Effect of Al–Zr co-doping on the electrical properties of graphene/ZnO Schottky contact

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Abstract
The Al–Zr–ZnO films was deposited on the surface of n-Si (111) by sol-gel method. The results showed that the average grain size of Al–Zr–ZnO films decreases due to ion doping concentration. Based on XPS analysis, the surface defect oxygen of Al–Zr–ZnO films decreases. As for graphene/Al–Zr–ZnO Schottky contact, barrier height increased and ideality factor decreased with the increasing of Al ion or Zr ion doping, indicating that the rectifying characteristics of graphene/Al–Zr–ZnO Schottky contacts was enhanced due to ion co-doping. It can be explained that oxygen vacancies of Al–Zr–ZnO films decreases due to the ion doping and weakens Fermi level pinning.

1. Introduction

Zinc oxide (short for ZnO) is a common II–VI compound semiconductor, which is widely used to the preparation of optoelectronic devices owing to the special physical properties [1]. Especially for ZnO-based Schottky optoelectronic devices, the vacancy defects at the interface have an important influence on device performance, which mainly comes from ZnO films [2]. According to the literature, it is found that the vacancy defects at the interface of devices can lead to the decrease of barrier height and the increase of leakage current [3]. In order to reduce the vacancy defects of ZnO films, the researchers have found that the ion doping can significantly solve this problem, for instance, Li$^{2+}$, Mg$^{2+}$, Al$^{3+}$, and so on [4–6]. Compared with single ion doping, the co-doping also has become one of the hot issues of doping, such as, Li–Mg, Al–N, Al–Fe, and so on [7–9]. Therefore, it is of great significance to study the effect of co-doping on the electrical properties of ZnO Schottky optoelectronic devices.

In addition, for ZnO-based Schottky optoelectronic devices, palladium is usually used as electrodes [10]. Due to the problems about transmittance and resistance of metals electrodes, it is urgent to find a new material with high optical transmittance and low contact resistance [11]. At presents, the graphene is widely used in the field of optoelectronic devices owing special structure and properties [12]. It has been reported that graphene as an electrode can significantly improve the performance of ZnO-based Schottky optoelectronic devices [13]. Therefore, it will be a meaningful work to analyze the effect of co-doping on the graphene/ZnO Schottky contact properties.

At present, the sol gel method has become one of the common methods to prepare ZnO films due to its adjustable composition and simple operation [14–16]. So, the sol-gel method was used to fabricate the Al–Zr–ZnO films. The phase structure, surface micromorphology and optical properties of Al–Zr–ZnO films were analyzed in detailed. Meanwhile, the surface states of Al–Zr–ZnO films were analyzed by x-ray photoelectron spectroscopy. Then, graphene by chemical vapor deposition method is transferred to the surface of the Al–Zr–ZnO films to fabricate graphene/Al–Zr–ZnO Schottky contact. Finally, by the current-voltage testing, the electrical properties of graphene/Al–Zr–ZnO Schottky contact was discussed in detailed.
Table 1. Doping ion concentration of Al–Zr–ZnO films.

| Sample no | Co doping ion concentration |
|-----------|----------------------------|
|           | Zr(at%) | Al(at%) |
| S1        | 1%      | 1%      |
| S2        | 3%      |         |
| S3        | 5%      |         |
| S4        | 7%      |         |
| S5        | 3%      | 1%      |
| S6        | 5%      |         |
| S7        | 7%      |         |

2. Experiment

In this experiment, the Al–Zr–ZnO films was fabricated on n-Si(111) substrates by the sol-gel method. Zinc acetate hexahydrate is the solute and ethylene glycol is the solvent. The solubility of Zn$^{2+}$ ion is 0.5 mol l$^{-1}$. The concentration of doped ions depends on the percentage of Al$^{3+}$/Zn$^{2+}$ ions and Zr$^{4+}$/Zn$^{2+}$ ion, as shown in table 1. Zinc acetate hexahydrate was added to ethylene glycol, stirred for 15 min, and the diethanolamine as stabilizer was added. Meanwhile, doped ions are added proportionally according to table 1. Finally, the mixing solution is stirred for 2 h, and held for 24 h. The main parameters of spinning coating are as follows: 3000 rpm, 30 s. After each spin coating is finished, the sample is baked in oven for 15 min. After 8 times of the above process, the Al–Zr–ZnO films with the thickness about 740 nm was obtained. All samples are placed in an annealing furnace at 600 °C for 1 h.

By the means of x-ray diffraction and atomic force microscopy, the phase structure and surface morphology of the Al–Zr–ZnO films was measured. Meanwhile, the core level of the Al–Zr–ZnO films were analyzed by x-ray photoelectron spectroscopy. All the core levels of Al–Zr–ZnO films are corrected by Au4f (84 eV). The transmittance of the Al–Zr–ZnO films was measured by ultraviolet-visible spectrophotometer. Then, the graphene by chemical vapor deposition was transferred to the surface of Al–Zr–ZnO films for the formation of graphene/Al–Zr–ZnO Schottky contact, as shown in figure 1(a). The transfer and preparation of graphene can be referred to in the report of Li reports [17]. Meanwhile, the graphene was analyzed by SEM and Raman spectrum, as shown in figure 1(b). It is observed that some wrinkles present on the surface of graphene. Meanwhile, two obvious peaks with the position at 2715.6 cm$^{-1}$ and 1583.7 cm$^{-1}$ appear Raman spectrum. According to the literature report, the peak D at 1362 cm$^{-1}$ did not appear, indicating that the graphene has the low-density defects [18, 19]. Meanwhile, the current-voltage(I–V) measurements of graphene/Al–Zr–ZnO Schottky contact were measured by a Keithley 2400 source meter.

2.1. Phase structure analysis

Figure 2 shows the XRD of Al–Zr–ZnO films. As seen in figure 2, all the main diffraction peaks of Al–Zr–ZnO films present in region from 30° and 40°. The corresponding angles of the diffraction peaks (100), (002), (101) are 31.95°, 34.6°, 36.4°, respectively. It can be obtained that the Al–Zr–ZnO films has the wurtzite structure, and this result coincides with the standard card of ZnO powder diffraction [20, 21]. With the doping concentration of Al ions increasing to 7%, the diffraction peak intensity decreases gradually from S1 to S4. When the concentration of Zr ion increases to 7%, the intensity of the diffraction peak changes in the same way as Al ion doping. Meanwhile, the position of all diffraction peaks remained unchanged, indicating that the addition of graphene does not change the structure of ZnO films. In addition, full width half maximum values (FWHM) of Al–Zr–ZnO films (002) increased, which may be related to the stresses caused by different atomic radius [22].

Based on the Scherer model [23]:

$$D = \frac{k\lambda}{(\beta_{2\theta} \cos \theta)}$$  

where $k$ is a constant about 0.94, $\lambda$ is 1.54 Å and $\beta_{2\theta}$ is the full width at half maximum of (002) peak, $2\theta$ is around 34.6°. The average grain size of Al–Zr–ZnO films decrease from 42.8 nm to 21.6 nm with the increase of ion doping concentration. This phenomenon is consistent with the effect of Li–Co doping on the grain size of ZnO films [24].

2.2. Surface microscopic morphology analysis

Figure 3 shows the micro-morphology of the Al–Zr–ZnO films. As seen in figure 3(a), the surface roughness of the Al–Zr–ZnO films is 6.87 nm. With the doping concentration of Al ions increasing to 7%, the surface...
roughness of S4 in figure 2(b) decreases to 4.53 nm. With the doping concentration of Zr ion increasing to 7%, the surface roughness of S7 in figure 3(c) decreases significantly, and the value is 0.82 nm. It can be speculated that the growth perpendicular to the matrix are effectively limited both the doping of Zr ion and Al ions, which is mainly related to the stress caused by the different radius of the atom. Meanwhile, this phenomenon can also be considered to be related to the reduction of oxygen vacancies in ZnO films [25].

2.3. Core level analysis
Figure 4 illustrates the Zn2p of S1. The binding energy of Zn2p3/2 locates at 1021.6 eV. According to previous literatures, the binding energy at 1021.6 eV is the corresponding Zn–O bond [26]. Meanwhile, the O1s on the surface of Al–Zr–ZnO films are also analyzed, as shown in figure 5. As seen in figure 5(a), the O1s is mainly composed of two
peaks, and the corresponding binding energies are 529.2 eV, 530.8 eV, respectively. The peak at 529.2 eV represents $O_2^-$ in the Zn–O bond [27]. The other peak at 530.8 eV mainly comes from the oxygen vacancy in Al–Zr–ZnO films [28]. According to XPS semi-quantitative analysis, the variation of oxygen vacancy in the Al–Zr–ZnO films can be inferred by the ratio of two peak areas. Therefore, when the Al ion doping concentration reaches 7%, the oxygen vacancy of sample S4 in figure 5(b) decreases. With the Zr ion doping concentration increasing to 7%, the oxygen vacancy of sample S4 in figure 5(c) also decreases significantly. Compared with Al ion doping, Zr ion doping can significantly reduce oxygen defect states in Al–Zr–ZnO films, which may be related to the electronegativity of atoms. Figure 5 shows the Al2p of S4 and Zr2d of S7. From the figure 6(a), the binding energy of Al2p is 73.3 eV, with the corresponding to Al–O bond. The Zr2d of S7 in figure 6(b) is 181.1 eV, with the corresponding to Zr–O bond. This indicates that doping atomic exists mainly in the form of ions.

2.4. Optical performance analysis

Figure 7 shows the transmittance of Al–Zr–ZnO films at the wavelength ranges from 300 nm to 800 nm. With the increase of wavelength, the transmittance of the Al–Zr–ZnO films remains above 80%, indicating that the Al–Zr–ZnO films has high quality. When the doping concentration of Al ions increases from 1% to 7%, at the
wavelength of 360 nm, the blue shift occurs in the transmittance of Al–Zr–ZnO films, which shifts to the direction of wavelength reduction. However, with Zr ion doping concentration increasing from 1% to 7%, the red shift appears at the wavelength of 360 nm in the Al–Zr–ZnO films.

2.5. Electrical characteristics analysis

The electrical properties of the graphene/Al–Zr–ZnO/graphene Schottky contacts were measured, as shown in figure 8. With the doping concentration of Al ions increasing from 1% to 7%, the forward saturation current of graphene/Al–Zr–ZnO/graphene Schottky contacts increases. The doping effect of Zr ion is better than that of Al ion. Combined with XPS analysis in figure 5, this phenomenon is mainly related to the decrease of defective oxygen in Al–Zr–ZnO films [29, 30]. Herein, for the electrical properties of graphene/Al–Zr–ZnO Schottky contact, the thermionic emission (TE) can be used to analyze the carrier transport mechanism, as follows [31]:

\[ I = I_s \exp\left(\frac{qV}{nkT}\right) \left\{ 1 - \exp\left(\frac{-qV}{kT}\right) \right\} \]

(2)

where \( I_s \) is saturation current and can be written as \( I_s = AA^*T^2 \exp\left(-\frac{q\Phi_b}{kT}\right) \), \( V \) is applied voltage, \( q \) is the electron charge, \( n \) is the ideality factor and can be written as \( n = \frac{q}{kT} \frac{dV}{d\ln(I)} \), \( k \) is the Boltzmann constant, \( T \) is the absolute temperature. Herein, \( A \) is the contact area about 2 × 2 mm² and \( \Phi_b \) is the barrier height of graphene/Al–Zr–ZnO Schottky contact, \( A^* \) is the effective Richardson constant about 32 A cm⁻² K⁻² [32]. For the calculation of barrier height and, the calculated linear voltage range is 0.2V–1V, as shown in insert map of figure 7. Therefore, barrier height and ideality factor are obtained by linear fitting, with corresponding to intercept and slope of the forward bias lnI versus V plot, as shown in table 2. It is observed that the barrier height increases and ideal factor decreases in table 2. Based on XPS analysis, it is obtained that the oxygen vacancy introduces defect levels at the interface, leading to pinning of Fermi levels [33, 34]. After ions doped, oxygen vacancies decrease, which can weaken Fermi level pinning and lead to the barrier height increasing [34]. For the ideal factor deviation from 1, it is mainly due to the existence of tunneling current in carrier transport mechanism [35]. Our results are helpful for the fabrication of graphene/ZnO Schottky optoelectronic devices.
3. Conclusion

In this paper, it is observed that the average grain size of Al–Zr–ZnO films decreases by increasing Al or Zr ion doping concentration. Meanwhile, the surface defect oxygen of Al–Zr–ZnO films decreases due to ion doping. In addition, barrier height of graphene/Al–Zr–ZnO Schottky contact increased and ideality factor decreased, indicating that the rectifying characteristics of graphene/Al–Zr–ZnO Schottky contacts was enhanced due to ion co-doping, which is considered that oxygen vacancies of Al–Zr–ZnO films decreases due to the ion doping and weakens Fermi level pinning.

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References

[1] Muchuweni E, Sathiara J S and Nyakotyo H 2017 Synthesis and characterization of zinc oxide thin films for optoelectronic applications _Heliyon_ **3** 1
[2] Rotella H, Mazel Y, Brochen S, Valla A, Pautrat A, Licitra C, Rochat N, Sabbione C, Rodriguez G and Nolot E 2017 Role of vacancy defects in Al doped ZnO thin films for optoelectronic devices _J. Phys. D: Appl. Phys._ **50** 485106
[3] Lee S, Lee Y, Kim D Y and Kang T W 2010 Impact of defect distribution on transport properties for Au/ZnO Schottky contacts formed with H2O2-treated unintentionally doped n-type ZnO epilayers _Appl. Phys. Lett._ **96** 293
[4] Srinivasan G, Kumar R T R and Kumar J 2007 Li doped and undoped ZnO nanocrystalline thin films: a comparative study of structural and optical properties J. Sol–Gel Sci. Technol. 43 171
[5] Qiu X, Li L, Jing Z, Liu J, Sun X and Li G 2008 Origin of the enhanced photocatalytic activities of semiconductors: a case study of ZnO doped with Mg$^{2+}$ J. Phys. Chem. C 112 2242
[6] Lee D, Kim H, Kwon J, Choi H, Kim S and Kim K 2011 Structural and electrical properties of atomic layer deposited Al-doped ZnO films Adv Fun Mater 21 448
[7] Aksoy S, Caglar Y, Ilican S and Caglar M 2012 Sol–gel derived Li–Mg co-doped ZnO films: preparation and characterization via XRD, XPS, FSEM J. Alloy Compd 512 171
[8] Dutta M, Ghosh T and Basak D 2009 N doping and Al–N co-doping in sol–gel ZnO films: studies of their structural, electrical, optical, and photoconductive properties J. Electron. Mater. 38 2335
[9] Ahn G Y, Park S I and Kim C S 2010 Enhanced ferromagnetic properties of diluted Fe doped ZnO with an Al co-doping Phys. Status Solidi 204 4037
[10] Singh S and Park S H 2015 Fabrication and characterization of Al:ZnO based MSM ultraviolet photodetectors Superlattices Microst 86 412
[11] Jian L, Chen H and Xue J 2014 Transparent electrodes for organic optoelectronic devices: a review. J Photon Energy 4 040990
[12] Kusmartsev F V, Wu W M, Pierpoint M P and Yung K C 2015 Application of graphene within optoelectronic devices and transistors Progress in Optical Science & Photonics 2 191
[13] Lee H, An N, Jeong S, Kang S, Kwon S, Lee J, Kim D Y and Lee S 2017 Strong dependence of photocurrent on illumination-light colors for ZnO/graphene Schottky diode Curr. Appl Phys. 17 552
[14] Lee J H, Ko K H and Park B O 2003 Electrical and optical properties of ZnO transparent conducting films by the sol–gel method J. Cryst. Growth 247 119
[15] Shahid M U, Deen K M, Ahmad A, Akram M A, Aslam M and Akhtar W 2016 Formation of Al-doped ZnO thin films on glass by sol–gel process and characterization Appl. Nanomater 6 235
[16] Jun M C, Park S U and Koh J H 2012 Comparative studies of Al-doped ZnO and Ga-doped ZnO transparent conducting oxide thin films Nanoscale Res. Lett. 7 639
[17] Li Y, Ma K, Li Y, Xia P, Wang H, Zou X, Liu Y and Zhang, J Q 2019 Carrier transport mechanism and barrier height of B–, Al– and B–Al-doped ZnO film/graphene schottky contacts prepared using the sol–gel method Elec. Mater. 48 3713
[18] Xie C et al 2012 Schottky solar cells based on graphene nanoribbon/multiple silicon nanowires junctions Appl. Phys. Lett. 100 193103
[19] Jin W F, Ye Y, Gan L, Yu B, Wu P, Dai Y, Meng H, Guo X and Dai L 2012 Self-powered high-performance photodetectors based on CdSe nanobelts/graphene junctions J. Mater. Chem. 22 2863
[20] Djouadi D, Meddouri M and Chelouche A 2014 Structural and optical characterizations of ZnO aerogel nano powder synthesized from zinc acetate ethanolic solution Opt. Mater. 37 567
[21] Azam A, Ahmed F, Arshin N, Charman M and Naqui A H 2010 Formation and characterization of ZnO nanopowder synthesized by sol–gel method J. Alloy Compd 496 399
[22] Pan C T, Yang R Y, Weng M H and Huang C W 2013 Properties of low-temperature deposited ZnO thin films prepared by cathodic vacuum arc technology on different flexible substrates Thin Solid Films 539 290
[23] Kahouli M, Barhoumi A, Bouzid A, Al-Hajry A and Guermazi S 2015 Structural and optical properties of ZnO nanoparticles prepared by direct precipitation method Superlattices & Microstructures 85 7
[24] Awan S U, Hasanain S K and Aftab M 2016 Influence of Li$^{+}$ co-doping effects on luminescence and bandgap narrowing of ZnO: Co$^{2+}$ nanorods due to band tailing effects J. Lumin. 172 231
[25] Bhuvana K P, Elanchezhiyan J, Gopalakrishnan N, Shin B C, Lee W J and Balasubramanian T 2009 A novel approach for Co doping in ZnO by AIN Vacuum 83 1081
[26] Kamarulzaman N, Kasim M F and Chayed N F 2016 Elucidation of the highest valence band and lowest conduction band shifts using XPS for ZnO and ZnO$_{0.95}$Cu$_{0.05}$O thin film gap changes Results Phys 6 217
[27] Hsieh P T, Chen Y C, Kao K S and Wang C M 2008 Luminescence mechanism of ZnO thin film investigated by XPS measurement Appl. Phys. A 90 517
[28] Chen H, Ding J, Guo W, Chen G and Ma S 2013 Blue-green emission mechanism and spectral shift of Al-doped ZnO films related to defect levels RSC Adv. 3 12327
[29] Li Y, Li Y, Zhang H, Tang L and Zhang Q 2018 The effect of annealing on electrical properties of graphene/ZnO Schottky contact J. Mater. Sci.: Mater. Electron 29 21408
[30] Hwang J D, Chen H Y, Chen Y H and Ho T H 2018 Effect of nickel diffusion and oxygen behavior on heterojunction Schottky diodes of Au/NiO/ZnO with a NiO interlayer prepared by radio–frequency magnetron sputtering Nanotechnology 29 295705
[31] Trushin M 2018 Theory of thermionic emission from a two-dimensional collector and its application to a graphene–semiconductor Schottky junction Appl. Phys. Lett. 112 171109
[32] Li Y, Li Y, Zhang J, Tong T and Ye W 2018 Influence of b doping on the carrier transport mechanism and barrier height of graphene/ ZnO Schottky contact J. Phys. D: Appl. Phys. 51 095104
[33] Tsai C H, Lin S X, Hung C J, Liu C C and Hsung M P 2009 Platinum Schottky contacts on single–crystal ZnO with hydrogen peroxide treatment J. Appl. Phys. 106 895
[34] Kashiwaba Y, Sakuma M, Abe T, Nakagawa A, Nikiura I, Kashiwaba Y, Masahiro D and Osada H 2013 Fabrication of Schottky barrier diodes using H$_2$O$_2$–treated non–polar ZnO (1010) substrates Appl. Surf. Sci. 286 126
[35] Kim H, Sohn A and Kim D W 2012 Silver Schottky contacts to Zn–polar and O–polar bulk ZnO grown by pressurized melt–growth method Semicond. Sci. Technol. 27 811