Journal of the European Ceramic Society 19 (1999) 1473–1476

PII: S0955-2219(98)00455-5
0955-2219/99/$ - see front matter

Photoconductive Properties of $Bi_4Ti_3O_{12}$/Si Heterostructures with Different Thickness of the $Bi_4Ti_3O_{12}$ Film

L. Pintilie,[a]* I. Pintilie[a] and M. Alexe[b]

[a]National Institute of Materials Physics, Bucharest-Magurele, PO Box MG-7, 76900, Romania
[b]Max Planck Institute for Microstructure Physics, Weinberg 2, 06200 Halle/Saale, Germany

Abstract

Ferroelectric $Bi_4Ti_3O_{12}$ (BiT) thin films of different thicknesses were deposited on p-type Si substrates using the Chemical Solution Deposition (CSD) method. The films were crystallized by the conventional thermal annealing for 30 min at temperatures in the 500–700°C range. It was found that the shape of the photoconductive signal spectral distribution is dependent on the film thickness. For thin films (150 nm) four peaks were observed (400, 500, 860 and 1075 nm) and the photoconductive signal occurs only if the Si substrate is negatively biased. For thicker films (500 nm) only two peaks were observed (370 and 1075 nm) and the photoconductive signal occurs no matter the polarity of the applied voltage. © 1999 Elsevier Science Limited. All rights reserved

Keywords: bismuth titanate, sol–gel processes, optical properties, perovskites.

1 Introduction

Ferroelectric thin films and ferroelectric/semiconductor heterostructures were subjected to an intensive study in the last decade due to their potential use in memory devices.[1,2] There is also a significant trend to integrate other applications of ferroelectric materials (pyroelectric detectors, piezoelectric transducers, electro-optic devices, etc.) with the standard semiconductor technology.[3] This imply optimization of ferroelectric thin films deposition methods and an intensive analysis of the physical phenomena taking place at the ferroelectric/semiconductor interface. The photoelectric investigation could be, in some cases, an useful tool allowing the determination of gap energy, the detection of impurity induced photoconductivity and of the internal electric fields, etc.[4–6]

In the past years we have studied the photoelectric properties of some complex ferroelectric/semiconductor heterostructures based on lead titanate ($PbTiO_3$) thin films.[7–9] Several types of signal (photovoltaic, photoconductive, pyroelectric) were observed in such structures. It was shown that they can be used as photovoltaic cells on a broad wavelengths range (0·3–3 μm) or can be used in photosensitive field effect controlled devices.

In the present paper the $PbTiO_3$ film was replaced by a $Bi_4Ti_3O_{12}$ (BiT) film, the template material from the Bi-layered perovskite class. The use of this material in a ferroelectric field effect devices imply a careful analysis of the BiT/Si interface. Photoelectric measurements can give information about the interface quality and physical phenomena taking place there.

2 Experimental

The BiT films were deposited on p-type Si substrates (1–10 Ωcm) by Chemical Solution Deposition (CSD) described elsewhere. The stock solution was prepared using Bi-diethylhexanoate and Ti-isopropylate as metal precursors and xylene as solvent. A metalorganic film was deposited on Si wafer by spin coating at 2500 rpm for 1 min. After deposition the metalorganic film was pyrolised onto a hot plate at 350°C for 5 min. Films with various thicknesses were obtained by repeating several times the spinning-pyrolise cycle. For photoelectric investigations two thickness of the BiT

*To whom correspondence should be addressed. Fax: +40-1423-1700; e-mail: pintilie@alpha1.infim.ro

film have been chosen: 150 nm (sample F1) and 500 nm (sample F2). The films were crystallized by thermal annealing in air for 30 min at temperatures ranging between 500 and 700°C. Details about solution preparation, deposition process and structural analysis are given in a previous paper.[10] We will remind only that the X-ray diffraction spectra show the characteristic lines of a policrystalline BiT film, with perovskite structure, and that the TEM cross-section analysis shows a rough BiT/Si interface with a significant interaction between Si and the BiT film.[11]

A continuous aluminum electrode was evaporated on the Si surface (the back electrode) after removing the native oxide in diluted HF and semitransparent gold electrodes were evaporated on the BiT film. The top Au electrodes with 3×3 mm^2 area were defined by standard photolithography and etching in K:KI solution. Photoconductive measurements were performed in continuous light, using the experimental set-up presented in Fig. 1. For spectral distribution measurements a voltage of 1·5 V was applied on the sample, usually with the minus polarity on the Si substrate, and the photocurrent was measured using a Keithley 6517 electrometer. For spectral distribution measurements, a grating monochromator (Spex 270) was used. The light source was an UV lamp model SVX 1000 calibrated with a Hamamtsu S1227-66BQ Si photodiode in the 200–1100 nm wavelength range.

The normalized spectral distributions of the photoconductive signal are presented in Fig. 2 (F1 films) and Fig. 3 (F2 films). It can be seen that there are major differences between the photoconductivity spectral distributions obtained for thin and thick BiT films. For F1 films two sensitivity peaks can be observed at low annealing temperatures (550–600°C), one located around 500 nm and the other located around 1075 nm. There are also some shoulders in the spectral distribution, located at 380, 820 and 900 nm. For the highest

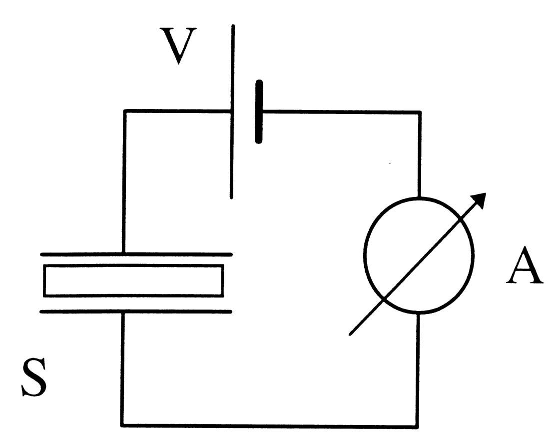

Fig. 1. The experimental set-up used for photoconductivity measurements: S, the sample; V, the d.c. voltage source; A, the electrometer.

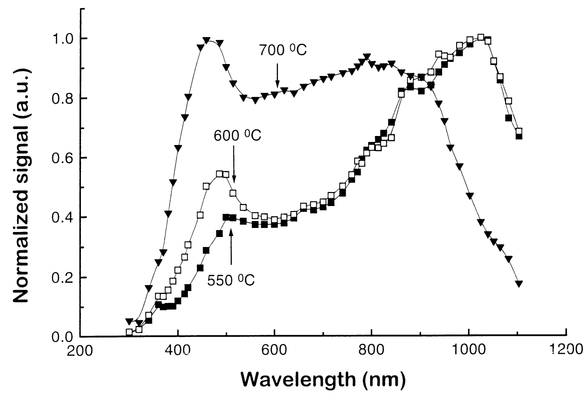

Fig. 2. The photoconductivity spectral distributions in case of BiT/Si heterostructures with a thin film of BiT (150 nm).

annealing temperature (700°C) the peak from 1075 nm is no longer occurring while the peak located at 500 nm is developing very much and is becoming dominant in the spectral distribution. The peak located at about 390–400 nm is practically included in the peak located at 500 nm. The shoulders at 820 and 900 nm are developing in a single, broad, peak centered around 860 nm. For the F2 films, no matter the annealing temperature, only two peaks occur in the spectral distribution, one at 1075 nm and the second at 370 nm. A possible third peak is occurring around 860 nm, but its relative amplitude is very small and remains practically constant with increasing the annealing temperature. The relative amplitude of the peak located at 370 nm is increasing with increasing the annealing temperature, reaching a value of about 2–3% from the amplitude of the one located at 1075 nm, which is the main peak in the spectral distribution. An important aspect which has to be underlined is that the photoconductive signal in case of F1 films occurs only when the minus polarity of the d.c. voltage source is applied on the Si substrate. If a positive polarity is applied on the Si substrate no photoconductive signal was detected. In fact the leakage current in this case is very high as it can be seen from the current–voltage (I–V) characteristic presented in Fig. 4. In case of the F2 films the photoconductive signal occurs irrespective of the polarity of the voltage applied on the Si

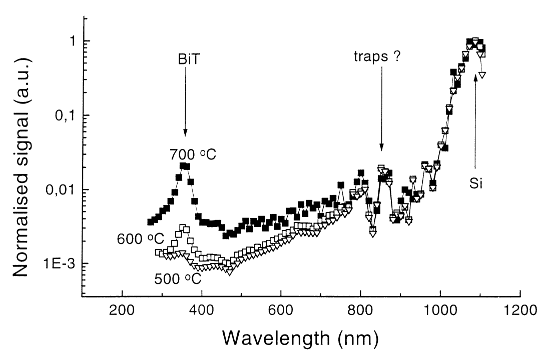

Fig. 3. The photoconductivity spectral distributions in case of BiT/Si heterostructures with a thick film of BiT (500 nm).

substrate (see Fig. 5). In this figure the photocurrent dependence on the applied voltage is presented for a wavelength of 350 nm. The measurement was performed on the heterostructure annealed at 700°C. As it can be seen the photocurrent is continuously increasing with increasing the applied voltage. The fact that at zero voltage the photocurrent is non-zero shows the presence of a photovoltaic effect, probably due to the internal electric field existing at the BiT/Si interface. Finally, the dependence of the photoconductive signal on the applied voltage in case of F1 films was raised. An example of this dependence, in case of the sample annealed at 700°C is presented in Fig. 6. The photocurrent reaches a saturation value for any wavelength and similar behavior was found for the samples annealed at lower temperatures.

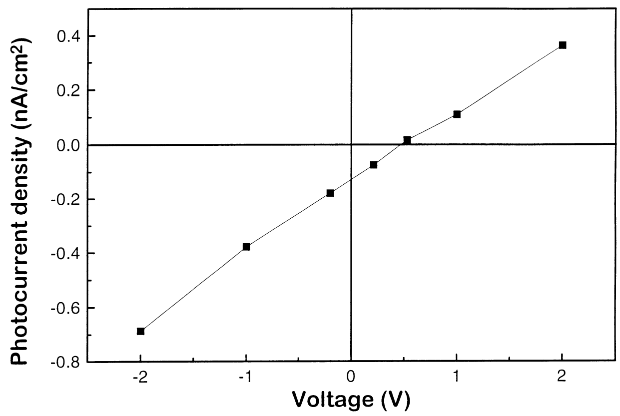

Fig. 5. The voltage dependence of the photocurrent in case of the BiT (thick)/Si heterostructure annealed at 700°C. The wavelength of the incident light was 350 nm.

3 Discussion

To explain the above experimental results we have to admit that the BiT films behave differently if they are thin or thick. Starting with the thinner BiT films (F1), the I–V characteristic presented in Fig. 4 shows a diode behavior and make us to believe that in this case the BiT film acts like a semiconducting material. The BiT/Si heterostructure is forward biased when a positive voltage is applied on the Si substrate and the forward current increases rapidly with increasing the applied voltage. The heterostructure is reverse biased if a negative voltage is applied on the Si substrate. The reverse current values are small and increase almost linearly with the applied voltage (see the inset in Fig. 4). Such an I–V characteristic was also found for other ferroelectric/Si heterostructures[12] and was explained considering a band structure specific for a heterojunction. The presence of the ferroelectric polarization can be considered as an additional band bending, similar with that produced by a voltage applied on the sample. The BiT film acts like a semiconductor due to the Si atoms diffusing into it during the thermal annealing. For thin films this doping process could affect the entire BiT film and could introduce some discrete levels in the forbidden band acting like trapping levels. These levels could be filled with carriers photogenerated either in Si or in BiT film and are emptied every time the wavelength of the incident light corresponds to their activation energies. This is the so called impurity induced photoconductivity[13] and can explain the occurrence of the peaks located at 860 and 500 nm. In our opinion, the peak located at 500 nm can be associated with a punctual defect such as an interstitial or a substitutional Si atom in the crystalline lattice of the BiT film. The peak is sharp and increases with increasing the annealing temperature, denoting that the density of this punctual defect is also increasing. The other peak, located at 860 nm, is a broad peak and can be associated with some defects at the BiT/Si interface. It can be assumed that a large interface states density acting as trapping levels with a broad spectrum of activation energies occurs at the interface due to the interaction of the two materials.

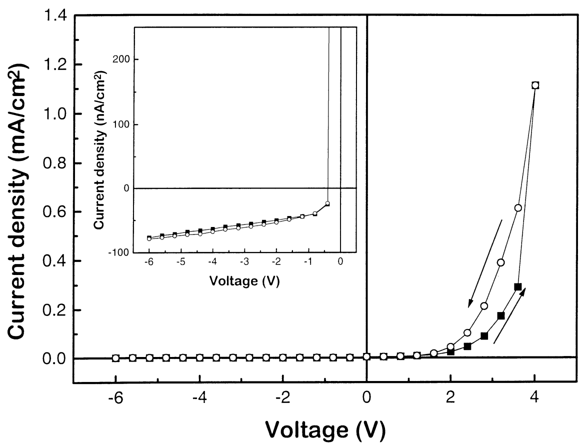

Fig. 4. The I–V characteristic in case of the BiT (thin)/Si heterostructure annealed at 700°C.

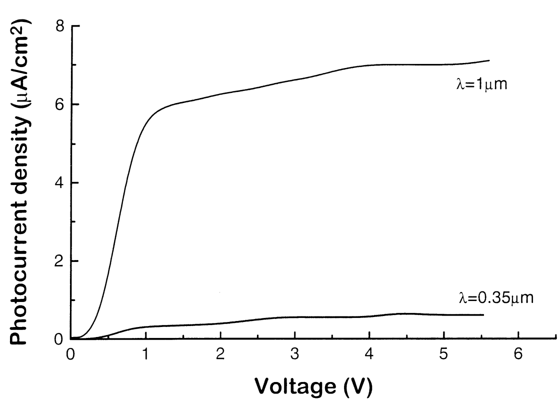

Fig. 6. The voltage dependence of the photocurrent in case of the BiT (thin)/Si heterostructure annealed at 700°C.

The other two peaks or shoulders occurring in the spectral distribution of photoconductivity in case of the F1 samples could be associated with the band-to-band generation in Si (1075 nm) and BiT (390–400 nm), respectively. The second peak, due to the 500 nm neighboring peak, is slightly displaced towards higher wavelengths than in case of the BiT films deposited on Pt/Si (370 nm).[14] The activation energy of the four peaks can be estimated using the peak wavelengths and the obtained values are: 3·2 eV (for the 390 nm peak, possible the gap of the BiT film), 2.48 eV (500 nm, possible interstitial or substitutional Si atoms in the BiT films), 1·43 eV (860 nm, interface defects) and 1·2 eV (1075 nm, the Si gap).

Referring to the dependence of the measured photocurrent on the applied reverse voltage (Fig. 6) it can be seen that no signal can be detected for a bias lower than 0·20–0·4 eV, therefore, one can suppose the existence of a threshold voltage. For all samples and for all wavelengths increasing the reverse bias the photoconductive signal increases reaching very rapid a saturation. The saturation of the photoconductive signal with the increasing of the applied reverse voltage could be due to the fact that all the photogenerated carriers are separated and collected by the applied electric field.

In the case of thicker BiT films (F2) the influence of the Si diffusion on the photoconductive properties of the ferroelectric/Si heterostructure is diminished. In this case only the peaks corresponding to band-to-band generation in Si (1075 nm) and BiT film (370 nm) occur. The fact that in this case the photoconductive signal occurs no matter the polarity of the applied voltage and that this signal increases almost linearly with the applied voltage make us to believe that the Si substrate plays the role of an electrode for the BiT film. In this case the BiT film can be regarded as a highly insulating film with ferroelectric properties. Due to the ferroelectric polarization the Si substrate is either in accumulation or in inversion near the interface. In both cases, a highly conductive layer exist in the Si substrate near the interface and the remaining Si volume can be regarded as a small value resistor in series with the ferroelectric film. Photocarriers can be generated in the Si bulk but only a few of them can overcome the potential barrier between the two materials. This can explain why the photogenerated current is so small at waveengths where the band-to-band generation in Si take place.

4 Conclusion

Photoconductive properties of the BiT/Si heterostructures were investigated. It was found that the shape and the number of peaks occurring in spectral distribution is dependent on the BiT film thickness. In case of thin films the semiconducting properties of the BiT film are dominant and a doping process can occur by Si diffusion in the film during the thermal annealing. For thick BiT films the influence of Si diffusion is negligible, the BiT film having very good insulating properties.

The results are explained considering that for thin BiT films the heterostructure can be regarded as a semiconducting heterojunction while for thick films the heterostructure can be regarded as an insulating layer with electrodes. Further studies are need to clarify the role of Si atoms over the transport and photoconducting properties of the BiT films deposited on Si substrates.

References

1. Scott, J. F. and Paz de Araujo, C. A., Ferroelectric memories. *Science*, 1989, **246**, 1400–1405.
2. Chen, F. Y., Fang, Y. K., Sun, M. J. and Chen, J. R., A nonvolatile ferroelectric memory device with a floating gate. *Appl. Phys. Lett.*, 1996, **69**(21), 3275–3276.
3. Watton, R., Ferroelectric materials and devices in infrared detection and imaging. *Ferroelectrics*, 1989, **91**, 87–108.
4. 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.
5. 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.
6. Thakoor, S. and Maserjian, J., Photoresponse probe of the space charge distribution in ferroelectric lead zirconate titanate thin film memory capacitors. *J. Vac. Sci. Technol. A*, 1994, **12**, 295–299.
7. Pintilie, L., Alexe, M., Pintilie, I. and Botila, T., Photovoltaic effects in $PbS/PbTiO_3/Si$ heterostructures. *Appl. Phys. Lett.*, 1996, **69**(11), 1571–1573.
8. Pintilie, I., Pintilie, L., Dragoi, V., Petre, D. and Botila, T., Indirect enhancement of PbS photoconductivity by ferroelectric field effect in a $PbS/PbTiO_3/Si$ heterostructure. *Appl. Phys. Lett.*, 1997, **71**(8), 1104–1106.
9. Alexe, M., Pintilie, I., Pintilie, L., Pignolet, A., Senz, S. and Hesse, D., Photoelectric properties of $PbTiO_3/Si$ heterostructures. Proc. MRS–Spring Meeting, Vol. 433, April 1996, San Francisco, USA, **433**, 425–430.
10. Alexe, M., Pignolet, A., Senz, S. and Hesse, D., Physical properties of spin-on solution deposited $Bi_4Ti_3O_{12}$ thin films on Si substrates. *Ferroelectrics*, 1997, **201**, 157–165.
11. Alexe, M., Kästner, G., Hesse, D. and Gösele, U., Ferroelectric-semiconductor heterostructures obtained by Direct Wafer Bonding. *Appl. Phys. Lett.*, 1997, **70**(25), 3416–3418.
12. Xu, Y., Chen, C. J., Xu, R. and MacKenzie, J. D., The self-biased heterojunction effect of ferroelectric thin film on silicon substrate. *J. Appl. Phys.*, 1990, **67**(6), 2985–2991.
13. Bube, R. H., *Photoelectronic Properties of Semiconductors*, Cambridge University Press, Cambridge, UK, 1992, chap. 4.
14. Pintilie, L., Alexe, M., Pignolet, A. and Hesse, D., Photoelectric effects in chemical solution deposited $Bi_4Ti_3O_{12}$ thin films. *2nd European Meeting on Integrated Ferroelectrics*, Jouy-en-Josas, Paris, 29–30 September 1997. *J. Phys. IV France*, 1998, **8**, Pr9-101–Pr9-104.