown on *n*-type and *p*-type silicon wafers, using the oxidation of isopropanol as a model system. Direct *in vacuo* mass spectrometry measurements were performed under irradiation above the TiO<sub>2</sub> bandgap. We present a model consistent with our experimental results, which indicate that only near-surface electron-hole pair generation is relevant and that the reaction rate can be controlled by varying the substrate Fermi level in going from *n*-type to *p*-type silicon, by approximately a factor of 2. © 2009 American Institute of Physics. [DOI: 10.1063/1.3196314]

There has been extensive research in the past 35 years on the photocatalytic oxidation of compounds on ionic oxide surfaces, particularly titanium dioxide, following the work by Fujishima and Honda<sup>1</sup> in 1972, on the photocatalytic cleavage of water. Photocatalysis has widespread potential applications<sup>2,3</sup> from the cleavage of water under solar irradiation to oxidative mineralization for pollutant remediation. More recently, there has also been interest in photocatalytic lithography<sup>4,5</sup> and in the use of photocatalytic materials as capping layers in the fabrication of extreme ultraviolet lithography self-cleaning optics.<sup>6</sup>

In this letter we examine the photocatalytic properties of ultrathin films of TiO<sub>2</sub> grown on Si substrates. Using direct *in vacuo* mass spectrometry measurements of the photocatalysis of isopropyl alcohol to acetone as a model system, we find that the photocatalytic effect is observed in TiO<sub>2</sub> films with thicknesses down to 2 nm. In addition, the substrate Fermi level has an effect on the photocatalytic efficiency: lowering the Fermi level using a *p*-type Si substrate (as opposed to an *n*-type substrate) increases the photocatalytic effect by approximately a factor of 2. Our results indicate that only near-surface electron-hole pair generation is relevant for the photocatalysis. We further show evidence that the photocatalytic reaction rate on the TiO<sub>2</sub> surface is limited by the annihilation rate of surface or subsurface oxygen vacancies.

Titanium dioxide films with thicknesses from 2 to 50 nm were deposited at 300 °C on Si (111) wafers, in an ultrahigh-vacuum (UHV) molecular beam epitaxy system. The wafers were treated with an HF dip prior to loading into the vacuum chamber to create a native-oxide-free silicon surface. A transmission electron microscopy (TEM) image of a typical sample is shown in the lower inset of Fig. 1. The TiO<sub>2</sub> films are polycrystalline with an ultrathin (<1.8 nm) amorphous interfacial SiO<sub>x</sub>/TiO<sub>x</sub> layer created between the TiO<sub>2</sub> film and the Si substrate during the TiO<sub>2</sub> film formation. This amorphous layer, due to its much larger bandgap, is not expected to participate in the photocatalytic process, as it would require light of a very short wavelength (<150 nm). The few structural defects that are found in the oxide are also not expected to influence the results in a significant manner,

as the measurements are performed on whole wafers and nondefective sites will dominate. The photocatalytic experiments were carried out in vacuum, using the setup shown in the top inset of Fig. 1. The Si/TiO<sub>2</sub> substrates faced a nozzle, which is used to introduce isopropyl alcohol (IPA) through a UHV leak valve, as well as a guide tube leading onto a mass spectrometer. The incident light came from a strobe system with a Xe lamp pulsed at 55 Hz. The mass spectrometer analog signal was fed into a lock-in amplifier tuned to the strobe frequency in order to enhance the sensitivity of the detection. All measurements were carried out at room temperature, and the typical pressures during the experiment were in the 10<sup>-7</sup> Torr range. The IPA molecules arriving on the TiO<sub>2</sub> surface possess a certain residence lifetime, after which they desorb. Under UV illumination above the TiO<sub>2</sub> bandgap, some of the IPA molecules resident on the TiO<sub>2</sub> surface will photocatalytically dissociate, with subsequent desorption of the dissociation products (acetone, in this case). We tracked the oxidation of IPA to acetone by measuring atomic mass unit (amu) 43 (CH<sub>3</sub>CO-) through the mass spectrometer in order to monitor the photocatalytic activity.

A typical acetone signal response to the UV irradiation of a fresh TiO<sub>2</sub> surface is shown in Fig. 1. We observe an

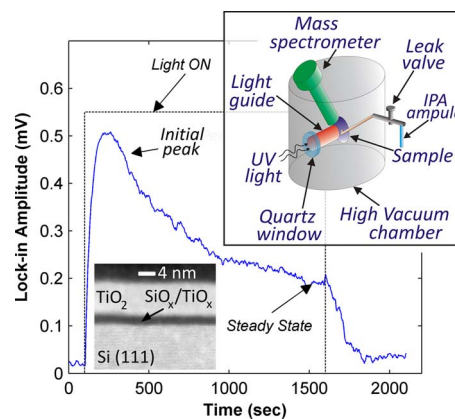


FIG. 1. (Color online) Typical acetone signal response upon UV irradiation. The initial peak in the signal is followed by a transient decay. A schematic of the measurement setup is shown in the top inset, while a TEM image of a typical sample is shown in the bottom inset.

<sup>a)</sup>Electronic mail: guha@us.ibm.com.

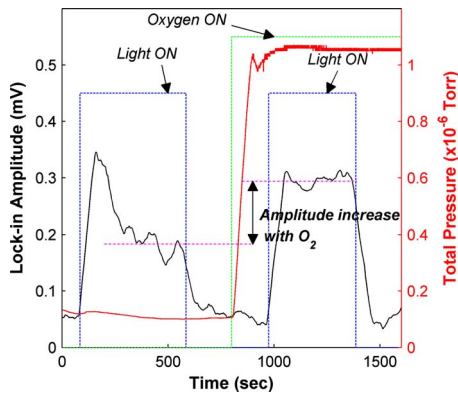


FIG. 2. (Color online) Smoothed lock-in amplifier response for acetone, showing the mean amplitude increase in the signal in increased presence of  $O_2$  in the chamber.

initial peak in response to the light irradiation, followed by a transient decay to a steady state. This is related to an accumulation of adsorbed oxygen on the surface of the  $TiO_2$  as will be discussed later. Figure 2 shows the results of experiments, in which the mass spectrometer response to 43 amu was tracked under illumination and IPA injection, as a function of oxygen presence in the vacuum system. In the absence of oxygen, as the UV irradiation is turned on, an initial peak followed by a transient decay is observed in the acetone signal, followed by a return to the baseline signal upon turning off the light source. When oxygen is now deliberately bled into the system and the UV irradiation turned on, the acetone signal rises to a higher level compared to the case without oxygen. This clearly indicates an oxygen-mediated enhancement in the conversion of IPA to acetone in the presence of oxygen. The role of oxygen also explains the initial transient peak in the response upon irradiation when the sample has been left idle for long periods of time. The initial peak is due to the buildup of adsorbed oxygen on the sample surface resulting in a higher rate for the reaction. During irradiation, the adsorbed concentration of oxygen on the surface drops, reaching a steady state that depends upon the arrival rate of oxygen from the ambient. Subsequent figures will show the steady-state signal after the initial surface oxygen-induced transient peak has decayed, as in Fig. 1.

In Fig. 3 we show the response of the acetone signal as a function of the UV light source irradiation, for a set of samples with  $TiO_2$  thicknesses of 50, 5, and 2 nm on  $n$ -Si, as

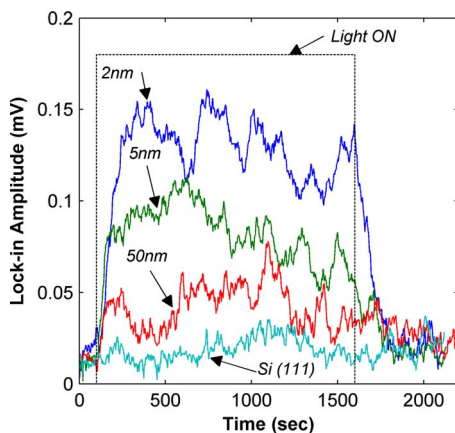


FIG. 3. (Color online) Steady-state response of the acetone signal upon UV light irradiation for ultrathin  $TiO_2$  samples, as well as a bare  $n$ -type Si (111) wafer for control. The dashed line shows when the light is on.

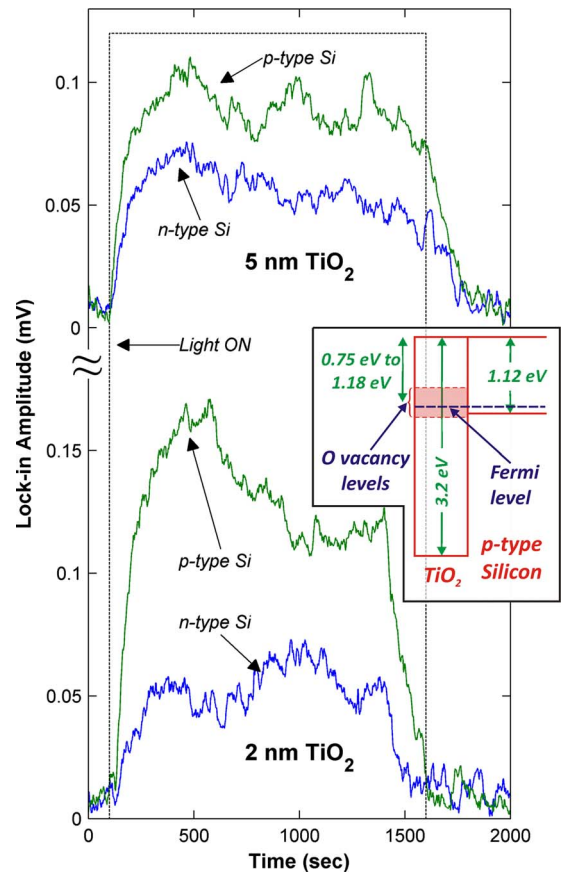


FIG. 4. (Color online) Comparison of the effect of  $n$ -type and  $p$ -type substrate doping on the photocatalytic response for 2 and 5 nm thick  $TiO_2$  films. A simplified band diagram of a  $TiO_2/p$ -Si system is shown in the inset.

well as a bare  $n$ -Si wafer for control. All three samples with the  $TiO_2$  layer exhibit a clear photocatalytic response, which is absent in the bare silicon control wafer case. The response occurs only for above bandgap illumination in  $TiO_2$ , as filtering the UV light to  $\lambda < 436$  nm (below  $TiO_2$   $E_G \approx 3.2$  eV) led to no response. Importantly, the photocatalytic responses of the films are within a factor of three for films with thicknesses from 50–2 nm (a factor of 25), implying that the conversion is controlled by surface or near-surface processes rather than the bulk, since in the latter case one would have expected much higher conversion for the thicker films.

There is a clear and repeatable dependence of the photocatalytic rate upon the Fermi level of the silicon substrate, which can be changed by altering the doping in the silicon. Figure 4 shows the photocatalytic response tracked by monitoring amu 43 for 2 and 5 nm thick  $TiO_2$  films grown on  $n$ -type (phosphorus doped, 0.0016–0.0034  $\Omega$  cm) and  $p$ -type (boron doped, 10–20  $\Omega$  cm) Si substrates, under otherwise identical conditions. It is clear from Fig. 4 that there is a significant enhancement in the photocatalytic rate for the  $p$ -type substrate for both thicknesses. We tie together the above observations to put together a simple model based on three observations. First, as is known<sup>7,8</sup> and further confirmed by us, increase in the ambient oxygen content promotes the photocatalytic reaction. Second, it appears that the presence of near-surface oxygen vacancies is necessary for the photocatalytic reaction.<sup>8,9</sup> Finally, we note that the oxygen vacancy concentrations in thin films of ionic oxides can be increased when the oxide is in contact with a high work

function electrode whose Fermi level lies below the energy level of the neutral oxygen vacancy in the oxide.<sup>10–12</sup> In our case, the Si substrate acts as the electrode, with the Fermi level dependent on the substrate doping, as shown in the inset of Fig. 4. Electron transfer from the neutral oxygen vacancy level into the metal electrode enables charged oxygen vacancy formation by the following reaction expressed using Kröger-Vink notation as:



with the free oxygen either absorbed into the electrode, or released into the ambient—the process is discussed in detail by Guha and Narayanan<sup>10</sup> and Shiraishi *et al.*<sup>12</sup> If the metal electrode Fermi level lies below the neutral oxygen vacancy level, then the process for charged oxygen vacancy creation is favored—it may be interpreted as being due to the energy gain in the transfer of electrons from the neutral oxygen level to the metal. The superscripts “ $x$ ” and “ $••$ ” refer to neutral and doubly positively charged species, respectively.  $\text{O}_0$  is an oxygen atom on an oxygen site and  $V_0$  is an oxygen vacancy. We now consider this possibility for  $\text{TiO}_2$ , whose conduction band is nearly aligned to that of Si.<sup>13</sup> The oxygen vacancy level in  $\text{TiO}_2$  is found to be between 0.75–1.18 eV below the conduction band edge.<sup>9,14</sup> Consider now the case of  $\text{TiO}_2$  layers on  $n$ - and  $p$ -types silicon. For the case of highly doped  $n$ -type Si, the Fermi level lies close to the conduction band of the  $\text{TiO}_2$  layer and is therefore expected to be above the vacancy level in the oxide. However for  $p$ -type Si substrates, the Fermi level could lie below the oxygen vacancy energy level in the  $\text{TiO}_2$  layer, (see inset of Fig. 4) favoring the generation of oxygen vacancies. Thus, very thin  $\text{TiO}_2$  layers on  $p$ -type substrates are expected to have higher charged oxygen vacancy concentrations compared to  $n$ -type ones. In order to directly measure these concentrations, x-ray photoelectron spectroscopy (XPS) was attempted, but the results were inconclusive as the oxygen vacancy concentrations are insufficient for the XPS Ti  $2p_{3/2}$  peak to show vacancy-related features.<sup>15,16</sup>

Using the same notation, we can now write the reaction for generation of oxygen by a photogenerated hole in the  $\text{TiO}_2$  as:



so that holes react with oxygen in the oxygen sublattice, to create a positively charged oxygen vacancy and nascent oxygen, which is available for the oxidation of the IPA. The rate for reaction (2),  $R_2$ , will have a dependence  $R_2 = k_2G$ , where  $G$  is the electron-hole generation rate under irradiation. The oxygen vacancy is in turn replenished by oxygen that has been adsorbed on the  $\text{TiO}_2$  surface from the ambient as:



with the electrons available from the  $n$ -type  $\text{TiO}_2$  layer. Photogenerated holes thus result in the generation of nascent oxygen and the creation of oxygen vacancies on the surface; the oxygen vacancies are then replenished by adsorbed oxygen from the ambient for the process to continue.

The rate for reaction (4),  $R_4$ , will have a dependence upon the concentration of the adsorbed oxygen molecules and the probability that there are two vacancies within a

characteristic capture distance for reaction (4) to proceed. Since  $\text{TiO}_2$  is  $n$ -type, we assume that the electron concentration is high enough that it does not limit the reaction. Keeping in mind that the concentration of adsorbed oxygen molecules is proportional to the oxygen partial pressure,  $R_4$  is then given by:

$$R_4 = k p_{\text{O}_2}^{0.5} [V_0^{**}]. \quad (5)$$

If the electron-hole pair generation rate is higher than the rate at which the created oxygen vacancies are annihilated, i.e.,  $R_2 > R_4$ , then the overall rate for the photocatalysis will be limited by  $R_4$ . In that case the photocatalytic rate will depend both upon the oxygen vacancy concentration as well as the oxygen content in the ambient. All of our observations are consistent with this model. The photocatalytic rates are enhanced when oxygen is introduced into the system, as shown in the data of Fig. 2. The enhancement in the photocatalytic rates observed for the  $p$ -type Si substrates (compared to  $n$ -type Si) is also consistent with the higher vacancy concentrations expected in the  $\text{TiO}_2$  due to the lowering of the Fermi level as discussed earlier.

In conclusion, we have examined the photocatalytic activity of  $\text{TiO}_2$  thin films on silicon using *in situ* mass spectrometry and the IPA to acetone conversion as a test reaction. Correlating the experimental data, we have developed a model that points out the relevance of the oxygen vacancy concentration in the near-surface region of the  $\text{TiO}_2$  and shown that when the electron hole pair generation rate is high enough, the reaction is controlled by the rate at which surface oxygen vacancies are annihilated. Finally, we have shown that by using semiconductor- $\text{TiO}_2$  structures, one can use the Fermi level of the semiconductor to control the photocatalytic reaction.

The work at Brown University has been supported by the NSF (Award No. ECCS-0701635). The authors would like to thank Dr. T. Topuria, Dr. P. M. Rice, and L. Krupp from IBM Almaden Research Center for their help in the TEM characterization of the material.

<sup>1</sup>A. Fujishima and K. Honda, *Nature (London)* **238**, 37 (1972).

<sup>2</sup>M. Gratzel, *Nature (London)* **414**, 338 (2001).

<sup>3</sup>K. Hashimoto, H. Irie, and A. Fujishima, *Jpn. J. Appl. Phys., Part 1* **44**, 8269 (2005).

<sup>4</sup>L. P. Lee and M. M. Sung, *J. Am. Chem. Soc.* **126**, 28 (2004).

<sup>5</sup>W. Kubo, T. Tatsuma, A. Fujishima, and H. Kobayashi, *J. Phys. Chem. B* **108**, 3005 (2004).

<sup>6</sup>S. Bajt, N. V. Edwards, and T. E. Madey, *Surf. Sci. Rep.* **63**, 73 (2008).

<sup>7</sup>A. Furube, T. Asahi, H. Masuhara, H. Yamashita, and M. Anpo, *J. Phys. Chem. B* **103**, 3120 (1999).

<sup>8</sup>M. Formenti and S. J. Teichner, *Catalysis* **2**, 87 (1978).

<sup>9</sup>I. Nakamura, N. Negishi, S. Kutsuma, T. Ihara, S. Sugihara, and K. Takeuchi, *J. Mol. Catal. A: Chem.* **161**, 205 (2000).

<sup>10</sup>S. Guha and V. Narayanan, *Phys. Rev. Lett.* **98**, 196101 (2007).

<sup>11</sup>E. Cartier, F. R. McFeely, V. Narayanan, P. Jamison, B. P. Linder, M. Copel, V. K. Paruchuri, V. S. Basker, R. Haight, D. Lim, R. Carruthers, T. Shaw, M. Steen, J. Sleight, J. Rubino, H. Deligianni, S. Guha, R. Jammy, and G. Shahidi, Dig. Tech. Pap. - Symp. VLSI Technol. **2005**, 230.

<sup>12</sup>K. Shiraishi, K. Yamada, K. Torii, Y. Akasaka, K. Nakajima, M. Konno, T. Chikyow, H. Kitajima, and T. Arikado, *Jpn. J. Appl. Phys., Part 2* **43**, L1413 (2004).

<sup>13</sup>J. Robertson, *J. Vac. Sci. Technol. B* **18**, 1785 (2000).

<sup>14</sup>D. C. Cronemeyer, *Phys. Rev.* **113**, 1222 (1959).

<sup>15</sup>U. Diebold, *Surf. Sci. Rep.* **48**, 53 (2003).

<sup>16</sup>Y. He, O. Dulub, H. Cheng, A. Selloni, and U. Diebold, *Phys. Rev. Lett.* **102**, 106105 (2009).