Preparation of ZnO:Al,F powder and its electrical property

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As a kind of interesting transparent conductive material, aluminum and fluorine codoped ZnO (ZnO:Al,F, FAZO) powder which is necessary for obtaining sputtering target was prepared for the first time by improved solid state synthesis. The influences of mixing way of raw materials, doping elements, calcining temperature and doping concentration on electrical property of FAZO were investigated in detail. The measurement results show improved solid state synthesis and codoping are in favor of low resistivity. When calcining temperature was at 1100℃ and the doping concentrations of Al and F were both 1.5at%, FAZO powder has the lowest resistivity.

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1. Introduction

Zinc oxide (ZnO) is a ⅡB-ⅥA wide band-gap semiconductor with hexagonal wurtzite crystal structure. It is a kind of important, stable and nontoxic material due to its excellent optoelectronic properties [1-7]. But pure ZnO cannot meet the requirements for optoelectronic devices application well. So it must be doped with other elements designedly to regulate carrier concentration. As a result, the electrical property of ZnO is improved. To date, there are many research works about doped ZnO such as aluminum doped zinc oxide (ZnO:Al, AZO) [8-10] and fluorine doped zinc oxide (ZnO:F, FZO) [11-12]. Doping limit issue of ZnO is 3 wt.% usually. Both AZO and FZO thin films have been applied in many optoelectronic devices such as solar cells and flat panel displays because of their low resistivity and high transparency in the visible wavelength range. The conducting mechanism of AZO is that Al^{3+} replaces Zn^{2+}, carrier concentration increases and the resistivity of ZnO thin film decreases. Compared with AZO, F^- in FZO replaces O^{2-}, electron concentration increases because of electron releasing from every F^- incorporated into matrix lattice. Regarding the difference of conducting mechanism between AZO and FZO, aluminum and fluorine codoped ZnO (ZnO:Al,F, FAZO) thin film should be of lower resistivity through incorporating the benefits of both dopants. Therefore, some researchers studied the electrical property of FAZO thin film and found that it had high conductivity indeed [13-14]. All of researches were carried out around thin films.

Deposition technologies of thin film include sputtering, CVD, sol-gel, and so on [15-17]. Among these, sputtering has been applied widely for film preparation [18-20]. Its mechanism is that ions with high energy which come from gas ionization bombard target. Atoms escape from surface of target and then are deposited on substrate. According to this, the quality of target must affect the properties of thin films. Furthermore, considering that the target is obtained with compacted powders by calcining, the properties of powders would influence the quality of target so that the properties of thin films maybe changed [21]. Hence, it is important to study the properties of powders.

There is no report about studying on properties of FAZO powder to date. In this paper, FAZO powder was prepared by improved solid state synthesis. The influences of mixing way of raw materials, doping elements, calcining temperature, doping concentration on electrical property of FAZO were investigated in detail.

2. Experiment

ZnO was used as matrix. Aluminum nitrate nanohydrate [$Al(NO_3)_3 \cdot 9H_2O$] and ammonium fluoride (NH_4F) were used as aluminum and fluorine sources, respectively. ZnO:Al,F (Al:1.5at%, F:1.5at%) powders were prepared by improved solid-state synthesis and traditional solid-state synthesis. The difference between these two synthesis methods was in raw materials mixing way. Specifically, for the former, the dopants were dissolved in ethanol, after that ZnO was added into this solution, stirred fully and then the slurry was obtained.

These steps were called as liquid mixing. The slurry was dried at 100 °C in oven, ground and pressed to be tablets. At last, the tablets were calcined at 700, 900, 1100 °C for 1h, respectively. For the later, except that all of raw materials were mixed by manual grinding, other steps were same to the former. In addition, to studying the effects of doping elements and doping concentration on electrical property of FAZO, AZO(Al:3at%), FZO(F:3at%), FAZO (Al:1.5at%, F: 1.5at%) and FAZO (Al:3at%, F: 3at%) were prepared.

The crystal structure of the FAZO powder was analyzed by X-ray diffraction (XRD) using a Empyrean X'pert diffractometer with Cu radiation (λ=0.1506 nm). The square resistances ($R_□$) of tablets were measured at room temperature by Loresta EP MCP-T360 four-point probe. The thicknesses (d) of sintered tablets were measured by vernier caliper. The resistivity (ρ) was obtained by calculation according to the formula: $\rho = R_□ \cdot d$.

3. Results and discussion

3.1 Raw materials mixing way

For the sake of effect investigation of raw materials mixing way on electrical property of FAZO (Al:1.5at%, F: 1.5at%), different samples were prepared by traditional and improved solid-state synthesis, respectively. Considering that the calcining temperature of ZnO:Al powder which was studied widely is ≧ 1100℃ usually, we chose this temperature value in experiments. The values of calcining temperature, $R_□$, d and ρ are shown in Table 1.

Table 1. The values of calcining temperature, R□, d and ρ of samples prepared by different methods.

Methods	Calcining temperature（℃）	$R_□$(10^4Ω/□)	d(cm)	ρ(10^4Ω·cm)
Improved	1100	0.227	0.60	0.1362
Traditional	1100	0.453	0.61	0.2763

In order to make comparison obviously, the relation between raw materials mixing way and resistivity of samples is shown in Fig. 1. It can be found that ρ of sample prepared by traditional method is twice as many as that of sample prepared by improved method. This indicates the electrical property of sample synthesized by improved method is better. It is attributed to uniform dispersion of the dopants in matrix. When $Al(NO_3)_3 \cdot 9H_2O$ and NH_4F were dissolved in ethanol, they were ionized and existed as ionic state. Al^{3+} and F^- would come into the interspaces among ZnO particles. They adsorbed on the surface of ZnO. This reduced the energy needed which doping ions came into the matrix lattice and made effective doping more easily [22]. As a result, improved solid-state synthesis is better for obtainment of lower resistivity than the traditional. Hence, other experiments were carried out by improved solid-state synthesis method.

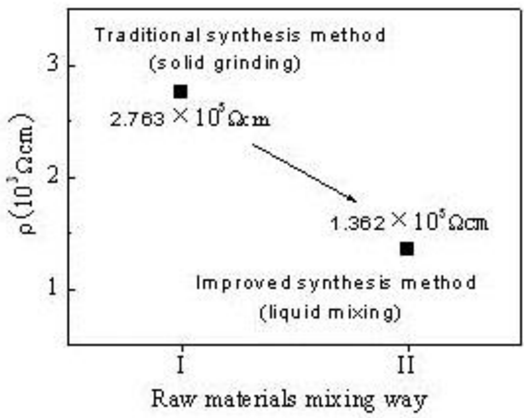

Fig. 1. The effect of raw materials mixing ways on electrical properties of samples.

3.2 Doping elements

Some reports about FAZO thin film showed electrical property of codoped sample was better than that of mono-doped sample [13,23]. According to this, it is deduced that the electrical property of FAZO powder should has the same phenomenon with that of thin film. For validation, mono-doped [AZO (Al: 3 at%), FZO (F: 3 at%)] and codoped [FAZO(Al: 1.5at%, F: 1.5at%)] samples were prepared by improved method calcined at 1100℃ for 1h.

The XRD patterns of three samples are shown in Fig. 2. All the powders show three strongest diffraction peaks located at 2θ of 31.7 °, 34.4 ° and 36.2 ° in order. It indicates that all the samples have polycrystalline hexagonal wurtzite structure [24]. The results reveal that the dopants Al and F do not change the hexagonal wurtzite structure of ZnO matrix. No characteristic peaks related to compounds of Al and F phase are found.

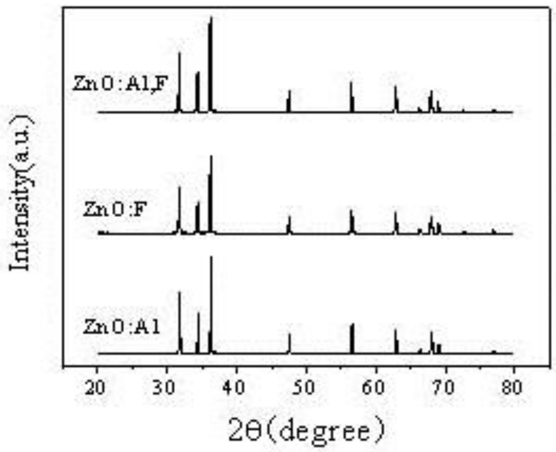

Fig. 2. XRD patterns of mono-doped and codoped samples calcined at 1100 ℃.

The $R_□$, d and ρ values of ZnO doped with different elements (AZO, FZO, FAZO) are shown in Table 2. In order to make comparison obviously, the resistivity ρ of these samples are shown in Fig. 3. Under the same synthesizing conditions, the resistivity relation of three samples is as follows: AZO (Al: 3 at%) > FZO (F: 3 at%) > FAZO(Al: 1.5at%, F: 1.5at%). The conducting mechanisms of AZO and FZO are doping ions replace matrix lattice ions. The radius of F^- is similar to radius of O^{2-}, so that O^{2-} can be replaced by F^- easily. This is the reason for AZO (Al: 3 at%) > FZO (F: 3 at%). Furthermore, the benefits of both doping elements are integrated and this results in the lowest resistivity of FAZO(Al: 1.5at%, F: 1.5at%).

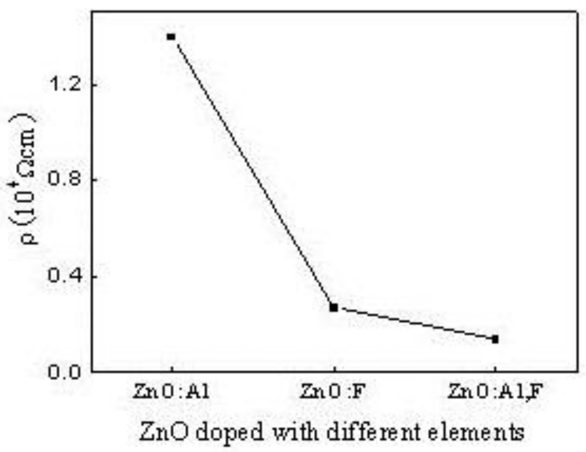

Fig. 3. The effect of doping elements on electrical properties of samples.

Table 2. The values of R□, d and ρ of mono-doped and codoped samples calcined at 1100 ℃.

ZnO doped with different elements	$R_□(10^4Ω/□)$	d(cm)	$ρ(10^4Ω·cm)$
ZnO:Al (3 at%)	2.25	0.62	1.395
ZnO:F (3 at%)	0.453	0.59	0.2673
ZnO:Al,F (Al: 1.5at%, F: 1.5at%)	0.227	0.60	0.1362

Table 3. The values of R□, d and ρ of FAZO(Al: 1.5at%, F: 1.5at%) calcined at different temperatures.

Calcining temperature (℃)	$R_□$ $(10^4Ω/□)$	d(cm)	$ρ(10^4Ω·cm)$
700	78	0.58	45.24
900	4.99	0.60	2.994
1100	0.227	0.60	0.1362

3.3 Calcining temperatures

Sputtering target can be obtained with compacted powder by calcining. Calcining temperature would have effect on the quality of target. FAZO(Al: 1.5at%, F: 1.5at%) tablets were calcined at 700, 900, 1100 ºC for 1h, respectively. The $R_□$, d and ρ values of all samples are shown in Table 3.

In order to make comparison clearly, Fig. 4 shows the resistivity of samples as a function of calcining temperature. Under the same synthesizing conditions, the resistivity decreases with the increasing calcining temperature. FAZO calcined at 1100 ºC has the best electrical property. One reason is the particles sizes are smaller at the lower calcining temperature. So the carriers are scattered by grain boundary heavily and mobility of carriers is lower so that sample has higher resistivity. With the increasing of calcining temperature, the particles grow to the bigger. The carrier scattering decreases and mobility increases so that the resistivity decreases. The other reason is the compact density of tablets varies with the calcining temperature. The densities were measured using Archimedes method. The values are $3.2g/cm^3$ (700 ºC), 3.9 g/cm^3 (900 ºC), $4.6g/cm^3$ (1100 ºC). The higher calcining temperature used, the higher density tablets have. The higher density tablets have, the higher mobility carriers have.

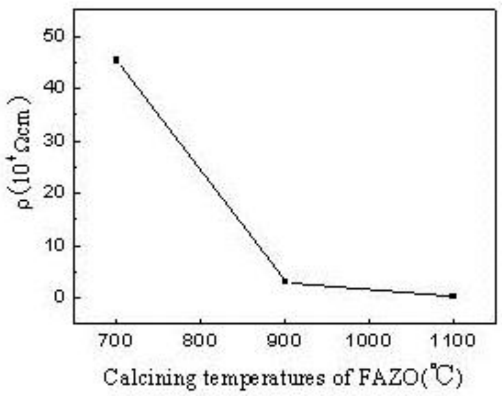

Fig. 4. The effect of calcining temperature on electrical properties of samples.

3.4 Doping concentration

In order to investigate the effect of doping concentration on resistivity, FAZO(Al: 1.5at%, F: 1.5at%) and FAZO(Al: 3at%, F: 3at%) were prepared. The $R_{\square}$, d and ρ values are shown in Table 4.

Table 4. The values of R□, d and ρ of FAZO with different doping concentration.

FAZO with different doping concentration (at%)	Calcining temperature（℃）	$R_{\square}$（$10^4\Omega/\square$）	d(cm)	ρ($10^4\Omega\cdot$cm)
Al: 1.5at%, F: 1.5at%	1100	0.227	0.60	0.1362
Al: 3at%, F: 3at%	1100	0.408	0.61	0.2489

Acorrding to Table 4, resistivity of the former is lower than that of the later. Resistivity is in inverse proportion to the product of carriers concentration and mobility, This relation is governed by equation: $1/\rho = ne\mu$, where n is carriers concentration, e is electron charge, μ is mobility. When doping concentration reaches a certain value, it has almost no effect on carriers concentration [25]. But the ionized impurity scatter would be enhanced with increased doping concentration, which makes mobility decrease. Therefore, resistivity is increased.

4. Conclusions

Aluminum and fluorine codoped ZnO (ZnO:Al,F, FAZO) powder was prepared by improved solid state synthesis for the first time. The mixing way of raw materials in this synthesis method is good for uniform dispersion of dopants. In addition, the influences of doping elements, calcining temperature and doping concentration on electrical property of FAZO powder were discussed. XRD patterns of either mono-doped or codoped samples show hexagonal wurtzite structure without any other diffraction peaks corresponding to the compounds of Al and F. FAZO has lower resistivity than both AZO and FZO owing to the benefits integration of both doping elements. The higher calcining temperature is in favor of the lower resistivity of FAZO. The appropriate doping concentration is 1.5at% for Al and F.

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