

Analysis of photocarrier mobility in BaSnO₃ thin films

BaSnO₃ 薄膜の光キャリア移動度評価

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1. Introduction

Photoelectrochemical water splitting (Fig. 1) has received extensive attention as a potential method for hydrogen fuel production from water utilizing solar energy. Although a large number of materials have been studied since the discovery of the water splitting reaction [1], the energy conversion efficiency of this process is still too low for practical use. One factor that limits the solar energy harvesting efficiency is the low diffusion rate of photoexcited carriers in water-stable oxide semiconductors.

Many photocatalytic transition metal oxide materials that have been studied, such as SrTiO₃, contain metal ions with a d⁰ electronic configuration. The conduction band is usually composed of d-orbitals [1] that tend to exhibit relatively low carrier mobilities at room temperature. On the other hand, BaSnO₃ contains Sn⁴⁺ ions with a d¹⁰ electronic configuration and the conduction band is composed of s-orbitals which has large dispersion due to a large overlap between s-orbitals. La-doped BaSnO₃ single crystals show high electron Hall mobility of 320 cm²/sV [2]. Therefore, it can be expected that photoexcited electrons in BaSnO₃ would also show higher diffusivity at room temperature, making BaSnO₃ an interesting starting point for high-efficiency photocatalyst development.

In this work, I focus on the analysis of photocarrier drift mobility in BaSnO₃. The drift mobility of BaSnO₃ thin films were analyzed by time-of flight measurement and photoelectrochemical measurement.

2. Experiment

2.1 BaSnO₃ thin film growth

BaSnO₃ thin films were prepared by pulsed laser deposition with a 248 nm KrF excimer laser as shown Fig. 2. The growth conditions of BaSnO₃ thin films were optimized with the help of x-ray diffraction, atomic force microscopy and x-ray fluorescence composition analysis.

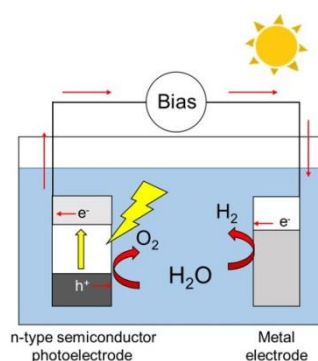


Fig.1 Photoelectrochemical water splitting

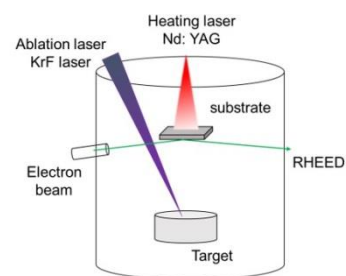


Fig.2 Pulse laser deposition (PLD)

2.2 Time-of-flight measurement

Time-of-flight (TOF) measurement can be used for transport studies of transient charge in insulating samples if the carrier lifetime is sufficiently long [3]. In this study, a time-of-flight measurement system was set up to measure the electron drift mobility in BaSnO₃ films. Fig. 3 shows a schematic illustration of the self-made TOF measurement system. A thin semitransparent electrode was deposited on the sample surface. A Nd:YAG laser at a wavelength 266 nm with a 350 ps pulse width was used to excite photocarriers in the film. The carriers excited near the top surface of the sample drift towards the bottom electrode under an applied bias and the displacement current as a function of time was measured with a 500 MHz storage oscilloscope, detecting voltage pulses across a resistor placed in series with the sample. A 750 nm BaSnO₃ thin film was grown on a 0.5 wt% Nb-doped SrTiO₃ substrate for TOF measurement. The 0.5 wt% Nb-doped SrTiO₃, which has sufficiently low resistivity, was used as a bottom electrode.

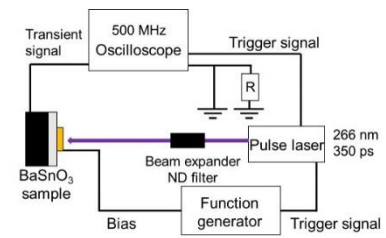


Fig.3 Time of flight measurement system

2.3 Photoelectrochemical measurement

The photocatalytic performance of BaSnO₃ films with various thicknesses (20 - 500 nm) were analyzed under UV irradiation (240-300 nm). BaSnO₃/Sr₂RuO₄/SrTiO₃ heterostructure samples were prepared for this measurement. Sr₂RuO₄ is a metallic oxide material which can be used as a bottom electrode and doesn't affect the photoelectrochemical performance. From a simulation of photoelectrochemical performance in which an equivalent model for analyzing solar cell performance was used [4], the photocarriers lifetime and mobility were estimated.

3. Results and discussion

3.1 Drift mobility of BaSnO₃

Fig. 4 shows the transient signals of BaSnO₃ film measured with the TOF system. The kinks of transient signal in $\log(V)$ vs $\log(t)$ plot correspond to the transit time of photocarriers across the BaSnO₃ film thickness. The position of the kinks depends on the magnitude of the applied bias. From this result, the electron drift mobility of BaSnO₃ can be calculated as $\mu = 6.3 \times 10^{-3} \text{ cm}^2/\text{sV}$. This mobility is much smaller than the reported Hall mobility (70 cm²/sV) of La-doped BaSnO₃ films grown on SrTiO₃ [2]. There are several reasons that may cause this difference such as too strong excitation laser intensity, insufficient BaSnO₃ film thickness compared to the penetration depth of the laser and the space charge effect of trapped carriers. These factors may make the calculation of mobility inaccurate. However, when the laser intensity or the film thickness were changed to exclude these effects, the kink in the time response disappeared, indicating that photocarriers cannot reach the bottom electrode due to heavy trapping and short carrier lifetime.

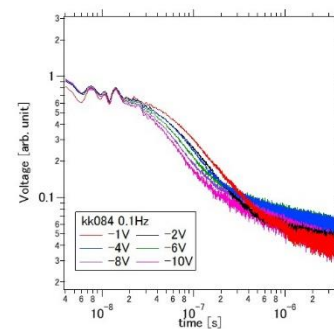


Fig.4 Transient signal of BaSnO₃ thin film measured by TOF system.

3.2 Photoelectrochemical analysis of BaSnO₃

The photoinduced current density of BaSnO₃ films at -0.1V vs a reversible hydrogen electrode as a function of thickness is shown with red dots in Fig. 5. The thickness of the BaSnO₃ thin film clearly affects the photoelectrochemical performance. This thickness dependence can be understood in terms of light absorption and charge transport efficiency. Simulation

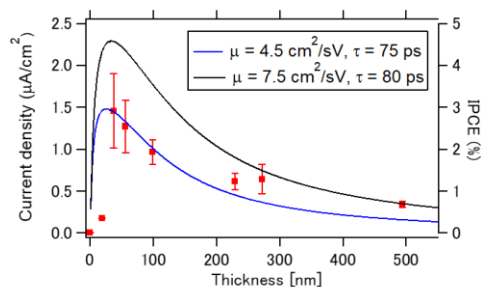


Fig.5 Photocurrent density of BaSnO₃ thin films.

results of the incident photon to current efficiency (IPCE) is plotted with a blue line with $\mu = 4.5 \text{ cm}^2/\text{sV}$ and $\tau = 75 \text{ ps}$. The black line corresponds to simulation parameters $\mu = 7.5 \text{ cm}^2/\text{sV}$ and $\tau = 80 \text{ ps}$. Although the simple model doesn't allow perfect fitting, a carrier lifetime estimate can be found. The simulation doesn't consider possible thickness-dependent crystallinity changes of the films caused by a large lattice mismatch between the film and the substrate. Thinner films have lower crystallinity, resulting in lower performance as shown by the blue line. Crystallinity improves as the BaSnO₃ films become thicker, following the black line. Thus, the electron drift mobility and lifetime of BaSnO₃ were estimated in the range of $\mu = 4.5 - 7.5 \text{ cm}^2/\text{sV}$ and $\tau = 75 - 80 \text{ ps}$.

4. Conclusion

High drift mobility of photocarriers and high efficiency of photoelectrochemical performance cannot be expected even for BaSnO₃, even though the material has a highly dispersive conduction band. The obtained (long range) electron mobility was $6.3 \times 10^{-3} \text{ cm}^2/\text{sV}$ by TOF analysis. The simulated IPCE was a few percent under UV irradiation. These results are most probably due to heavily trapping that limits the photocarrier lifetime to picosecond order. Accurate measurement of the drift mobility by TOF is almost impossible if the lifetime is too short, and the efficiency of photoelectrochemical performance is low because photocarriers cannot migrate to the semiconductor surface. In general, non-doped oxide materials have empty trap states due to intrinsic vacancies or defects. This means that the photocarrier mobility is much lower than the Hall mobility obtained by doping the insulating oxide to a metallic state. In conclusion, high-crystallinity material such as Si, where the photocarrier lifetime is much longer than in oxide materials, should be used for solar energy conversion.

References

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Publication and Presentation list

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