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Formation Mechanism and Properties of In, P Codoped p-type ZnO Thin Film

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Abstract: In, P codoped ZnO [ZnO: (In, P)] films were grown on quartz by radio frequency magnetron sputtering, the ZnO target was mixed with 1.5% P_2O_5 and 0.3% In_2O_3, and the mixing gas of Ar and O_2 was used as the sputtering gas. The as-grown ZnO: (In, P) film shows insulating conduction, but n-type conductivity after annealing at 600 ℃ for 5 min, and p-type conduction after annealing at 800 ℃ for 5 min. The p-type ZnO: (In, P) has a resistivity of 12.4 Ω·cm, a carrier concentrativity of 1.6×10^{17} cm^{-3} and a Hall mobility of 3.29 $cm^2\cdot V^{-1}\cdot s^{-1}$. XRD measurement indicates that both the as-grown and annealed ZnO: (In, P) films have a preferred (002) orientation and larger (002) diffraction angles than that of undoped ZnO prepared at the same conditions, implying that both In and P occupy Zn site in the ZnO: (In, P). The XPS result confirm that the P substitutes Zn site (P_{Zn}) but not O site in the ZnO: (In, P). Therefore, it was suggested that both In and P substitute at Zn sites in the ZnO: (In, P) and the P_{Zn} combines with two Zn vacancies(V_{Zn}) to form a P_{Zn}-$2V_{Zn}$ acceptor complex, which is responsible to p-type conductivity of the ZnO: (In, P).

Key words: ZnO; codoping; RF magnetron sputtering; XPS
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1 Introduction

In the recent years, wide band gap optoelectronic research based on ZnO has been stimulated by the need for blue and ultraviolet solid-state light emitters and detectors. ZnO-based optical devices are expected to be highly efficient and practical due to the large exciton binding energy (~60 meV), the high radiation resistance, the availability of large area ZnO substrates, the amenability to wet chemical etching, and relatively low materials costs[1,2]. However, ZnO has several drawbacks, including lack of reproducible and high quality p-type material. The n-type ZnO with high carrier density is easily realized via chemical doping with group Ⅲ elements (Al, Ga, and In) or intrinsic defects[3,4]. In contrast, achieving p-type ZnO is difficult due to the relatively deep location of the ZnO valence band as well as the self-compensation effect from native donor defects, such as oxygen vacancies (V_O), zinc interstitials (Zn_i), and hydrogen. The hydrogen can easily diffuse into ZnO at moderate temperatures[5~9]. In the more recent years, many groups have reported to obtain the p-type ZnO by mono-

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doping with Ⅰ group element (Li) or Ⅴ group element (N, P, As, *etc.*) and co-doping with Ⅲ and Ⅴ group elements[10~21]. Among them, phosphorus-doped ZnO films exhibited low resistivities, high carrier concentrations and reasonable mobilities[12,13], so phosphorus is considered as good p-type dopant for ZnO, and P-doping has been studied. However, the microscopic structure of dominant acceptors in P-doped ZnO is not yet clear, and there are open questions regarding the specific doping mechanism as well as processing conditions necessary to activate the acceptor states. And it is difficult to obtain the heavy phosphorus doping ZnO film. It has been theoretically predicted that the codoping of acceptor and donor will reduce the Madelung energy[22], enhance the solubility of p-type dopant in ZnO and give rise to a shallower acceptor level in the band gap. Recently, a few literatures reported some co-doping methods, such as (In, P), (In, N), (Al, N)[23~25]. However, there is little work reported on p-type ZnO co-doped by P and In (P-In) using radio frequency magnetron sputtering technique. In this letter, p-type ZnO films codoped by In and P were prepared by radio frequency magnetron sputtering technique in the Ar-O_2 ambient, and the formation mechanism of the P, In codoping p-type ZnO was investigated.

2 Experimental Procedures

A sputtering target was prepared by sintering ZnO powder (99.99% in purity) mixed with 0.3% In_2O_3 (99.99% purity) powder and 1.5% P_2O_5 (99.99% purity) at 1 000 ℃ in air ambient. Before deposition, the quartz substrate was treated for 10 min with acetone and ethanol in an ultrasonic bath, respectively, to remove surface contamination, and then rinsed in deionized water (18.2 MΩ · cm) and blow-dried using high-purity nitrogen. The deposition chamber was evacuated to a base pressure of 5×10^{-4} Pa, and filled by a flow of mixture of Ar (99.99%) and O_2 (99.99%) with ratio of 36 and 4 sccm. A ZnO film codoped by P and In [ZnO: (In, P)] was deposited on the quartz at 500 ℃ by magnetron sputtering the target for 1 h. Prior to deposition, the target was presputtered for 10 min to remove contaminant from the surface. In order to improve crystal quality and change electric properties, the as-grown ZnO: (In, P) films were annealed in temperature ranging from 600 to 800 ℃ for 5 min.

Crystal structure of the sample was measured by using a Rigaku O/max-RA X-ray diffractometer with Cu Kα radiation (λ = 0.154 18 nm). Electrical properties were measured in the Van der Pauw configuration by a Hall effect measurement system at room temperature. Optical transmission and absorption spectra were recorded by a UV-3101PC spectrometer. The temperature-dependent PL spectra of the p-type ZnO: (In, P) film were measured in temperatures ranging from 80 K to 300 K by using an UV Labran Infinity Spectrophotometer made by Jobin Yvon, and excited by the 325 nm line of a He-Cd laser with power of 50 mW.

3 Results and Discussion

The Hall measurement results showed that the as-grown ZnO: (In, P) film behaved as insulator, but n-type semiconductor by annealing at 600 ℃ and p-type semiconductor after annealing at 800 ℃. The p-type ZnO: (In, P) films possess a resistivity of 12.4 Ω · cm, a carrier concentration of 1.6×10^{17} cm^{-3} and a Hall mobility of 3.29 $cm^2 \cdot V^{-1} \cdot s^{-1}$. To understand the formation mechanism of ZnO: (In, P), the structure and compositions of ZnO: (In, P) as well as the chemical environment of In and P in the ZnO: (In, P) were studied by XRD, XPS and EDX.

Fig. 1 (a ~ c) shows the XRD patterns of the as-grown, 600 ℃-annealed and 800 ℃-annealed ZnO: (In, P) films, respectively. It can be seen that only one diffraction peak corresponding to the (002) plane of ZnO is observed for the three films, no other peak appears, indicating that the ZnO: (In, P) films have a high (002) preferential orientation and no other phases (*e. g.*, P_2O_5, In_2O_3) are formed. It is also found that diffraction angles of (002) peak of all the three ZnO: (In, P) is larger than that of undoped ZnO prepared at the same condition as ZnO: (In, P), indicating that the lattice constant *c* of the

ZnO: (In, P) is always smaller than that of undoped ZnO, as shown in Table 1. Obviously, the decrease in lattice constant c is attributed to incorporation of In and P into the ZnO: (In, P). It is known that In should substitute for Zn site of ZnO when it incorporates into ZnO. However, ionic radius of In is 0.092 nm, larger than Zn ionic radius of 0.083 nm. So, the incorporation of In should lead to increase of the lattice constant, in disagreement with the XRD results. P is amphoteric element. It can substitute for Zn of ZnO as a P^{3+} ion, and also substitute for O of ZnO as P^{3-} ion. However, P^{3-} ionic radius is 0.186 nm, larger than O^{2-} ionic radius of 0.135 nm, while P^{3+} ionic radius is 0.044, smaller than Zn^{2+} ionic radius. Therefore, substitution of P for Zn should result in decrease of the lattice constant c, in agreement with the XRD results. EDX measurement indicates that concentration of P in the ZnO: (In, P) is 1.5%, and the concentration of In is about 0.3%, as shown in Table 2. Since concentration of P is much larger than that of In in the ZnO: (In, P), so codoping of In and P makes lattice constant decrease, though substitution of In for Zn can increase lattice constant c. This conclusion is consistent with the XRD results mentioned above.

Fig. 1 XRD patterns of as-grown ZnO: (In, P) film (a) and the films annealed at 600 ℃ (b) and 800 ℃ (c), respectively.

Table 1 2θ diffraction angles and lattice constant c of In-P codoped ZnO and undoped ZnO

Annealing temperature (℃)	ZnO: (In, P)		ZnO	
	2θ(°)	c(nm)	2θ(°)	c(nm)
As-deposited	34.44	0.520 4	34.39	0.521 6
600	34.49	0.519 7	34.41	0.521 2
800	34.60	0.518 1	34.54	0.519 4

Table 2 Compositions of the 800 ℃-annealed ZnO: (In, P) measured by EDX

Element	O	P	In	Zn
%	29.50	1.50	0.32	48.68

In order to confirm chemical environment of In and P in the ZnO: (In, P), XPS measurements were performed for the three samples, which have similar XPS spectra. Fig. 2 illustrates the typical XPS spectra of the ZnO: (In, P) annealed at 800 ℃. Fig. 2 (a) shows $P2p_{1/3}$ XPS spectrum, indicating that the binding energy of the $P2p_{1/3}$ is 133.3 eV, which is different from the binding energy of 135.5 eV observed in pure P_2O_5. This implies that no P_2O_5 clusters exist in the ZnO: (In, P) and the P of the P_2O_5 is incorporated into ZnO films during growth process, in agreement with XRD results mentioned above. It is reported that binding energy of $P2p_{1/3}$ is 128.3 eV in Zn_3P_2 and 129.8 eV in ZnP_2, smaller than the value in ZnO: (In, P), implying that no Zn-P bond is formed in the ZnO: (In, P) film, that is, P does not substitute O. Onyiriuka[26] investigated chemical environment of P in the zinc phosphate glass composed mainly of ZnO and P_2O_5 by XPS, and found that binding energy of $P2p_{1/3}$ in P—O—P and P—O—Zn bonds is in the rangs of 133.3 to 133.8 eV, which is closed to the binding energy of $P2p_{1/3}$ in the ZnO: (In, P). Furthermore, the binding energy of $P2p_{1/3}$ in the ZnO: (In, P) is also closed to that in $InP_{0.23}O_{2.6}$ (133.3 eV). Fig. 2 (b) shows the XPS spectrum of $In3d_{5/2}$, the binding energy of the $In3d_{5/2}$ is 444.4 eV, which is close to that of In—P bond (444.4 eV) and In—O bond (444.3 eV). This result indicates that In substitute for Zn site in the ZnO: (In, P) and bonds with O or P. Taking ZnO structure as well as the XPS and XRD results into account, it is deduced that both P and In substitute at Zn site and P does not occupy O site in the ZnO: (In, P).

It is well known that substitutional P and In at Zn sites should form donor defects P_{Zn} and In_{Zn}, resulting in n-type conduction. However, the ZnO: (In, P) annealed at 800 ℃ behaves as p-type conductivity, implying that the p-type conductivity comes from other form of acceptor.

Fig. 2　XPS spectra of P2p(a) and In3d (b) of the In-P co-doped ZnO films

Lee *et al.* investigated electron structure of various P-related defects in ZnO using first-principle pseudopatiental calculation, indicating that substitutional P at a O site can form a deep acceptor P_O with energy of 620 ~ 900 meV, so it is difficult to be responsible for p-type semiconductor of P-doped ZnO[27]. While the P_{Zn} can combine with two Zn vacancies V_{Zn} to form a stable shallow acceptor complex (P_{Zn}-$2V_{Zn}$) under O-rich condition, which can compensate native donor defects, such as O vacancies and Zn interstitials, and realize the P-doped ZnO p-type conductivity. In the present work, both EDX and XPS measurements indicate that the annealed ZnO: (In, P) is O-rich, and as mentioned above, the P substitutes at a Zn site. Therefore, the p-type conductivity may be due to contribution of P_{Zn}-$2V_{Zn}$ complex acceptors. Since concentration of P (1.5%) is much larger than that of In (0.3%), the P_{Zn}-$2V_{Zn}$ complex acceptors is enough to compensate the effect of In_{Zn} donors.

As mentioned above, the as-grown, 600 ℃-annealed and 800 ℃-annealed ZnO: (In, P) show the insulator, the n-type and the p-type semconductor, respectively, therefore, annealing temperature is important for obtaining p-type ZnO: (In, P). The insulation or high resistivity is a common feature of as-grown ZnO prepared by magnetron sputtering technique, it is usually attributed to poor crystal quality. The n-type 600 ℃-annealed ZnO: (In, P) has resistivity of 0.24 Ω · cm, carrier concentration of 6.4×10^{19} cm^{-3} and Hall mobility of 0.43 $cm^2 \cdot V^{-1} \cdot s^{-1}$. The high carrier concentration implies that there are a lot of donor defects or impurities in the 600 ℃-annealed ZnO: (In, P). As we known, the main native donor defects are O vacancies (V_O) and Zn interstitials (Zn_i) in the ZnO, and donor impurities are main H atom. PL measurement indicates that the intensity of the emission bands located at visible range and related to V_O and Zn_i are very weak for the ZnO: (In, P), as shown in inset of Fig. 3, implying that the amount of the V_O and Zn_i are small. That is in agreement with EDX results, which show that the ZnO: (In, P) is O-rich. Since the insulation of as-grown ZnO: (In, P) transforms into n-type conductivity after annealing at 600 ℃, as well as p-type conductivity as annealed at 800 ℃, but H atom can escape from ZnO at above 500 ℃ and the amount of H atoms escaped increases with increasing temperature, we deduced that the P_{Zn}-$2V_{Zn}$ acceptors are mainly compensated by H donors. When the ZnO: (In, P) is annealed at 600 ℃ for 5 min, only a small amount of H escape from ZnO due to low temperature and short time. There still remain a lot of H donors in the ZnO: (In, P), which is enough to compensates P_{Zn}-$2V_{Zn}$ acceptor and make the ZnO: (In, P) conductivity in n-type. However, as annealing temperature increases to 800 ℃, most H atoms may leave the ZnO: (In, P), there is no enough H donors to compensate the P_{Zn}-$2V_{Zn}$ acceptors, resulting in p-type conduction of the ZnO: (In, P).

Fig. 3 shows low-temperature (80 K) PL spectrum of the p-type ZnO: (In, P). It can be divide into five sub-bands by using Gaussian fitting method, which are located at 3.366, 3.317, 3.267, 3.225 and 3.154 eV, respectively, they are different

Fig. 3　80 K PL spectrum of the p-type ZnO: (In, P) obtained at an annealing temperature of 800 ℃. Inset is the PL spectrum in wider photon energy range

from PL spectrum of P-doped p-type ZnO reported previously[28]. More detail fitting parameters are given in Table 3. The 3.366 eV subband is due to recombination of neutral donor-bound exciton (D^0X), and the subband at 3.317 eV comes from an electronic radiative transition from conduction band to neutral acceptor level (eFA). The subband at 3.267 eV is not observed in P-doped ZnO reported previously. Variable-temperature PL measurement indicates that the 3.267 eV subband disappear at 113 K, as shown in Fig.4, and its full-width at half maximum (FWHM) is small, implying that it may be related to a shallow donor, such as, a donor formed by substitutional In at Zn site. The origin of the subband at 3.267 eV need further study in experiment. The subband at 3.225 eV has close photon energy to donor-acceptor pair (DAP) band observed in P-doped ZnO and In-P codoped ZnO, and has a wider FWHM, as shown in Table 3. It is attributed to recombination of a DAP. Since the difference in photon energy between subbands at 3.225 eV and 3.154 eV is 71 meV, close to longitudinal optical-phonon energy, so the 3.154 eV band is due to replicas of the 3.225 eV band.

Fig.4 Temperature-dependent PL spectra of the p-type ZnO:(In,P) measured at temperatures ranging from 80 to 300 K

Table 3 Parameters of sub-bands obtained by Gaussian fitting of 80 K PL of the p-type ZnO:(In,P)

Subband No.	Photon energy (eV)	FWHM (eV)	Area
1	3.366	0.029	69
2	3.317	0.043	290
3	3.267	0.041	107
4	3.225	0.135	787
5	3.154	0.219	229

The temperature dependent eFA band centered at 3.317 eV can be well described as the following:

$$\mathrm{EFA}(T) = E_g(T) - E_A + kT/2 \qquad (1)$$

where $E_g(T)$ is the temperature-dependent band gap, and follows the Varshni-type equation[24], E_A, k, and T are acceptor level, Boltzmann constant, and temperature, respectively. By fitting the energies of the eFA band at different temperatures with Eq. (1), as shown in Fig.5, E_A is calculated to be 130 meV.

Fig.5 PL peak energies as a function of temperature for the p-type ZnO:(In, P). The dots are experimental data and the solid lines are fitting curves

4 Conclusion

A insulating P,In codoped ZnO film was grown on quartz by radio frequency magnetron sputtering technique with ZnO(P,In) alloy as target and mixture gas of Ar and O_2 as sputtering gas. A p-type ZnO:(In,P) thin film with resistivity of 12.4 Ω·cm, a carrier concentration of 1.6×10^{17} cm^{-3} and a Hall mobility of 3.29 $cm^2\cdot V^{-1}\cdot s^{-1}$ was fabricated by annealing the insulating as-grown ZnO:(In,P) at 800 ℃ for 5 min. XRD and XPS measurements indicate that both In and P occupy Zn site in the ZnO:(In,P), it is suggested that the P_{Zn} combines with two Zn vacancies(V_{Zn}) to form a P_{Zn}-$2V_{Zn}$ acceptor complex, which is responsible to p-type conductivity of the ZnO:(In,P) annealed at 800 ℃. PL measurements indicate that the 80 K PL spectrum consists of bands located at 3.366, 3.317, 3.267, 3.225 and 3.154 eV, respectively. The former two bands are due to D^0X and eFA emissions, respectively,

the latter two bands are attributed to DAP emission and its replicas. The band at 3.267 eV is related a shallow donor. The P_{Zn}-$2V_{Zn}$ acceptor complex level was estimated to be 130 meV above the valence band maximum.

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铟磷共掺杂p型氧化锌薄膜形成机理和性质

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摘要: 利用射频磁控溅射在石英衬底上生长出铟磷共掺氧化锌薄膜(ZnO: In, P),所用靶材为掺杂五氧化二磷(P_2O_5)和氧化铟(In_2O_3)的氧化锌(ZnO)陶瓷靶,掺杂质量分数分别为1.5%和0.3%,溅射气体为Ar和O_2的混合气体。原生ZnO薄膜是绝缘的, 600 ℃退火5 min后导电类型为n型,而800 ℃退火5 min后为p型。p型ZnO薄膜的电阻率、载流子浓度和霍尔迁移率分别为12.4 Ω·cm, 1.6×10^{17} cm^{-3}和3.29 $cm^2\cdot V^{-1}\cdot s^{-1}$。X射线衍射测量结果表明所有样品都只有(002)衍射峰,并与相同条件下生长的未掺杂ZnO相比向大角度方向偏移,意味着In和P都占据Zn位。XPS测试结果表明在共掺ZnO薄膜中P不是取代O而是取代Zn。因此,铟磷共掺ZnO薄膜中,In和P都取代Zn,并且P_{Zn}与2个锌空位(V_{Zn})形成P_{Zn}-2V_{Zn}复合受主,薄膜表现为p型。

关 键 词: 氧化锌; 共掺; 射频磁控溅射; XPS

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