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Influence of Ag–S codoping on silver chemical states and stable p-type conduction behavior of the ZnO films

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Abstract

The effects of Ag–S codoping on chemical states of Ag doped in ZnO, as well as electrical and optical properties of the ZnO film were investigated by comparative study of undoped ZnO, Ag-doped ZnO (ZnO:Ag) and Ag–S codoped ZnO (ZnO:(Ag, S)) films. It was found that the Ag occupied the Zn site and showed only positive univalence (${Ag_{Zn}}^{1+}$) in the ZnO:(Ag, S). Compared to the ZnO:Ag, the solid solubility of the ${Ag_{Zn}}^{1+}$ is greatly enhanced in the ZnO: (Ag, S) with incorporation of S. Stable p-type conduction was observed and proved further in the ZnO: (Ag, S) films. Low temperature photoluminescence measurement for the ZnO:(Ag, S) indicated that there were two kinds of acceptors of ${Ag_{Zn}}^{1+}$–S_O complex and ${Ag_{Zn}}^{1+}$ in the ZnO:(Ag, S), moreover, the ionization energy of the Ag_{zn}^{1+}–S_O was smaller than that of the ${Ag_{Zn}}^{1+}$. The stable p-type conduction of the ZnO:(Ag, S) was suggested to be attributed to the increase of the ${Ag_{Zn}}^{1+}$ content induced by S doping and to the formation of the ${Ag_{Zn}}^{1+}$–S_O complex acceptor.

Keywords: A. Films; C. Electrical conductivity; D. ZnO; Ag–S codoping

1. Introduction

ZnO semiconductor is considered as a promising material for preparation of ultraviolet light-emitting diodes and laser diodes, due to its wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature [1–3]. A premise of realization of these applications is to fabricate reliable and stable p-type ZnO. However, although a great deal of effort has been devoted to fabrication of p-type ZnO by doping group-I (Li, Na) and group-V (N, P, As, Sb) elements [4–10] in the recent years, the result is not so satisfactory. For instance, due to small ionic radius, Li tends to occupy both interstitial site (Li_i) and Zn site (Li_{Zn}) when it is doped in ZnO, resulting in the self-compensation of Li_i donor for Li_{Zn} acceptor. So, the Li-doped ZnO usually shows n-type or semi-insulating conductivity [11,12]. And for example, since N has similar radii and electrical structure to O, it was once considered as the most suitable candidate for p-type doping. However, due to low solubility of N in ZnO, high ionization energy of acceptor formed by substitution of N for O (N_O) and self-compensation of the donors (including native donors and the donor formed by substitution of N_2 for the O ($(N_2)_O$) for the N_O acceptor, p-type N-doped ZnO is obtained very difficultly [13,14]. In summary, the low dopant solubility, high ionization energy and self-compensation of native donor defects and dopant donors (such as Li_i and $(N_2)_O$) for acceptors have been key issues of preparation of stable p-type ZnO, which hinder the development and application of ZnO based optoelectronic devices and urgently need to be solved.

Recently, Yan et al. [15] predicated, based on first-principle calculation, that the formation energy of group IB-elements (Cu, Ag and Au) occupying Zn site (denoted as Cu_{Zn}, Ag_{Zn}

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and Au_{Zn}) were much lower than that of the elements occupying interstitial site, which implied that the atoms of the group IB prefer to substitute for Zn rather than occupy interstitial site when they were doped in ZnO. So the self-compensation of the interstitial dopant donors for the substitutional dopant acceptors can be restrained. Yan et al. also indicated that the Cu_{Zn}, Ag_{Zn} and Au_{Zn} ions with positive univalence (denoted as ${Cu_{Zn}}^{1+}$, ${Ag_{Zn}}^{1+}$ and ${Au_{Zn}}^{1+}$) could act as acceptors and had the ionization energies of 0.7, 0.4 and 0.5 eV, respectively, amongst which the ionization energy of the ${Ag_{Zn}}^{1+}$ was the smallest and closed to the ionization energy of the N_O acceptor in N-doped ZnO. So, Ag is considered as the most suitable candidate of p-type dopant of ZnO among the three elements. However, the ionization energy of the ${Ag_{Zn}}^{1+}$ acceptor is still too large to realize p-type conduction of Ag-doped ZnO (denoted as ZnO:Ag) [15,16]. So, it is necessary to decrease the ionization energy of the ${Ag_{Zn}}^{1+}$ acceptor.

Persson et al. [17] reported that a strong valence band offset bowing of ZnO occurred as S doped in ZnO, which would lead to shift-up of level of maximum valence band (MVB) of ZnO. The shift-up may reduce the acceptor ionization energy, enhancing doping efficiency and stability of the p-type ZnO. We have prepared stable p-type ZnO film successfully by Cu–S codoping in our previous work [18], suggesting that incorporation of S into ZnO is favorable to preparation of p-type group-IB element doped ZnO and that Ag–S codoping may be a good method for obtaining stable p-type ZnO.

In the present work, we prepared undoped, Ag-doped and Ag–S co-doped ZnO films (denoted as ZnO, ZnO:Ag and ZnO:(Ag, S), respectively) by radio frequency magnetron sputtering and post annealing techniques, and investigated the effects of Ag–S codoping on chemical states of Ag doped in ZnO as well as electrical and optical properties of the ZnO film by comparative study of the ZnO, ZnO:Ag and ZnO:(Ag, S) films.

2. Experimental section

2.1. Preparation of ZnO, ZnO:Ag and ZnO:(Ag, S) films

ZnO, ZnO:Ag and ZnO:(Ag, S) films were deposited on high-resistance single crystal Si (111) substrates with resistivity of 3.34×10^5 Ωcm and carrier density of 1.11×10^{11} cm^{-3} at room temperature by radio frequency magnetron sputtering of ZnO (99.99%) ceramic target, ZnO ceramic target with Ag wire on its surface and ZnO ceramic target with ZnS pieces and Ag wire on its surface, respectively. Before deposition, the Si substrates were cleaned with acetone, ethanol and deionized water in an ultrasonic bath, respectively, and then immersed in a mixed solution of H_3PO_4 and H_2SO_4 with mole ratio of 1:3 for 20 h and in diluted HF solutions for 10 min in sequence to get a clean and fresh surface, and finally blown dry with 99.999% pure nitrogen gas. The growth chamber was evacuated to a base pressure of 6×10^{-4} Pa, and then filled with mixture of 38 sccm 99.99% pure Ar and 2 sccm 99.99% pure O_2 up to 1.0 Pa, which was kept during the depositing process. All films were grown for 1 h at room temperature, and then rapidly annealed for 15 min at 450 °C under vacuum.

2.2. Characterization

The structures of the films were characterized by X-ray diffractometer (XRD) with $Cu_{K\alpha 1}$ radiation ($\lambda = 0.15405$ nm). The chemical states and contents of the Ag and S in the samples were detected by X-ray photoelectron spectroscopy (XPS) with $Al_{K\alpha}$ ($h\upsilon = 1486.6$ eV) X-ray radiation source, and XPS spectrum was calibrated by C1s peak (284.6 eV). Prior to XPS measurement, the films were etched by Ar^+ ions for 60 s. The electrical properties of the samples were measured by Hall effect measurement system in the Van der Pauw configuration at room temperature (Lakershore HMS 7707), and ohmic contact of the electrode was confirmed prior to the measurement. Low temperature photoluminescence (PL) measurement was performed by using the UV Labran Infinity Spectrophotometer with He-Cd laser line of 325 nm as an excitation source.

3. Results and discussion

Fig. 1(a)–(c) shows the XRD patterns of the ZnO, ZnO:Ag and ZnO:(Ag, S) films annealed at 450 °C, respectively. The (002) and (004) diffraction peaks of the wurtzite ZnO are only observed in the XRD pattern of the annealed ZnO, as shown in Fig. 1(a), indicating that the ZnO has full *c*-axis preferential

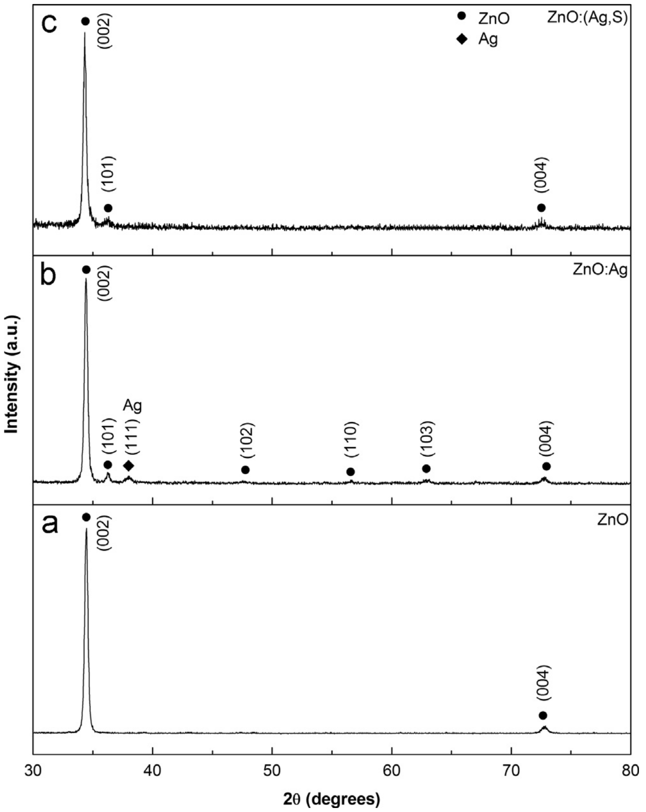

Fig. 1. XRD patterns of the (a) ZnO, (b) ZnO:Ag and (c) ZnO:(Ag, S) films annealed for 15 min at 450 °C under vacuum (● ZnO, ◆ Ag).

orientation. Fig. 1(b) shows the XRD pattern of the ZnO:Ag, where XRD peaks corresponding to the (002), (101), (102), (110), (103) and (004) diffractions of wurtzite ZnO are observed (PDF No. 36-1451). Besides, a diffraction peak of (111) plane of metal Ag that locates at 38.06° (marked as ◆) is also detected (PDF No. 87-0718), implying existence of metal Ag phase in the film, which probably comes from the participation of Ag from the ZnO:Ag. For the ZnO:(Ag, S), only XRD peaks corresponding to the (002), (101) and (004) diffractions of the wurtzite ZnO are observed, as shown in Fig. 1(c), and no XRD peak of metal Ag or phases related to Ag or S is detected, meaning that both Ag and S have incorporated into the ZnO to form ZnO:(Ag, S) solid solution with wurtzite structure.

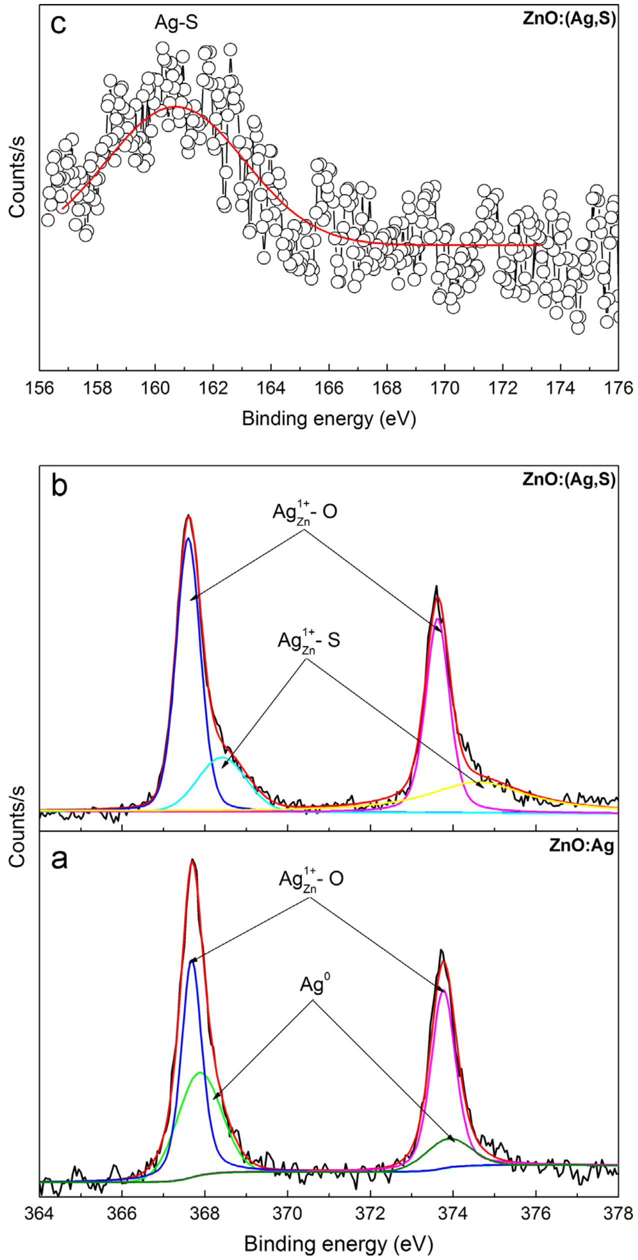

Fig. 2. XPS spectra of Ag 3d for the (a) ZnO:Ag, (b) ZnO:(Ag, S) and of S 2p for the (c) ZnO:(Ag, S).

XPS measurements were used to identify the chemical states of the Ag and S doped in ZnO as well as composition of the films. In order to clean up the surface contaminations and get accurate information about the interior of the film, the surface of the film was etched by Ar^+ ions for 60 s prior to measurement, and all XPS spectra were calibrated by C1s peak (284.6 eV). Fig. 2(a) and (b) shows the XPS spectra of the Ag 3d (Ag $3d_{5/2}$ and Ag $3d_{3/2}$) of the ZnO:Ag and ZnO:(Ag, S) films, respectively. Obviously, both the Ag $3d_{5/2}$ and the Ag $3d_{3/2}$ peaks are asymmetric, and can be disassembled into two sub-peaks by Lorentz fitting. For example, the Ag $3d_{5/2}$ peak of the ZnO:Ag can be disassembled into two sub-peaks with binding energy of 367.7 and 367.9 eV, respectively, as shown in Fig. 2(a), which are closed to the binding energies of Ag $3d_{5/2}$ of Ag_2O [19–21] and metal Ag [22], respectively. This result implies that the Ag exists in two forms of univalent ion (Ag^{1+}) and metal state in the ZnO:Ag. It is indicated that the Ag^{1+} ion located at Zn site (${Ag_{Zn}}^{1+}$) has formation energy lower than Ag at interstitial site (Ag_i) [15], therefore, it is deduced that the Ag doped in the ZnO occupies Zn site in univalent ion state and binds with O, while the metal Ag exists on the surface or in grain boundaries of the ZnO:Ag. For the ZnO:(Ag, S), the Ag $3d_{5/2}$ peak can be fitted into two sub-peaks with binding energy of 367.6 and 368.4 eV, respectively, which are closed to the binding energies of the Ag $3d_{5/2}$ of Ag_2O and Ag_2S [23,24], respectively. Meanwhile, a peak with binding energy of 160.8 eV is observed in XPS spectrum of the S 2p of the ZnO:(Ag, S), as shown in Fig. 2(c). The binding energy is much smaller than that of S $2p_{3/2}$ of S (164.15 eV) and ZnS (161.7 eV), but almost the same as that of S $2p_{3/2}$ of Ag_2S (160.7 eV) [25–27]. The results of Fig. 2(b) and (c) indicate that there exist Ag and S in the ZnO: (Ag, S), and that the Ag occupies Zn site in the form of ${Ag_{Zn}}^{1+}$ and the S occupies O site in bivalent ion state (S_O^{2-}), and some of the ${Ag_{Zn}}^{1+}$ bind with O^{2-} ion and others bind with S_O^{2-} ion. As the Ag^{1+}–S^{2-} bond has binding energy larger than Ag^{1+}–O^{2-} bond [28], hence the ${Ag_{Zn}}^{1+}$ prefers to bind with S_O^{2-} rather than O^{2-}, when Ag and S dope in ZnO simultaneously.

The concentrations of the Ag in the ZnO:Ag and ZnO:(Ag, S) are estimated by using the XPS data of Fig. 2 and following formula (1):

$$C_x = \frac{I_x/S_x}{\sum_i I_i/S_i} \qquad (1)$$

where I_x and S_x are the peak area and sensitivity factor of the selected element, respectively, and I_i and S_i are the peak area and sensitivity factor of the zinc, oxygen, sulfur or silver, respectively. The concentration of Ag in the ZnO:Ag and ZnO:(Ag, S) films (defined as $(C_{Ag}/(C_{Ag}+C_{Zn}))\times 100\%$, C_{Ag} and C_{Zn} are concentrations of Ag and Zn calculated using the formula (1), respectively) are estimated to be 2.8% and 7.5%, respectively. For the ZnO:Ag, the Ag exists in the chemical states of metal Ag and ${Ag_{Zn}}^{1+}$, and the relative content of the metal Ag (denoted as Ag^0) in the total Ag doping content is calculated to be 68.2% by using a formula of $A_{Ag^0}/(A_{Ag^0}+A_{{Ag_{Zn}}^{1+}})\times 100\%$, where the A_{Ag^0} and $A_{{Ag_{Zn}}^{1+}}$

Table 1
Electrical properties of the 450 °C-annealed ZnO, ZnO:Ag and ZnO:(Ag, S) films.

Sample	Resistivity (Ωcm)	Carrier density (cm^{-3})	Mobility ($cm^2\ V^{-1}\ s^{-1}$)	Type
ZnO	2.30	4.41×10^{17}	6.29	n
ZnO:Ag	2.65	5.80×10^{17}	4.09	n
	9.42	1.04×10^{16}	6.55×10^{1}	p
ZnO:(Ag, S)	1.73	2.44×10^{16}	1.48×10^{2}	p

are the fitted peak area of the Ag^{0} and $\mathrm{Ag_{Zn}}^{1+}$, respectively. As sensitivity factor is the same for the same shell of the same element, so the relative content is calculated by using the ratio of the fitted peak areas, as mentioned above. This result implies that most of Ag exists in the form of metal Ag in the ZnO:Ag film and only a small amount of Ag dope in the ZnO. While for the ZnO:(Ag, S), no metal Ag is detected, which is consistent with the XRD results, and all of the Ag dope in the ZnO in the state of $\mathrm{Ag_{Zn}}^{1+}$. Among the $\mathrm{Ag}^{1+}_{\mathrm{Zn}}$, 39.3% $\mathrm{Ag_{Zn}}^{1+}$ bond with $\mathrm{S}^{2-}_{\mathrm{O}}$, and 60.7% $\mathrm{Ag_{Zn}}^{1+}$ bond with O^{2-}. Obviously, the doping concentrations of $\mathrm{Ag_{Zn}}^{1+}$ in the ZnO:(Ag, S) is greatly enhanced compared to the ZnO:Ag, implying that the incorporation of S benefits for increasing the solid solubility of $\mathrm{Ag_{Zn}}^{1+}$ in ZnO.

Table 1 gives the electrical properties of the ZnO, ZnO:Ag and ZnO:(Ag, S) films annealed at 450 °C. The annealed ZnO film exhibits n-type conductivity with a resistivity of 2.30 Ω cm, an electron concentration of 4.41×10^{17} cm^{-3} and a mobility of 6.29 cm^2/Vs, which are common features for n-type ZnO deposited on Si substrate. The ZnO:Ag shows unstable conductivity, that is, some samples show n-type conduction, while others show p-type conduction in the first measurement, but changed into n-type conduction as measured repeatedly or laid in air for one day or several days, as shown in Table 1. The unstable p-type conductivity may be explain as following: when the ZnO:Ag is annealed at high temperature, some electrons in valence band can transit to the levels of the $\mathrm{Ag_{Zn}}^{1+}$ or native acceptors to generate holes, however, the amount of the hole is not abundant due to smaller doping concentration and high ionization energy of the $\mathrm{Ag_{Zn}}^{1+}$, but may be similar to that of the native electron, so the conduction type shows uncertain in the first Hall measurement. However, when the ZnO:Ag is performed Hall measurement repeatedly or is laid in air for 1 day or several days, on the one hand, most of the holes combine with electrons, resulting in decrease in amount of the hole, on the other hand, the electron in valence band jumps difficultly to the level of the acceptor at room temperature to generate new holes due to high ionization energy of the $\mathrm{Ag_{Zn}}^{1+}$ acceptors, hence the amount of the hole is much less than that of native electron, and the ZnO:Ag shows n-type conduction. Based on above analysis, it is concluded that it is difficult to prepare stable p-type ZnO by Ag mono-doping.

While the ZnO:(Ag, S) shows p-type conductivity with a resistivity of 1.73 Ωcm, a hole concentration of 2.44×10^{16} cm^{-3} and a mobility of 148 cm^2/Vs. As is known to all, the melting point of Ag_2S is 825 °C, much higher than that of Ag_2O (280 °C), so Ag^{1+}–S bond should be more stable than Ag^{1+}–O bond under annealing conditions. Hence, with the incorporation of S, more $\mathrm{Ag_{Zn}}^{1+}$ are retained in the ZnO:(Ag, S), leading to that the solid solubility of $\mathrm{Ag_{Zn}}^{1+}$ acceptor in the ZnO film is enhanced compared to the ZnO:Ag. In addition, the strong valence band offset bowing induced by the substitution of S for O can improve the level of the MVB of ZnO, so may reduce the ionization energy of the $\mathrm{Ag_{Zn}}^{1+}$ acceptor [35]. Therefore, the p-type conduction of the ZnO:(Ag,S) should be related to the increase of amount of the $\mathrm{Ag_{Zn}}^{1+}$ acceptor and the incorporation of S. It is worth noting that the mobility of the ZnO, ZnO:Ag and ZnO:(Ag, S) films are larger than that of the ZnO films grown on quartz or sapphire substrate. The high mobility is probably relevant to the high-resistance single crystal Si substrate we used. Moreover, it is found that the mobility of the p-type ZnO is much larger than that of the n-type ZnO, as shown in Table 1, suggesting that the mobility is associated with the conduction type. We guess that the high mobility of the p-type ZnO:(Ag, S) may be due to the formation of two-dimensional hole gas at the interface between the substrate and the p-type ZnO film, which will be studied in detail in our subsequent work.

In order to confirm further the p-type conduction, an I–V characteristic of a ZnO homojunction synthesized by deposition of the Al-doped n-type ZnO on the Ag–S codoped p-type ZnO layer is measured and shown in Fig. 3. The schematic structure of the ZnO p–n homojunction is shown in the upper left inset. Indium and Ni/Au electrodes are used to form Ohmic contacts to the n-type and p-type layer, respectively [29,30]. Ohmic nature of the contacts are demonstrated for both In on n-type and Ni/Au on p-type region before measurement. The *I–V* curve in Fig. 3 indicates that the homojunction shows a typical rectifying behavior, confirming the p-type conductivity of the ZnO:(Ag, S).

It is well known that time-related stability of p-type ZnO is an important issue for application of ZnO. It has been reported in many published literatures that p-type ZnO can revert into n-type ZnO once it is laid in air for several days or weeks [31–33]. Hydrogen-generated donors, light exposure, metastable acceptor defects and so on are speculated to be the possible reasons. However, in our present work, we found that the conduction type of the 450 °C-annealed ZnO:(Ag, S) had been in p-type in a period of seven months. We plot the resistivity, carrier density and hall mobility of the p-type ZnO:(Ag, S) film as a function of preservation time, as shown in Fig. 4. It is found that the variation of electrical property parameters is very small with the increasing preservation time, confirming that the p-type conduction of the ZnO:(Ag, S) film is stable.

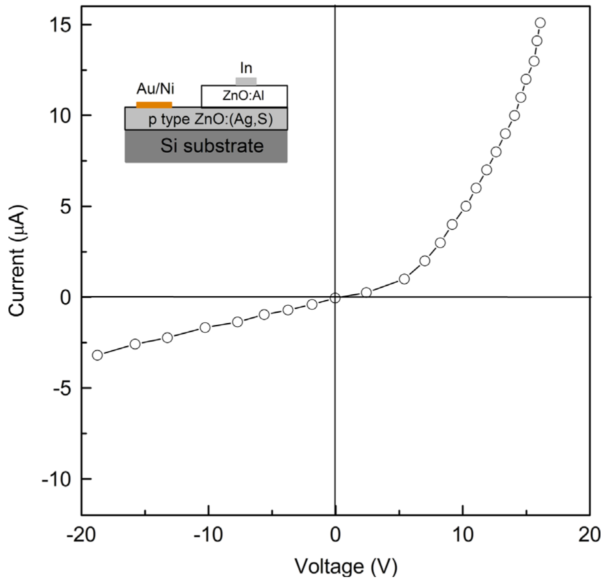

Fig. 3. *I–V* curve of the homojunction composed of Al doped n-type ZnO and Ag–S co-doped p-type ZnO. The upper left inset shows a schematic structure of the p–n homojunction.

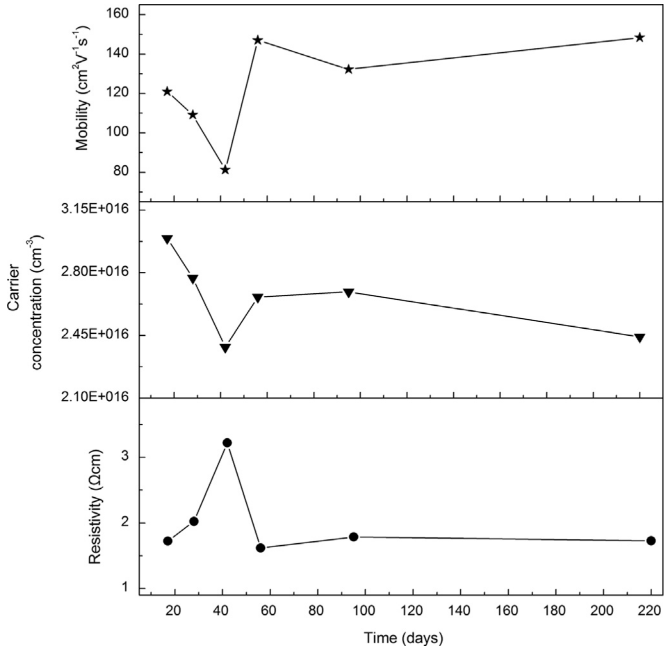

Fig. 4. The plots of the resistivity, carrier density and hall mobility of the 450 °C-annealed ZnO:(Ag, S) film as a function of time.

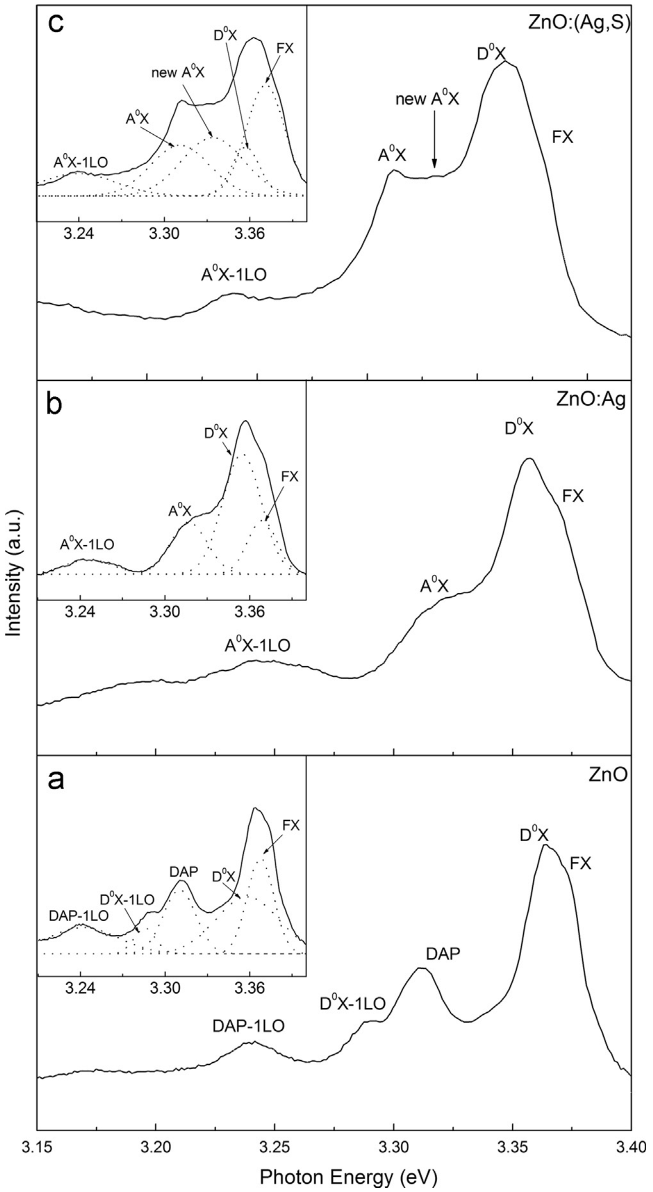

Fig. 5. Low temperature (95 K) photoluminescence spectra of the 450 °C-annealed (a) ZnO, (b) ZnO:Ag and (c) ZnO:(Ag, S) films.

To understand the stable p-type conduction mechanism of the ZnO:(Ag, S) and the effects of Ag–S codoping on electrical and optical properties of the ZnO films by comparative study, low temperature photoluminescence (PL) measurements were performed at 95 K for the ZnO, ZnO:Ag and ZnO:(Ag, S), respectively, as shown in Fig. 5. The PL spectrum of the ZnO consists of five emission peaks, located at 3.370, 3.358, 3.310, 3.286 and 3.239 eV, respectively, as shown in Fig. 5(a). The former three peaks are assigned to the free exciton (FX) recombination [34,35], the neutral donor bond exciton (D^0X) transition [36] and the donor–acceptor pair (DAP) transition [37], respectively. The peak at 3.286 and 3.239 eV exhibit phonon replicas of D^0X and DAP separated by approximately $\Delta E = 72$ meV, respectively, the ΔE is longitudinal optical phonon energy observed in ZnO [38]. For the ZnO:Ag film, as shown in Fig. 5(b), the PL spectrum consists of four peaks, located at 3.371, 3.356, 3.318 and 3.246 eV, respectively. The 3.371 and 3.356 eV peaks can be assigned to FX and D^0X, respectively, while the peak at 3.317 eV is due to the neutral acceptor bound exciton (A^0X) transition related to $Ag_{Zn}{}^{1+}$ acceptor [36]. The peak located at 3.246 eV exhibits a LO phonon replica of A^0X separated by approximate 72 meV, hence, it is denoted as A^0X-LO. It is found from the PL spectrum that small amounts of $Ag_{Zn}{}^{1+}$ acceptor exist in the ZnO:Ag, but the native donors are still dominant, resulting in n-type conductivity. Fig. 5(c) shows the low temperature PL spectrum of the ZnO:(Ag, S), revealing five peaks, located at 3.371, 3.357, 3.334, 3.312 and 3.239 eV, respectively. The peaks at 3.371 and 3.357 eV are assigned to FX and D^0X, respectively. The A^0X emission related to $\mathrm{Ag_{Zn}}^{1+}$ acceptor and its phonon replica (A^0X-LO) peaks are observed at 3.312 and 3.239 eV, respectively. It is noted that both peaks show slight red shift comparing with that of the ZnO:Ag, which is probably related to the valence band offset bowing induced by S doping. A new peak located at 3.334 eV is assigned to a new neutral acceptor bound exciton (new-A^0X) related to $\mathrm{Ag_{Zn}}^{1+}$–$\mathrm{S_O}$ acceptor induced by Ag–S codoping [35].

The ionization energies (E_A) of the $\mathrm{Ag_{Zn}}^{1+}$ and $\mathrm{Ag_{Zn}}^{1+}$–$\mathrm{S_O}$ acceptors are estimated by Haynes rules [39]:

$$E_b = \alpha E_A \tag{2}$$

where E_b is the exciton localization energy, which can be obtained from the difference in photon energy between the FX and A^0X in the PL spectra, and α is the Haynes factor. Based on the PL spectra shown in Fig. 5, the E_b of the $\mathrm{Ag_{Zn}}^{1+}$ and $\mathrm{Ag_{Zn}}^{1+}$–$\mathrm{S_O}$ are estimated to be 54 and 37 meV, respectively. By using the appropriate value $\alpha = 0.24$ [40], the ionization energies for $\mathrm{Ag_{Zn}}^{1+}$ and $\mathrm{Ag_{Zn}}^{1+}$–$\mathrm{S_O}$ acceptors are calculated to be 225 and 154 meV, respectively, suggesting that the incorporation of S can form the $\mathrm{Ag_{Zn}}^{1+}$–$\mathrm{S_O}$ complex acceptor with ionization energy smaller than that of the $\mathrm{Ag_{Zn}}^{1+}$ acceptor, which is advantageous to p-type conduction. Our previous first-principle calculation result [41] reveals that the $\mathrm{Ag_{Zn}}^{1+}$–$\mathrm{S_O}$ complex is stable with respect to the isolated $\mathrm{Ag_{Zn}}$ and $\mathrm{S_O}$ defects, and the ionization energy of $\mathrm{Ag_{Zn}}^{1+}$–$n\mathrm{S_O}$ is calculated to be 0.26 eV for $n=2$ and 0.18 eV for $n=4$, smaller than that of the $\mathrm{Ag_{Zn}}^{1+}$ in the ZnO (0.44 eV), which well explained the shallow $\mathrm{Ag_{Zn}}^{1+}$–$\mathrm{S_O}$ complex acceptor observed in the PL spectra and well supports our experimental results. The stable p-type conduction of the ZnO:(Ag, S) may be mainly attributed to contribution of the $\mathrm{Ag_{Zn}}^{1+}$–$\mathrm{S_O}$ complex acceptor.

4. Conclusions

Stable Ag–S codoped p-type ZnO films were grown on Si substrates by radio frequency magnetron sputtering and post annealing techniques. There is only one chemical state of $\mathrm{Ag_{Zn}}^{1+}$ in the ZnO:(Ag, S), compared to Ag-doped ZnO. Incorporation of S can greatly enhance the solid solubility of $\mathrm{Ag_{Zn}}^{1+}$ in ZnO. In the ZnO:(Ag, S), some of the $\mathrm{Ag_{Zn}}^{1+}$ bond with S and others with O, resulting in the existence of two kinds of $\mathrm{Ag_{Zn}}^{1+}$–$\mathrm{S_O}$ and $\mathrm{Ag_{Zn}}^{1+}$ acceptors. Moreover, it is deduced from PL measurement that ionization energy of the $\mathrm{Ag_{Zn}}^{1+}$–$\mathrm{S_O}$ complex acceptor is lower than that of the $\mathrm{Ag_{Zn}}^{1+}$ acceptor. The stable p-type conduction of the ZnO:(Ag, S) is mainly attributed to increase of the $\mathrm{Ag_{Zn}}^{1+}$ doping content and formation of shallow $\mathrm{Ag_{Zn}}^{1+}$–$\mathrm{S_O}$ complex acceptor.

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