Materials Research Express

PAPER

Fabrication of Pt/InGaZnO/PZT/LNO hetero-structure by one-step photochemical method

Zhen Li, Jianshe Yue, Nusrat Rafsani Eka and Qi Zhang

School of Chemistry and Chemical Engineering, Xianyang Normal University, Wenlin Rode, Xianyang, 721000, Shaanxi, People’s Republic of China

E-mail: Lizhen0408@163.com

Keywords: sol-gel method, photochemical, photovoltaic, ferroelectric

Abstract

The transparent InGaZnO (IGZO) film was fabricated on the surface of PZT film by photochemical sol-gel method, hence more UV light can penetrate IGZO film reaching the IGZO/PZT junction and produce photo-induced charge carrier to obtain a high photocurrent. To decrease the crystalline temperature of PZT film, and simplify the fabrication process, the UV photochemical treatment of IGZO and PZT happened at the same time. During photochemical process, the organic agents of both IGZO and PZT gel film were decomposed greatly, forming an active metal-oxygen bond, which facilitate crystallization at a low temperature. The obtained IGZO film show a uniform surface with homogeneous particles, the obtained Pt/IGZO/PZT/LNO hetero-structure shows a good photo-electric property.

1. Introduction

Lead zirconate titanate (Pb(Zr0.52Pb0.48)O3 (PZT)) ferroelectric film possesses good dielectric, piezoelectric and ferroelectric properties, which can be a potential application in ferroelectric devices [1–3]. Additionally, the good photovoltaic effect of PZT also has potential usage in photo-electronic devices to produce clean and renewable energy to satisfy newly increased energy demand. In the traditional solar device, no p–n junction or Schottky barrier was present in the PZT film, only an internal electric field was built throughout the bulk by polarization treatment [4], the internal electric field can separate the photo-induced electron-hole (e–h) charge pairs and produce the photocurrent [5]. To further enhance the photovoltaic efficiency of PZT film, an asymmetric interface that possesses p–n junction or Schottky barrier was fabricated intentionally between PZT film and electrodes, the e–h charge carrier pairs can be further separated by the asymmetric interface, and the photovoltaic efficiency was enhanced as well [6].

In the past decade, metallic oxide ZnO, CuO, and SnO2 were used as a top/bottom layer material to build an asymmetric interface and to form a p–n junction or Schottky barrier [7], both physical and chemical methods were employed to fabricate these layers. Physical magnetron sputtering can obtain a dense layer, but the equipment is expensive and vacuum condition is also required [8]. Although the chemical method is a simple and cheap process, which can improve the production efficiency greatly, however, some defects may be produced during the volatilization of solvent [9]. These defects may undermine the property of asymmetric interface as well as photovoltaic efficiency. To resolve above problems, ultraviolet (UV) light associated with the chemical solution method was used to decompose the organic agent of gel film at room temperature by photochemical activation [10]. Finally, a dense layer can be obtained and a full–contact junction was built.

The sol–gel method is an attractive chemical method with the merits of simple process, low price, and high productivity [11–13]. In this work, both PZT films and IGZO films are fabricated by the sol–gel method and treated by a photochemical process. Dense transparent IGZO film were fabricated on the PZT surface, which forms a p–n asymmetric junction which can depart the e–h charger carriers. UV light with high penetrability can cleave the organic bonds in the gel film and form active agents. After the final heat treatment, the active agents produce a dense matrix with a small defect, as a result, the photovoltaic efficiency is enhanced. The merit of this
work is that the photochemical treatment of PZT and IGZO were performed simultaneously, which facilitates high product efficiency and lowers the product price. After heat treatment, dense PZT and IGZO films were produced and a p–n junction was formed. To increase the photovoltaic efficiency, an internal electric field was built in the PZT film by polarization process, with the cooperation of the p–n junction and the internal electric field, the electron-hole charge carriers were separated greatly, and photovoltaic efficiency was enhanced as well.

2. Experimental

The Si wafers were used as a substrate with LaNiO3 (LNO) coated as the bottom electrode. The precursor solution of LNO with a concentration of 0.5 mol l⁻¹ was fabricated by dissolving lanthanum acetate (La(CH₃COO)₃) and nickel acetate (Ni(CH₃COO)₂) in a composition solution. The solution is composed of propionic acid and methanol with a molar ratio of 1:5. The solution was stirred for 1 h at 20 °C to form a transparent solution. The LNO precursor solution was deposited on the Si wafer by dip-coating method with a withdrawal rate of 5 mm s⁻¹. After that, LNO precursor film was heated at 700 °C for 10 min in ambient air. The above process was repeated ten times until the resistance of LNO was below 20 Ω cm⁻².

The PZT precursor solution was made by using lead acetate trihydrate (Pb(CH₃COO)₂·3H₂O), zirconium acetylacetonate, and tetra-n-butoxide (Ti(OC₄H₉)₄) as solute materials, methanol and acetylacetone (AcAcH) mixture with the molar ratio of 2:1 was used as the solvent. The solutes dissolved into the solvent with a total metallic ion concentration of 0.5 mol l⁻¹.

The IGZO precursor was made by using indium nitrate hydrate (InN₄O₄·4.5H₂O), gallium nitrate hydrate (GaN₄O₄·H₂O), and zinc acetate hydrate (ZnC₄H₆O₄·2H₂O) as solutes, the 2-methoxy ethanol was used as the solvent. The solutes dissolved into the solvent forming a solution with total metallic ion concentration of 0.3 mol l⁻¹.

The PZT precursor solution was deposited on the Si/LNO substrate by dip-coating method and formed PZT gel film, the withdrawal rate of dip-coating is 5 mm s⁻¹. The PZT gel film was dried at 120 °C for 10 min to remove the solvent. To build up the thickness, the dip-coating-drying process was repeated five times. The IGZO gel film was fabricated on PZT/LNO/substrate by the same process. Then using UV light with the wavelength of 185 nm (90%) and 254 nm (10%) to irradiate the IGZO/PZT gel films for 1 h at room temperature. After that, the IGZO/PZT/LNO/Si hetero-structure was heat-treated at 400 °C for 1 h. The film surface of IGZO/PZT were observed by scanning electron microscope (SEM, JSM-7000F, JOEL). The IGZO film was characterized by X-ray photoelectron spectroscopy (XPS, Kratos, UK). Pt electrodes with a diameter of 0.5 mm were fabricated by the DC-sputtering method, which was used for ferroelectric test, polarization hysteresis loops and the leakage current of Pt/IGZO/PZT/LNO/Si hetero-structure that was characterized by a TF-analyzer 2000. The photocurrent of PZT film was tested by a Keithley-2400 electrometer under a mercury lamp (wavelength of 405 nm, light intensity of 100 mW cm⁻²), the diagram of ferroelectric and photocurrent test as shown in figure 1.

3. Result and discussion

The ferroelectric hysteresis of Pt/IGZO/PZT/LNO/Si with and without UV irradiation is shown in figure 2. It is clearly shown that the remnant polarization value of UV irradiated Pt/IGZO/PZT/LNO/Si is 23 uc cm⁻², which is higher than that of non-irradiated Pt/IGZO/PZT/LNO/Si (16 uc cm⁻²). The leakage current value of UV irradiated Pt/IGZO/PZT/LNO/Si is 1.29 × 10⁻⁷ A cm⁻² at 100 kV cm⁻¹, however, the leakage current
The value of non-irradiated Pt/IGZO/PZT/LNO/Si increases to $1.27 \times 10^{-6}$ A cm$^{-2}$ at 100 kV. UV irradiated sample shows good ferroelectric properties than the non-irradiated sample. A higher remnant polarization value can build a higher internal electric field.

The photovoltaic property of UV irradiated Pt/IGZO/PZT/LNO/Si and non UV irradiated Pt/IGZO/PZT/LNO/Si were tested and shown in figure 3. The I–V curves clearly indicate that the UV irradiated Pt/IGZO/PZT/LNO/Si has a higher photocurrent value of 41 nA, however, the non UV irradiated Pt/IGZO/PZT/LNO/Si possesses a low photocurrent value of 20 nA. The photoelectrons were produced at the p–n junction of IGZO/PZT when the Pt/IGZO/PZT/LNO/Si hetero-structure was under UV illumination[14], and these photo-generated carriers were separated and transferred to electrodes effectively with the help of the internal electric field of the PZT and IGZO/PZT junction barrier. The UV irradiated Pt/IGZO/PZT/LNO/Si possesses a higher remnant polarization value, which means a higher internal electric field is present throughout the PZT film, therefore, resulting in high photocurrent.

Besides the internal electric field of PZT, IGZO film plays a key role in the improvement of photocurrent. The work function of PZT is 4.6 eV, which is higher than that of the LNO (4.5 eV) bottom electrode. Therefore, the contact between LNO and PZT is Ohmic contact. When the p-type IGZO contact with n-type PZT, a p–n junction barrier $E_{p-n}$ ($E_{p-n}$ direction from PZT to IGZO) is formed. The work function of IGZO is 4.89 eV, which is lower than that of the Pt electrode, therefore, the contact between IGZO and Pt is Ohmic contact, and a schematic of the band structure of LNO/PZT/IGZO/Pt is formed as shown in figure 4. Since there is no inner potential existing at both bottom and top electrodes, it facilitates the transfer of photo-induced carrier carrier[15].

The photo-induced carriers are produced at the interface of IGZO/PZT and separated by the p–n junction barrier when the PZT film is unpolarized, as denoted in figure 5(a). After polarization, the PZT possesses the depolarization field direction (internal electric field) along the p–n junction, the electron-hole pairs can be
separated easily, and the negative charges accumulate at the interface of PZT/LNO, and therefore, the concentration of positive chargers at IGZO/PZT interface is increased (as denoted in figure 5(b)), as a result, photocurrent is increased. The higher the remnant polarization value, the higher the depolarization field, and the easier the separation of the electron-hole pairs leading to the higher photocurrent.

To guarantee a higher remnant polarization value, higher crystallization of PZT is needed, in this work, heat treatment was performed at 400 °C, which is lower than that reported [16]. However, this degree of temperature is in favor of silicon substrate, avoiding being oxidized greatly. In the crystallinity of LNO/PZT/IGZO heterostructure, as shown in figure 6, it is revealed that both the PZT and IGZO have shown good crystallinity. For IGZO film, this heating temperature is fit for crystallization [17], but for PZT film, the crystallization temperature is always above 600 °C [18]. The good crystallization of both PZT and IGZO may be attributed to the UV irradiation during the gel film formation. In this work, UV light with a wavelength of 185 (90%) nm and 254 (10%) nm is used, the energy of irradiated UV light is 647 kJ mol⁻¹ (185 nm) and 472 kJ mol⁻¹ (254 nm), which is larger than that of the organic group of C–H (413 kJ mol⁻¹), C–C (348 kJ mol⁻¹) and C–O (352 kJ mol⁻¹). During the irradiation, high-energy UV light can cleave the organic bonds and form high activated metal-oxygen-metal (M–O–M) bonds inside the films, the M–O–M bonds can produce crystalline oxide at low temperature, and as a result, the crystallization temperature was decreased. More importantly, this UV irradiation made decomposition of the organic group happen at a low temperature and formed uniform M–O–M bonds, avoiding the solvent from volatilized greatly, therefore, a uniform and dense film was formed after the heat treatment.

The surface morphology of IGZO is shown in figure 7. It is a clear reveal that the UV irradiated surface shows a uniform structure and symmetrical particle size (figure 7(a)). Contrarily, the non-irradiated surface shows some defects and large size particles. These defects and large particles may attribute to decomposition and crystallization happening at high temperatures. The UV irradiated IGZO film has good contact with PZT film, the contact area is larger than that of non-irradiated IGZO film. As a result, shows a good photoelectric property.

To further confirm the appropriate UV irradiation time, UV–vis absorption of IGZO gel film versus different irradiation times graph is shown in figure 8. With the increase of UV irradiation time, the N–O peak and H–O peak undermine gradually, after 20 min irradiation, both N–O peak and H–O peak disappear, which means an appropriate irradiation time is 20 min. In this work, the UV irradiation time was 30 min, which guarantees the full decomposition of the organic agent.
To testify the effect of UV light on the decomposition of the organic agent, the IGZO and PZT films were investigated by XPS. The N1s spectra of IGZO were tested due to the precursor solution coming from the nitrate, as shown in figure 9. Before UV irradiation, the N1s spectral peak emerged at 475 eV (figure 9(a)), after UV irradiation, the N1s spectra disappeared (figure 9(b)), which means the UV light cleaves all N–O bonds.
In this work, the UV irradiation of IGZO and PZT was performed at the same time. To reveal the effect of UV light on the decomposition of the PZT organic agent, the IGZO layers were removed by ion etching technology. The O1s spectra of PZT were tested as shown in figure 10, after UV irradiation, the content of the M–OH bond decreased, and the M–O content increased (figure 10(b)), which means the UV light can penetrate the transparent IGZO gel film, arrive at PZT film and cleave the organic M–OH bonds to form M–O bonds. The formed M–O bonds have higher activity, which can decrease the crystalline temperature of PZT. As a result, the crystalline PZT can be obtained at a temperature of 400 °C.

4. Conclusion

The transparent IGZO film and PZT were fabricated by the sol-gel method associated with the photochemical method. During the photochemical reaction, high energy UV light penetrates the IGZO gel film and cleaves the organic bond and forms an active metal-oxide bond, which facilitates a decrease in the crystallinity temperature of PZT. The well crystalline PZT film guarantees a good ferroelectric property and high remnant polarization value. The decomposition of IGZO gel film happened at room temperature, which avoids coarse particles and defects formation, the obtained IGZO particles show symmetrical morphology and small size. An asymmetric interface p–n junction formation between IGZO and PZT interface, due to good contact interface of IGZO/PZT, the photovocurrent was increased greatly. With the help of the p–n junction and high internal electric field of PZT, the Pt/IGZO/PZT/LNO hetero-structure shows high photocurrent.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
References

[1] Veer E, Noheda B and Acuautla M 2021 J. Sol-Gel Sci. Technol. 100 517
[2] Zhi- Ming X, Chang-Guo W and Tan H F 2021 Extreme. Mech. Lett. 42 101102
[3] Sappati K K and Bhadra S 2020 IEEE Sens. J. 20 16310
[4] Yue J-S, Chen Y-Q, Li L-W, Zhang K-X and Li Z 2017 J. Sol-Gel Sci. Technol. 83 647
[5] Yang Y S, Lee S J, Yi S, Chae B G, Lee S H, Joo H J and Jang M S 2000 Appl. Phys. Lett. 76 774
[6] Pan D-F, Bi G-F, Chen G-Y, Zhang H, Liu J-M, Wang G-H and Wan J-G 2016 Sci Rep. 6 22948
[7] Li S, Pan J-Q, Li H-L, Liu Y-Y, Liu Q W, Wang J-J, Song C-S, Zhao W-J, Zheng Y-Y and Li C-R 2019 Chem. Eng. J. 366 305
[8] Chi C Y, Pan J Q, Jiang Z Y, Dong Z J and Li C R 2019 Appl. Catal. B Environ 242 92
[9] Song Y, Li L W, Chen Y Q, Li F Z, Qu W W, Wu H M, Yerramilli A S, Alford T L and Zheng H W 2018 J. Sol-Gel. Sci. Tech. 87 285
[10] Zhu Y, Li Q, Yang Z, Wang C and Wei Z 2021 AIP Adv. 11 035019
[11] Sharon V S, Gopalan V E, Al-Omari I A and Malini K A 2022 J. Supercond. Nov. Magn. 35 795
[12] Lu Y S and Dai J Q 2022 J. Alloy Compd. 899 163387
[13] Lee Y H, Tsai P T, Chang C J, Meng H F and Horng S F 2016 AIP Adv. 6 115506
[14] Ren L, Yu A, Wang W, Guo D, Jia M, Guo P, Zhang Y, Wang Z and Zhai J 2021 Nano Lett. 21 10099
[15] Wang Y R, Wang F, Wang Z X, Wang J J, Yang J, Yao Y Y, Li N N, Sendeku M G, Zhan X Y and Shan C 2021 Nano Res. 14 4328
[16] Song Y, Li L W, Chen Y Q, Li F Z, Qu W W, Wu H M, Yerramilli A S, Alford T L and Zheng H W 2018 J. Sol-Gel. Sci. Tech. 87 285
[17] Choi J H, Hwang S M, Chang M L, Ji C K, Park G C, Joo J H and Lim J H 2011 J. Crys. Growth 326 175
[18] Vandana, Gupta R, Tomar M, Tando R P and Gupta V 2021 Appl. Phys. A 127 1