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Photoconductivity of $SrBi_2Ta_2O_9$ Thin Films

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Abstract

Photoconductive properties of $SrBi_2Ta_2O_9$ thin films in the 250–400 nm wavelength range were investigated. The films were deposited on $Pt/SiO_2/Si$ substrates using the Chemical Solution Deposition and were crystallized by conventional thermal annealing at 850°C. One sensitivity maximum was observed in the spectral distribution of the photoconductive signal and was attributed to band-to-band generation in the film. The wavelength corresponding to this maximum was found to be dependent on the applied voltage, on the delay time, defined as the time between the application of light on the film and the reading of the generated photocurrent, and on the wavelengths sweeping direction (up or down). The gap value was estimated to be around 3·94–4 eV. © 1999 Elsevier Science Limited. All rights reserved

Keywords: Bi-layered perovskites, sol–gel processes, optical properties.

1 Introduction

Ferroelectric thin films were subjected to an intensive research in the last decade due to their potential use in memory devices.[1,2] The effort was focused mainly on the preparation method, structural quality and ferroelectric properties of the films. The major problems regarding the ferroelectric memories are the polarization fatigue in case of memory cells based on ferroelectric capacitors[3] and the low retention time in case of memory cells based on ferroelectric field effect transistors.[4] In both cases the read–write procedure used until now was purely electric and is based on ferroelectric polarization reversal. To overcome the above mentioned problems new optical read–write procedures were proposed.[5] Such procedures can be applied only if the ferroelectric films have photoelectric properties. Besides this aspect, the photoelectric properties investigation of ferroelectric thin films can give information about the semiconductor properties like energy gap, energetic trap distribution in the gap and presence of internal electric fields.[6–8] Even the switching behavior can be affected by the presence of the photogenerated carriers.[9] New applications for the ferroelectric films, such as UV detectors, can also be found.[10] Until now only a few studies were devoted to the investigation of photoelectric properties in ferroelectric thin films with perovskite or layered perovskite structure.[11–13] The present study investigates the photoconductive properties in $SrBi_2Ta_2O_9$ (SBT) thin films, which is known as a representative layered-perovskite material widely used in ferroelectric memories' devices.

2 Experimental

SBT thin films were deposited by Chemical Solution Deposition (CSD) method on $Pt/SiO_2/Si$ substrates. The metalorganic solution was prepared using Bi-diethylhexanoate, Sr-diethylhexanoate and Ti-isopropoxide as metal precursors and xylene as solvent. The films were obtained by solution spinning at 2500 rpm for 35 s followed by a pyrolize at 300°C for 5 min. Deposition–pyrolize process was repeated three times to obtain 550 nm thick SBT films. The films were crystallized by conventional thermal annealing in air for 30 min at 850°C. Semi-transparent gold electrodes were evaporated on the free SBT surface defining ferroelectric capacitors with an effective area of 0·63 mm^2. For photoconductive measurements the samples were placed in a electrically shielded black box having a window with 10 mm in diameter. The light source was a xenon lamp model SVX-1000. The light beam was collimated on the entrance slit of a grating monochromator model SPEX 270. The

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generated photocurrent was measured with an electrometer model Keithley 6517. The electrometer has a built-in d.c. voltage source which allows to apply a d.c. voltage on the sample. The polarity of the applied voltage was considered with respect to the illuminated top gold electrode, which is connected to the ground through the electrometer. Photoconductive measurements were performed for different values and polarities of the applied voltage. Two values of the delay time (1 and 30 s) were used and the wavelengths were swept up and down. The delay time is defined as the time between the moment when the light is applied on the surface of the SBT film and the moment when the photocurrent value is read.

Figure 1 presents the normalized spectral distribution of photoconductivity in case of a positive voltage of 0.01 V applied on the sample and for short delay times (1 s). It can be readily seen that the position of the maximum in the spectral distribution is dependent on the wavelength sweeping direction. This maximum is located at 324 nm when the wavelengths are swept up and at 304 nm when they are swept down. A small second peak occurs at short wavelengths (256 nm) but only when the wavelengths are swept up. The same 'hysteretic' behavior at short delay times was observed for negative polarity on the bottom electrode. The corresponding peak wavelengths are somewhat smaller than for positive polarities. A second maximum occurs around 260 nm, also only when the wavelengths are swept up.

As it can be seen from Fig. 2 the 'hysteretic' behavior in the spectral distribution disappears if long delay times (30 s) are used. In this case the maximum in the spectral distribution occurs at the same wavelength no matter the wavelengths are swept up or down. The wavelength corresponding to the maximum sensitivity is about 315 nm for positive polarity and about 310 nm for negative polarity.

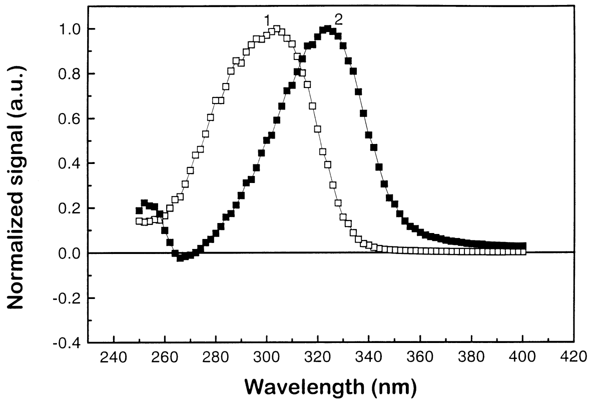

Fig. 1. Normalized spectral distribution of photoconductivity in SBT thin films in case of a 0·01 V positive voltage applied on the bottom electrode and for a delay time of 1 s: 1, wavelength swept down; 2, wavelength swept up.

Identical behavior can be observed for other values of the applied voltage (0·1 and 1 V). However it was observed that increasing the applied voltage the peak wavelength is moving towards longer wavelengths (312 nm for 0·01 V compared with 320 nm for 1 V) in case of negative polarities and towards shorter wavelengths (320 nm for 0·01 V compared to 312 nm for 1 V) in case of positive polarities. This fact can be seen from Figs 3 and 4 that present the wavelength dependencies of the photocurrent (non-normalized curves) for different values and polarities of the applied voltage. The same delay time (30 s) and the same sweeping direction (down) were used. It can be also seen that the polarity of the photogenerated current changes with increasing the applied voltage. At small bias the photocurrent has an opposite polarity compared with the applied voltage.

3 Discussions

There are several aspects which have to be considered when we start to judge the experimental results. First, depending on the polarity of the applied voltage, the photogenerated electrons or holes are extracted from the sample.[14] Second, the light penetration depth, defined as the reverse of the absorption coefficient α, is dependent on the incident light wavelength. For short wavelengths compared with the peak wavelength in the spectral distribution, the value of α can reach values as high as $10^6\,\mathrm{cm}^{-1}$. Consequently, the penetration depth can be of the order of 10 nm meaning that the entire light is absorbed in a very thin layer near the surface. In this case the carriers' generation is very non-uniform across the film thickness and the diffusion current is important. For long wavelengths

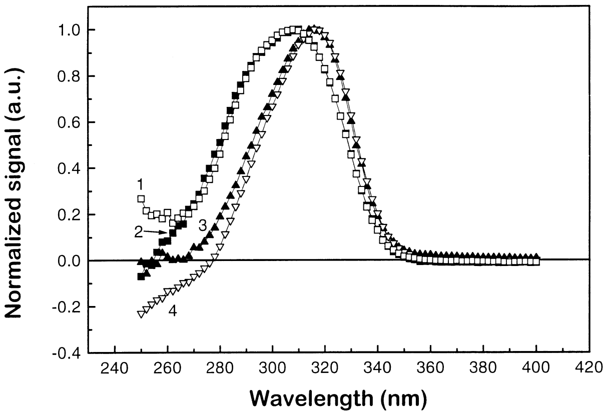

Fig. 2. Normalized spectral distribution of photoconductivity in SBT thin films in case of a 0·01 V voltage applied on the bottom electrode and for a delay time of 30 s: 1, negative polarity, wavelength swept up; 2, negative polarity, wavelength swept down; 3, positive polarity, wavelength swept up; 4, positive polarity, wavelength swept down.

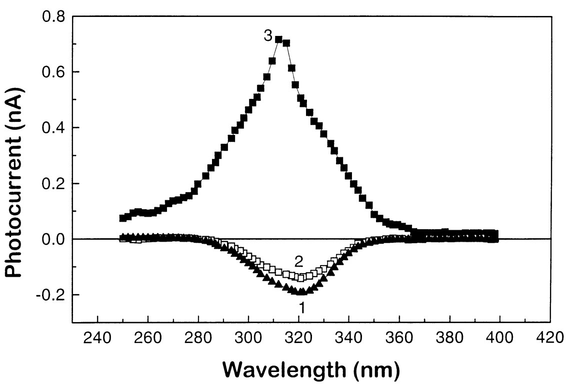

Fig. 3. Spectral distribution of photocurrent in SBT thin films in case of different positive voltages applied on the bottom electrode. The delay time was 30 s and the wavelengths were swept down. 1, 0·01 V; 2, 0·1 V; 3, 1 V.

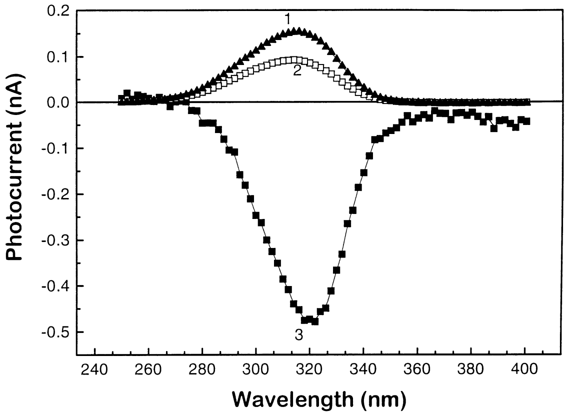

Fig. 4. Spectral distribution of photocurrent in SBT thin films in case of different negative voltages applied on the bottom electrode. The delay time was 30 s and the wavelengths were swept down: 1, 0·01 V; 2, 0·1 V; 3, 1 V.

the penetration depth becomes comparable with the film thickness and the carriers' generation can be considered uniform within the film. The diffusion current can be neglected in this case.

A third aspect is that the surface, or rather interface, recombination can not be neglected when the carriers' generation takes place near the one of the two ferroelectric/metal interfaces. The recombination rate is different at these interfaces due to different metals and processing.

A fourth aspect that has to be considered is that, generally, the ferroelectric films are good insulators, therefore the density of the equilibrium free carriers is much lower than that of the photogenerated carriers. In this case, the life time of the photogenerated carriers is dependent on the intensity and the wavelength of the incident light.[15] The consequence is that the time-dependence of the photogenerated current can change from one wavelength to another. The charge carriers' mobility could be, also, very low in such insulating films.

A fifth element that can influence the kinetics of photogenerated carriers is the presence of some internal electric fields in the ferroelectric film. An internal electric field can occur in a non-poled ferroelectric film due to the band bending near electrodes.[16] Depending if the charge carriers are generated near the top or bottom electrode, the band bending can change and the internal electric field can have different values. The presence of an internal electric field, which is opposite in orientation and larger than the applied field, is evidenced in Figs 3 and 4 by the fact that the photocurrent has an opposite sign with the applied voltage for small values. Finally, the possible presence of traps at the grain boundaries or near the electrodes can also affect the kinetic of photogenerated carriers. The traps could be responsible for the long time needed to reach a steady-state under illumination.

In case of the long delay time (30 s) it can be assumed that the system reaches a steady state. The photocurrent is constant in time and has almost the same value no matter if the wavelengths are swept up or down. The spectral distribution has the same shape and the maximum of photosensitivity occurs at the same wavelength. The peak wavelength (310–315 nm) can be used for the gap computation giving a value of about 3·94–4 eV. This value is in very good agreement with that reported in literature.[17]

For short delay time (1 s) the steady state cannot be reached, the photocurrent is in a transitory state and its value can be influenced by the elements mentioned above. All these can affect the wavelength at which the maximum in the spectral distribution occurs. The time dependence of the photocurrent being wavelength dependent it is possible to obtain the maximum sensitivity at different wavelengths for different delay times. The fact that the maximum in spectral distribution, in the case of short delay times, does not occur at the same wavelength when the wavelength domain is swept up or down can be due to a different carriers kinetic when the carriers' photogeneration starts from the bottom or from the top electrode. When the sweeping starts with short wavelengths the carriers are generated first near the top electrode leading to a high concentration gradient and, consequently, to an important contribution of the diffusion current. This current superimposes the drift current and generates the peaks observed at shorter wavelengths. If a negative polarity is applied to the bottom electrode (the top illuminated electrode positive) electrons will be subtracted from the film while the holes will be pushed to the sample volume. The situation reverses if a positive polarity is applied on the bottom electrode. Noting that in the first case the photocurrent is higher than in the second case (see Fig. 2) we can presume that the surface recombination rate near the top gold electrode is higher for electrons than for holes. For longer wavelengths the contribution of the diffusion current disappears because the carriers' generation takes place in whole volume and the surface recombination can be neglected.

If the wavelength sweeping starts with long wavelengths the carriers will be generated first near the bottom electrode. The carriers' photogeneration can be considered uniform and the current is dominated by the drift current. However, only a very small part of the photogenerated carriers will be collected due to their small mobility. Decreasing the wavelength the carriers' photogeneration becomes non-uniform and the concentration gradient increases, leading to an increased contribution of the diffusion current.

Depending on the photogenerated carriers which are extracted from the film when the generation takes place near the top or bottom electrode and depending on the type of traps that are dominant near electrodes the value of the internal electric field can be different. This fact can affect the position of the maximum in the spectral distribution, at least for short delay times when the photocurrent is in a transitory state. The consequence is the occurrence of a 'hysteresis' in the spectral distribution depending on the wavelengths sweeping direction.

4 Conclusions

Photoelectric properties of ferroelectric SBT thin films deposited on Pt/SiO_2/Si substrates by Chemical Solution Deposition method were investigated in the 250–400 nm wavelength range. A 3·94–4 eV gap value was determined. The wavelength corresponding to the maximum in spectral distribution is dependent on the delay time and on the wavelength sweeping direction (up or down). The presence of an internal electric field in the film and the non-equivalence of the two metal–ferroelectric interfaces was confirmed by the photoconductive measurements.

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References

1. Paz de Araujo, C. A., Cuchiaro, J. D., McMillan, L. D., Scott, M. C. and Scott, J. F., Fatigue-free ferroelectric capacitors with platinum electrodes. *Nature*, 1995, **347**, 627–629.
2. Scott, J. F. and Paz de Araujo, C. A., Ferroelectric memories. *Science*, 1989, **246**, 1400–1405.
3. Duiker, H. M., Beale, P. D., Scott, J. F., Paz de Araujo, C. A., Melnick, B. M., Cuchiaro, J. D. and McMillan, L. D., Fatigue and switching in ferroelectric memories: theory and experiment. *J. Appl. Phys.*, 1990, **68**, 5783–5791.
4. Wu, S. Y., Memory retention and switching behavior of metal-ferroelectric-semicondictor transistors. *Ferroelectrics*, 1976, **11**, 376–383.
5. Lee, J., Essayan, S., Prohaska, J. and Safari, A., Reversible pyroelectric and photogalvanic current in epitaxial Pb($Zr_{0.52}$ $Ti_{0.48}$)O_3 thin films. *Appl. Phys. Lett.*, 1994, **64**, 294–296.
6. Dulieu, B., Bullot, J., Wery, J., Richard, M. and Brohan, L., Dispersive photoconductivity in the layered perovskite $Nd_2Ti_3O_9$. *Phys. Rev B*, 1996, **55**, 10641–10650.
7. Li, L., Liu, C. T., Leung, M. S. and Lipeles, R. A., Effects of laser radiation on photoconductivity in PZT thin films. *Integrated Ferroelectrics*, 1995, **7**, 33–44.
8. Thakoor, S. and Maserjian, J., Photoresponse probe of the space charge distribition in ferroelectric lead zirconate titanate thin film memory capacitors. *J. Vac. Sci. Technol. A*, 1994, **12**, 295–299.
9. Warren, W. L. and Dimos, D., Photo-assisted switching and trapping in $BaTiO_3$ and Pb(Zr,Ti)O_3 ferroelectrics. *J. Non-Cryst. Sol.*, 1995, **187**, 448–452.
10. Pintilie, L., Alexe, M., Pignolet, A. and Hesse, D., $Bi_4Ti_3O_{12}$ ferroelectric thin film ultraviolet detectors. *Appl. Phys. Lett.*, 1998, **73**, 342–344.
11. Dubovik, E. and Fridkin, V., The bulk photovoltaic effect in ferroelectric Pb(Zr,Ti)O_3 thin films. *Integrated Ferroelectrics*, 1995, **9**, 285–290.
12. Liu, C. T., Li, L., Welb, J. S., Leung, M. S. and Lipeles, R. A., Deposition and characterization of photoconductive PZT thin films. *J. Electrochem. Soc.*, 1995, **142**, 1957–1960.
13. Nonaka, K., Akiyama, M., Hagio, T. and Takase, A., Bulk photovoltaic effect in reduced/oxidized lead lanthanum titanate zirconate ceramics. *Jpn. J. Appl. Phys.*, 1995, **34**, 2344–2349.
14. Goodman, A. M., Photoconductivity as a function of optical absorption. *J. Appl. Phys.*, 1159, **30**, 144–147.
15. Bube, R. H., *Photoelectronic Properties of Semiconductors.* Cambridge University Press, 1992, chap. 4.
16. Fridkin, V. M., *Photoferroelectrics.* Springer–Verlag, Berlin, 1979, chap. 8.
17. Hartmann, A. J., Lamb, R. N., Scott, J. F., Johnston, P. N., El Bouanani, M., Chen, C. W. and Robertson, J., Electronic and microstructure characterization of strontium-bismuth tantalate (SBT) thin films. *J. of Korean Phys. Soc.*, 1998, **32**, S1329–S1331.