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Application of photoacoustic technique for Characterization of thermal diffusivities of nanostructured TiO_2 films

光音響法のナノ構造酸化チタン薄膜の熱拡散率評価への応用

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1. Introduction

Nanostructured TiO_2 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 TiO_2 films. In the field of DSSCs, it has been reported that the electronic properties of the nanostructured TiO_2 films depend greatly on the preparation condition.[1] However, there was few report on the thermal property of nanostructured TiO_2 films. In this study, we characterize the thermal diffusivity of nanostructured TiO_2 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 TiO_2 films on Ti substrates.[3] In the TDC, the light is incident on the TiO_2 surface and the PA signal is detected from the rear surface of the Ti substrate.

2. Experiments

2.1 Sample preparations

TiO_2 films were formed on Ti sheet substrate (thickness: 0.2 mm) by the following two kinds of methods, (1) the use of TiO_2 nanoparticles and (2) hydrolysis of $TiCl_4$ solutions[4]:

(1) TiO_2 paste was prepared by mixing nanocrystalline TiO_2 powders (with average diameter of 15nm, anatase structure) in pure water (30 wt%) with acetylacetone (10 wt%) and polyethylene glycol (PEG: 40 wt% relative to TiO_2) as binder addition for 30 minutes. Then, TiO_2 paste was coated on the Ti sheet substrate. Finally, TiO_2 film (termed as (TiO_2(15nm)) was annealed at 450℃ for 30 min in air.
(2) First, two drops of $TiCl_4$ (in methanol) solution was dropped onto the surface of Ti sheet substrate. After hydrolysis for 30 min, the Ti sheet was annealed at 125 ℃ for 5 min, and then at 450 ℃ for 25 min. The TiO_2 film (termed as TiO_2($TiCl_4$)) was formed on the Ti substrate by repeating the above process several times.

For both kinds of TiO_2 films, the nanostructures in the films have been confirmed and the average diameters of TiO_2 nanoparticles are found to be about 15-20 nm from scanning electronic 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.[2] A 300 W xenon arc lamp is used as the light source. A monochromatic light is obtained through a monochromater 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

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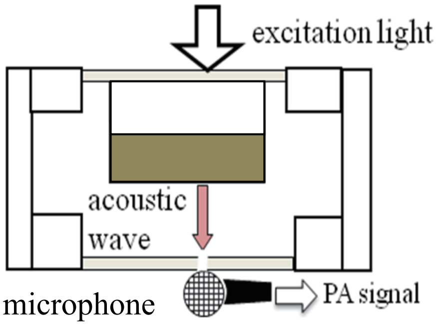


Fig. 1 Schematic diagram of the PA measurement under a transmission detection configuration (TDC).

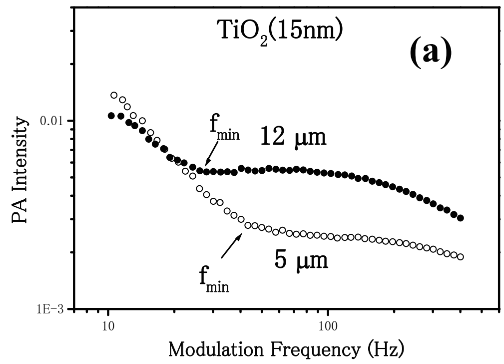
experiment, the excitation. wavelength was fixed at 340 nm and the modulation frequency was changed between 10 Hz and 400 Hz.

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_{min}) with increasing modulation frequency. The f_{min} moves to the lower frequency region as the TiO_2 thickness increases. It is known that, for the frequency region lower than f_{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_{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.[3,5] We assumed that the two-layered TiO_2/Ti samples are effectively homogenous samples. Then, the effective thermal diffusivities α for the two-layered samples can be estimated from f_{min} using eq. (1),

$$\sqrt{\alpha/\pi f_{\min}} \approx L/5 \qquad (1),$$

in which α is the effective thermal diffusivity, and L is the sample thickness. Table I shows the values of f_{min} and effective thermal diffusivity for both kinds of TiO_2 films. From the results, we found that the effective thermal diffusivity of nanostuructured TiO_2 films are about two orders smaller than that of TiO_2 crystal (TiO_2 crystal: 0.15 cm^2/s).[6] The effective thermal diffusivity α 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 increasees, f_{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.



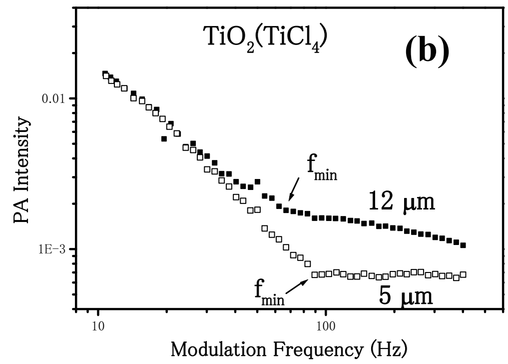


Fig. 2 Modulation frequency dependence of PA signal intensity for (a) TiO_2(15nm) and (b) $TiO_2(TiCl_4)$.

Table I f_{min} and effective thermal diffusivity of the nanostructred TiO_2 films on Ti substrates.

Sample	TiO_2(15nm)		$TiO_2(TiCl_4)$	
Thickness (μ m)	5	12	5	12
f_{min} (Hz)	45	25	95	60
Effective Thermal diffusivity (cm^2/s)	2.4×10^{-3}	1.4×10^{-3}	5.0×10^{-3}	3.4×10^{-3}

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