Application of photoacoustic technique for Characterization of thermal diffusivities of nanostructured TiO₂ films

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1. Introduction
Nanostructured TiO₂ films have attracted much interest for the applications of photocatalyst and dye sensitized solar cells (DSSCs). In these applications, it is important to study electronic properties of nanostructured TiO₂ films. In the field of DSSCs, it has been reported that the electronic properties of the nanostructured TiO₂ films depend greatly on the preparation condition.¹ However, there was few report on the thermal property of nanostructured TiO₂ films. In this study, we characterize the thermal diffusivity of nanostructured TiO₂ films using photoacoustic (PA) technique. PA technique is a photothermal methods and has advantages as follows:²

1. It is available for light absorption measurement of opaque or strong scattering sample.
2. It is a nondestructive and noncontact method.
3. It is useful for the simultaneous characterization of thermal property, optical property and carrier relaxation processes.
4. It is possible for depth profile analysis of a sample by changing incident light modulation frequency.

In this study, we have applied the PA method under a transmission detection configuration (TDC) to study the thermal diffusivity of two kinds of nanostructured TiO₂ films on Ti substrates.³ In the TDC, the light is incident on the TiO₂ surface and the PA signal is detected from the rear surface of the Ti substrate.

2. Experiments
2.1 Sample preparations
TiO₂ films were formed on Ti sheet substrate (thickness: 0.2 mm) by the following two kinds of methods, (1) the use of TiO₂ nanoparticles and (2) hydrolysis of TiCl₄ solutions ⁴:

1. TiO₂ paste was prepared by mixing nanocrystalline TiO₂ powders (with average diameter of 15 nm, anatase structure) in pure water (30 wt%) with acetylacetone (10 wt%) and polyethylene glycol (PEG: 40 wt% relative to TiO₂) as binder addition for 30 minutes. Then, TiO₂ paste was coated on the Ti sheet substrate. Finally, TiO₂ film (termed as TiO₂(TiCl₄)) was annealed at 450°C for 30 min in air.
2. First, two drops of TiCl₄ (in methanol) solution was dropped onto the surface of Ti sheet substrate. After hydrolysis for 30 min, the Ti sheet was annealed at 125°C for 5 min, and then at 450°C for 25 min. The TiO₂ film (termed as TiO₂(TiCl₄)) was formed on the Ti substrate by repeating the above process several times.

For both kinds of TiO₂ films, the nanostructures in the films have been confirmed and the average diameters of TiO₂ nanoparticles are found to be about 15-20 nm from scanning electron microscope (SEM) images and X-ray diffraction (XRD) measurements. The thicknesses of both kinds of samples are fixed to be 5 and 12 μm.

2.2 PA measurements
PA measurements are carried out by using a gas-microphone PA technique.⁵ A 300 W xenon arc lamp is used as the light source. A monochromatic light is obtained through a monochrometer and its intensity is modulated using a mechanical chopper. The modulated light is irradiated on the sample placed inside the PA cell. The light absorbed by the sample is converted into heat by nonradiative relaxation processes, which result in a pressure fluctuation of the air inside the cell. The pressure fluctuation oscillating is detected as the PA signal by a microphone enclosed in the PA cell and amplified by a preamplifier and a two-phase lock-in amplifier.

Fig. 1 shows the schematic diagram of the PA measurement under TDC. Under the TDC, the PA signals are measured from the rear surface opposite to the irradiated surface. The PA signals are due to both thermal diffusion and photo-excited electron-hole pair (excess-carrier) diffusion processes. These two processes can be selectively measured by changing the modulation frequency of the excited light. PA detection under TDC has proved to be useful in the study of carrier transport and thermal properties of semiconductors.³ In this
Results and Discussion

Fig. 1 Schematic diagram of the PA measurement under a transmission detection configuration (TDC).

experiment, the excitation wavelength was fixed at 340 nm and the modulation frequency was changed between 10 Hz and 400 Hz.

3. Results and Discussion

Fig. 2 shows modulation frequency dependences of the PA signal intensities for both kinds of TiO$_2$ films on Ti substrates with different thicknesses under TDC ((a) TiO$_2$(15nm) and (b) TiO$_2$(TiCl$_4$)), respectively. The PA signal intensity decreases for each sample and shows a minimum at a particular frequency ($f_{\text{min}}$) with increasing modulation frequency. The $f_{\text{min}}$ moves to the lower frequency region as the TiO$_2$ thickness increases. It is known that, for the frequency region lower than $f_{\text{min}}$, the samples are thermally thin and the “thermal wave” components caused by the heat sources generated at the irradiated surface are dominant. For frequencies higher than $f_{\text{min}}$, the samples are thermally thick and the carrier transport contribution to the PA signals, i.e., the heat source generated at the rear surface by nonradiative recombination of the carriers, is predominant.\textsuperscript{3,5} We assumed that the two-layered TiO$_2$/Ti samples are effectively homogenous samples. Then, the effective thermal diffusivities $\alpha$ for the two-layered samples can be estimated from $f_{\text{min}}$, using eq. (1),

$$\sqrt{\alpha / \sigma_{\text{min}}} \approx L/5 \quad (1),$$

in which $\alpha$ is the effective thermal diffusivity, and $L$ is the sample thickness. Table 1 shows the values of $f_{\text{min}}$ and effective thermal diffusivity for both kinds of TiO$_2$ films. From the results, we found that the effective thermal diffusivity of nanostructured TiO$_2$ films are about two orders smaller than that of TiO$_2$ crystal (TiO$_2$ crystal: 0.15 cm$^2$/s).\textsuperscript{6} The effective thermal diffusivity $\alpha$ of TiO$_2$(15nm) is smaller than that of TiO$_2$(TiCl$_4$). It may be due to larger thermal resistances at the TiO$_2$-TiO$_2$ interfaces and Ti-TiO$_2$ interfaces in TiO$_2$(15nm) compared to TiO$_2$(TiCl$_4$). In addition, for both kinds of samples, when the thickness increases, $f_{\text{min}}$ becomes smaller, i.e., the effective thermal diffusivity decreases with the increase of the sample thickness. It corresponds to the increase of TiO$_2$-TiO$_2$ interfacial resistances as the TiO$_2$ film thickness increasing.

Table I $f_{\text{min}}$ and effective thermal diffusivity of the nanosturctured TiO$_2$ films on Ti substrates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TiO$_2$ (15nm)</th>
<th>TiO$_2$(TiCl$_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness ($\mu$m)</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>$f_{\text{min}}$ (Hz)</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>Effective</td>
<td></td>
<td></td>
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<tr>
<td>Thermal diffusivity</td>
<td>$2.4 \times 10^{-3}$</td>
<td>$1.4 \times 10^{-3}$</td>
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<td>($\text{cm}^2/\text{s}$)</td>
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References