Photoconductivity of CaH$_2$-reduced BaSnO$_3$ thin films

C. W. Zhao, B. C. Luo and C. L. Chen

Incorporation of foreign chemical elements in oxides can significantly alter their optoelectronic performances, and thus it is widely used to seek new transparent conductive oxides. Chemical-doping BaSnO$_3$ systems, like La-doped BaSnO$_3$, are of increasing interest with extremely high electrical mobility and excellent oxygen stability, exhibiting the potential application in next-generation all-perovskite optoelectronic devices. In this work, hydrogen was introduced into BaSnO$_3$ through CaH$_2$ reduction of BaSnO$_3$ thin films, and the electrical properties, as well as the photo-response behavior, were investigated. Secondary ion mass spectroscopy demonstrated the uniform distribution of hydrogen within the BaSnO$_3$ thin film. The addition of hydrogen greatly enhanced the conductivity of the BaSnO$_3$ thin film, exhibiting a carrier concentration $\sim$8.04 x 10$^{19}$ cm$^{-3}$ and mobility $\sim$9.52 cm$^2$ V$^{-1}$ s$^{-1}$ at 300 K, and thus resulted in a fast relaxation process in the transient photoconductivity, which was characterized by a double exponential function indicating two physical contributions.

Experimental

The insulating epitaxial BaSnO$_3$ (BSO) thin films of thickness $\sim$100 nm were deposited on (LaAlO$_3$)$_{0.3}$(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$ (LSAT)
(001) substrates in one-shot by radio-frequency (RF) magnetron sputtering technique with BSO ceramic target, as described in detail in our previous publications. Here, the LSAT substrate was chose due to its inertness against CaH$_2$. The as-growth BSO thin film was embedded with CaH$_2$ powder in an evacuated Pyrex tube and then the tube was sealed in a vacuum (<0.3 mTorr), which were all done under nitrogen in a glovebox. Subsequently, the tubes were annealed under optimized conditions (annealing temperature ~630 °C and time ~20 h) for obtaining the lowest resistivity. Finally, the films were washed with ethanol and deionized water for 2 times to remove the excess CaH$_2$ and CaO byproduct, and then naturally dried at nitrogen-flowing environment (labeled as BSO-H). For comparison purpose, the above-mentioned processes were also done except that the films were not embedded with CaH$_2$ powder (labeled as BSO-V).

The phase structures of the films were characterized by X-ray diffraction (XRD) (PANalytical Empyrean), with Cu $K_{\alpha}$ radiation in the usual $\theta$–2$\theta$ geometry. The valence states of O ions were checked using X-ray photoelectron spectroscopy (XPS) (ESCA-LAB 250) with Al $K_{\alpha}$ radiation. For excluding the effect of the top surface, the XPS probing was performed after a thin top layer (~8 nm) of the films was removed away by Ar$^+$ ion beam. The hydrogen content in the films was examined using secondary ion mass spectrometry (SIMS). Temperature-dependent resistivity of the films was measured along the in-plane direction by a four-probe method, while the carrier mobility and concentration were determined through Hall measurement using van der Pauw geometry. Two platinum electrodes were vacuum-evaporated onto the film, through which a 6487 Keithley electrometer/Tektronix 4054 was connected by a probe station for photoconductivity measurements. A Xenon lamp coupled into a grating monochromator (Oriel Cornerstone 260) was used for the light source. The light uniformly illuminated the film between the two electrodes. The photocurrent was recorded under a constant bias voltage, and normalized with the incident power at each value of the wavelength. For time dependent photoconductivity measurement, the wavelength of the illuminated light was fixed at 360 nm. All the photo response measurements were performed under vacuum environment to exclude the effect of the absorbed molecules.

Results and discussion

Fig. 1(a) presents XRD patterns of BSO-H and BSO-V thin films (001) substrates in one-shot by radio-frequency (RF) magnetron sputtering technique with BSO ceramic target, as described in detail in our previous publications. Here, the LSAT substrate was chose due to its inertness against CaH$_2$. The as-growth BSO thin film was embedded with CaH$_2$ powder in an evacuated Pyrex tube and then the tube was sealed in a vacuum (<0.3 mTorr), which were all done under nitrogen in a glovebox. Subsequently, the tubes were annealed under optimized conditions (annealing temperature ~630 °C and time ~20 h) for obtaining the lowest resistivity. Finally, the films were washed with ethanol and deionized water for 2 times to remove the excess CaH$_2$ and CaO byproduct, and then naturally dried at nitrogen-flowing environment (labeled as BSO-H). For comparison purpose, the above-mentioned processes were also done except that the films were not embedded with CaH$_2$ powder (labeled as BSO-V).

The phase structures of the films were characterized by X-ray diffraction (XRD) (PANalytical Empyrean), with Cu $K_{\alpha}$ radiation in the usual $\theta$–2$\theta$ geometry. The valence states of O ions were checked using X-ray photoelectron spectroscopy (XPS) (ESCA-LAB 250) with Al $K_{\alpha}$ radiation. For excluding the effect of the top surface, the XPS probing was performed after a thin top layer (~8 nm) of the films was removed away by Ar$^+$ ion beam. The hydrogen content in the films was examined using secondary ion mass spectrometry (SIMS). Temperature-dependent resistivity of the films was measured along the in-plane direction by a four-probe method, while the carrier mobility and concentration were determined through Hall measurement using van der Pauw geometry. Two platinum electrodes were vacuum-evaporated onto the film, through which a 6487 Keithley electrometer/Tektronix 4054 was connected by a probe station for photoconductivity measurements. A Xenon lamp coupled into a grating monochromator (Oriel Cornerstone 260) was used for the light source. The light uniformly illuminated the film between the two electrodes. The photocurrent was recorded under a constant bias voltage, and normalized with the incident power at each value of the wavelength. For time dependent photoconductivity measurement, the wavelength of the illuminated light was fixed at 360 nm. All the photo response measurements were performed under vacuum environment to exclude the effect of the absorbed molecules.

Results and discussion

Fig. 1(a) presents XRD patterns of BSO-H and BSO-V thin films with a logarithmic scale. All the films show only the (00l) peaks corresponding to the substrate without any secondary phases, suggesting that the films are well (00l) oriented along the normal to the substrate. From these (00l) peaks, the out-of-plane lattice parameter was calculated to be about 0.414 and 0.417 nm for BSO-H and BSO-V thin films, respectively. The out-of-plane lattice parameter of BSO-H thin film is slightly smaller than that of BSO-V thin film. In analogy to the CaH$_2$-reduction ATIO$_3$ (A = Ba, Sr, Ca) thin films deposited on LSAT substrates, this lattice change might also be attributed to the compositional change. Previous experiment indicated that oxygen deficiency in BSO thin films could result in the expansion of the out-of-plane lattice parameter. Consequently, the O 1s spectra investigated by XPS analysis are plotted in Fig. 1(b). The O 1s spectrum from BSO-H thin film exhibits a symmetric peak at 529.9 eV, corresponding to the lattice oxygen (O$_{\text{L}}$). However, the O 1s spectrum from BSO-V thin film are asymmetric and can be deconvoluted into two peaks at 530.0 and 531.5 eV, corresponding to the lattice oxygen (O$_{\text{L}}$) and oxygen vacancies (O$_{\text{V}}$), respectively. This result demonstrates that only the BSO-V thin film is oxygen-deficient. Consequently, if considering H$^-$ with the close ionic radius to O$^{2-}$, the larger lattice parameter in BSO-V thin film is due to oxygen vacancies, and H$^-$ substitution for the O$^{2-}$ (H$_{\text{O}}$) in BSO-H film is mostly expectable due to CaH$_2$ reduction.

To clarify whether hydrogen is incorporated into film, the SIMS depth-profiles of H ion in BSO-H and BSO-V thin films were measured, as depicted in Fig. 2. The observed intensity of the H secondary ion signal in BSO-H thin film is >2 orders of magnitude larger than that in BSO-V thin film, and the intensity over the entire depth profile is nearly constant. These data implied that H ion was basically uniform in BSO-H thin film although the precise hydrogen concentration was determined difficulty due to the absence of a hydrogen quantification standard. Generally,
Interestingly, the BSO-V thin film resistivity was beyond the measurement limit of our equipment. Based on aforementioned XRD analysis, it is understandable that the resistivity of BSO-V film is smaller than that of as-grown BSO film due to oxygen vacancies. While for BSO-H thin film, it is believable that the H\textsuperscript{+} charge transition level lies virtually constant at \( \sim 4.5 \) eV below the vacuum level\textsuperscript{12,29,30} and thus easily form a shallow donor inside the conduction band of BSO film, resulting in highly conductive performance. On the other hand, the electrical property of interstitial H doping BSO thin film can be reversible through high vacuum annealing (i.e., from conductor to insulator)\textsuperscript{12}, whereas the BSO-H thin film is still conductive at 300 K, even annealed under high vacuum at 600 °C (see the inset of Fig. 3(a)), indicating that the primary of hydrogen species in BSO-H thin film are H\textsuperscript{+}, not proton. Accordingly, replacing the oxide ions with hydride ions in BSO film could also give rise to insulator–metal transition, analogous to ATiO\textsubscript{3} (A = Ca, Sr, Ba) thin films upon annealing with CaH\textsubscript{2}\textsuperscript{28}. Further, the temperature-dependent carrier concentration and mobility of BSO-H thin film were measured, as shown in Fig. 3(b). At 300 K, the carrier concentration and mobility are \( 8.04 \times 10^{19} \) cm\textsuperscript{-3} and 9.52 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}, respectively. Note that the mobility of our BSO-H thin film is still relatively low, but it is very much comparable to previous report in La-doping BSO thin film deposited on LSAT substrate\textsuperscript{23,31,32}, demonstrating H\textsuperscript{+} as dopant is another advantageous choice to induce metallic conductivity for insulating BSO thin film.

Fig. 4 illustrates the spectral response of the BSO-H thin film as function of wavelengths at 0.2 V and 1 V bias. Both the spectral response exhibit a sharp increase at 390 nm (\( \sim 3.18 \) eV), corresponding the band-to-band absorption of the BSO-H thin film. The response turned to be more prominent with the increasing voltage in the UV region, because the photo-generated carriers could migrate toward the electrodes under the external bias to form the current. With a 1 V bias, the responsivity can be above 0.8 A W\textsuperscript{-1} below the wavelength of 360 nm. Usually, BSO-based thin films were grown on lattice-mismatched substrates, leading to an inevitably high density of dislocations, which strongly weakened their electrical and photoconductive properties\textsuperscript{23,31,32}. However, the response value of our BSO-H thin film in the UV region is very much comparable to the wide band-gap oxide thin films\textsuperscript{33}. What’s more, the current–voltage characteristics under different light power were measured, as shown in the inset of Fig. 4, confirming the ohmic contact between electrode and film. Meanwhile, the current

---

**Fig. 2** SIMS depth profile of the H secondary ion in BSO-H and BSO-V thin films.

**Fig. 3** (a) Temperature-dependent resistivity of BSO-H and BSO-V thin films. Inset shows the temperature-dependent resistivity of BSO-H thin film annealed in vacuum. (b) Temperature dependence of the mobility and carrier concentration for BSO-H thin film.
increases monotonically with increasing the light power, indicating that the electron–hole pair generation is the main origin for the photo response.

To further explore the photo response performance of BSO-H thin film, the time dependent response was subsequently investigated. Fig. 5 presents the time dependence of the resistance ratio $R_l/R_D$ ($R_l$ is the resistance under illumination and $R_D$ is the dark resistance) at 100 K, 200 K and 300 K. Firstly, all the resistances rapidly decrease to the minimum values during illumination, corresponding to the band-to-band excitation, and then exhibit a long recovery process after illumination, relating with the relaxation process of carriers. Notably, the recovery process is complete in several seconds and much shorter than that had been reported on undoped BSO thin film, which is mostly due to the high carrier density and mobility in BSO-H thin film. Secondly, the recovery process reflects the carrier’s dynamics of recombination, and the carrier transit time ($\tau_1$) and the excess life-time of trapped carriers ($\tau_2$, $\tau_2 > \tau_1$) are well-known to be the main parts of the recovery time in oxide semiconductors. Therefore, the experimental data should be well fitted by a double exponential function (see red solid lines in Fig. 5), and the fitting parameters are summarized in inset of Fig. 5. At 300 K, the carrier transit time and the excess life-time of trapped carriers are 7.06 ms and 118.9 ms, respectively. Clearly, the excess lifetime of trapped carriers is the main reason for the recovery time. It has been proved in BSO-based thin films that the trapped states associated with defects including dislocations, ionized impurity, oxygen vacancies, etc., were widely existed. After illumination, some of electron–hole pairs may not recombine, and instead, may be trapped by defects. Consequently, release of these trapped carriers will have a definitive influence on the recovery process. Finally, we noticed that the variable value of resistances under illumination was almost independent of the measured temperatures. Through photo-Hall measurements, previous investigations demonstrated that the increased carrier concentration is the determination of the contribution to the photoconductivity in oxide thin films (WO$_3$ and Ti$_{1-x}$Nb$_x$O$_2$). In present case, the short photo response time of BSO-H thin film is beyond the time resolution of our photo-Hall measurement, and thus it is hard to briefly verify that the variable resistance is due to carrier concentration or mobility or both. However, considering the weak temperature-dependent carrier concentration in BSO-H thin film (see Fig. 3(b)), it is reasonable to assume that the change of resistances under illumination is still involved with the increased carrier concentration like the Ti$_{1-x}$Nb$_x$O$_2$ thin films, although the deep mechanisms need to be investigated further.

**Summary**

In summary, we fabricated hydrogen-doping BaSnO$_3$ through CaH$_2$ reduction of epitaxial BaSnO$_3$ thin films, and mainly investigated the optoelectronic properties. XRD and SIMS measurements revealed that the hydrogen unchanged the structure of BaSnO$_3$ thin film and uniformly existed in the film. The addition of hydrogen significantly improved the conductivity of BaSnO$_3$ thin film, transiting from the insulator to metallic property with a carrier concentration $\sim 8.04 \times 10^{19}$ cm$^{-3}$ and mobility $\sim 9.52$ cm$^2$ V$^{-1}$ s$^{-1}$ at 300 K. Through the spectral response measurements, a wavelength cutoff at $\sim 3.18$ eV was observed, and the responsivity could be above 0.8 A W$^{-1}$ with a 1 V bias in the ultraviolet range. Additionally, hydrogen doping in BSO thin film could enhance the photoelectric response characteristic due to the high carrier density and mobility. Meanwhile, the recovery process could be analyzed by a double exponential function, indicating the influence of the carrier transit and release of trapped carriers, and simultaneously demonstrating that release of trapped carriers has a definitive role on the recovery process.

**Acknowledgements**

This work was partly supported by National Natural Science Foundation of China (No. 51202195).
References

1 N. F. Mott, *Rev. Mod. Phys.*, 1968, 40, 677.

2 T. Minami, *Semicond. Sci. Technol.*, 2005, 20, S35.

3 J. Ravichandran, W. Siemons, H. Heijmerikx, M. Huijben, A. Majumdar and R. Ramesh, *Chem. Mater.*, 2010, 22, 3983–3987.

4 H. J. Kim, U. Kim, T. H. Kim, J. Kim, H. M. Kim, B. G. Jeon, W. J. Lee, H. S. Mun, K. T. Hong, J. Yu, K. Char and K. H. Kim, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, 86, 165205.

5 S. C. Dixon, D. O. Scanlon, C. J. Carmalt and I. P. Parkin, *J. Mater. Chem. C*, 2016, 4, 6946–6961.

6 K. C. Wilson, E. Manikandan, M. B. Ahamed and B. W. Mwakikunga, *J. Alloys Compd.*, 2014, 585, 555–560.

7 E. Manikandan, V. Murugan, G. Kavitha, P. Babu and M. Maaza, *Mater. Lett.*, 2014, 131, 225–228.

8 X. Luo, Y. S. Oh, A. Sirenenko, P. Gao, T. A. Tyson, K. Char and S. W. Cheong, *Appl. Phys. Lett.*, 2012, 100, 172112.

9 H. F. Wang, Q. Z. Liu, F. Chen, G. Y. Gao, W. B. Wu and X. H. Chen, *J. Appl. Phys.*, 2007, 101, 106105.

10 U. S. Alaan, P. Shafer, A. T. N’Diaye, E. Arenholz and Y. Suzuki, *Appl. Phys. Lett.*, 2016, 108, 042106.

11 H. J. Kim, U. Kim, H. M. Kim, T. H. Kim, H. S. Mun, B. G. Jeon, K. T. Hong, W. J. Lee, C. Ju, K. H. Kim and K. Char, *Appl. Phys. Express*, 2012, 5, 061102.

12 C. A. Niedermeier, S. Rhode, S. Fearn, K. Ide, M. A. Moram and H. Hiramatsu, *Appl. Phys. Lett.*, 2016, 108, 172101.

13 S. Sallis, D. O. Scanlon, S. C. Chae, N. F. Quackenbush, D. A. Fischer, J. C. Woicik, J. H. Guo, S. W. Cheong and L. F. J. Piper, *Appl. Phys. Lett.*, 2013, 103, 042105.

14 Q. Z. Liu, J. J. Liu, B. Li, H. Li, G. P. Zhu, K. Dai, Z. L. Liu, P. Zhang and J. M. Dai, *Appl. Phys. Lett.*, 2012, 101, 241901.

15 R. H. Wei, X. W. Tang, Z. Z. Hui, X. Luo, J. M. Dai, J. Yang, W. H. Song, L. Chen, X. G. Zhu, X. B. Zhu and Y. P. Sun, *Appl. Phys. Lett.*, 2014, 105, 109106.

16 C. Shan, T. Huang, J. Z. Zhang, M. J. Han, Y. W. Li, Z. G. Hu and J. H. Chu, *J. Phys. Chem. C.*, 2014, 118, 6994–7001.

17 S. Raghavan, T. Schumann, H. Kim, J. Y. Zhang, T. A. Cain and S. Stemmer, *APL Mater.*, 2016, 4, 016106.

18 P. V. Wadekar, J. Alaria, M. O’Sullivan, N. L. O. Flack, T. D. Manning, L. J. Phillips, K. Durose, O. Lozano, S. Lucas, J. B. Claridge and M. J. Rosseinsky, *Appl. Phys. Lett.*, 2014, 105, 052104.

19 K. Fujiwara, K. Nishihara, J. Shioigai and A. Tsukazaki, *AIP Adv.*, 2016, 6, 085014.

20 W. J. Lee, H. J. Kim, E. Sohn, T. H. Kim, J. Y. Park, W. Park, H. Jeong, T. Lee, J. H. Kim, K. Y. Choi and K. H. Kim, *Appl. Phys. Lett.*, 2016, 108, 082105.

21 S. Yu, D. Yoon and J. Son, *Appl. Phys. Lett.*, 2016, 108, 262101.

22 D. O. Scanlon, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2013, 87, 161201.

23 J. Park, U. Kim and K. Char, *Appl. Phys. Lett.*, 2016, 108, 092106.

24 B. C. Luo, J. Zhang, J. Wang and P. X. Ran, *Ceram. Int.*, 2015, 41, 2668–2672.

25 B. C. Luo, X. S. Cao, K. X. Jin and C. L. Chen, *Curr. Appl. Phys.*, 2016, 16, 20–23.

26 T. Yajima, A. Kitada, Y. Kobayashi, T. Sakaguchi, G. Bouilly, S. Kasahara, T. Terashima, M. Takano and H. Kageyama, *J. Am. Chem. Soc.*, 2012, 134, 8782–8785.

27 Q. Z. Liu, J. M. Dai, Y. Zhang, H. Li, B. Li, Z. L. Liu and W. Wang, *J. Alloys Compd.*, 2016, 655, 389–394.

28 X. Liu, T. S. Bjorheim and R. Haugrød, *J. Mater. Chem. A*, 2017, 5, 1050–1056.

29 C. G. Van de Walle and J. Neugebauer, *Nature*, 2003, 423, 626.

30 S. A. Chambers, T. C. Kaspar, A. Prakash, G. Haugstad and B. Jalan, *Appl. Phys. Lett.*, 2016, 108, 152104.

31 H. Mun, U. Kim, H. M. Kim, C. Park, T. H. Kim, H. J. Kim, K. H. Kim and K. Char, *Appl. Phys. Lett.*, 2013, 102, 252105.

32 U. Kim, C. Park, T. Ha, R. Kim, H. S. Mun, H. M. Kim, J. H. Kim, T. H. Kim, N. Kim, J. Yu, K. H. Kim, J. H. Kim and K. Char, *APL Mater.*, 2014, 2, 056107.

33 L. J. Mandalapu, F. X. Xiu, Z. Yang and J. L. Liu, *Solid-State Electron.*, 2007, 51, 1014–1017.

34 V. N. Smolyaninova, E. Talanova, R. Kennedy, R. M. Kolagani, M. Overby, L. Aldaco, G. Yong and K. Karki, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, 76, 104423.

35 M. Poloju, N. Jayababu, E. Manikandan and M. V. R. Reddy, *J. Mater. Chem. C*, 2017, 5, 2662–2668.

36 J. Sun, F. J. Liu, H. Q. Huang, J. W. Zhao, Z. F. Hu, X. Q. Zhang and Y. S. Wang, *Appl. Surf. Sci.*, 2010, 257, 921–924.

37 K. X. Jin, W. Lin, B. C. Luo and T. Wu, *Sci. Rep.*, 2015, 5, 8778.

38 J. H. Hao, S. A. Studenikin and M. Cocivera, *J. Appl. Phys.*, 2001, 90, 5064.

39 N. Golego, S. A. Studenikin and M. Cocivera, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, 61, 8262.