Photoelectric and photocatalytic properties of ZnO:Ga powders prepared by sol-gel method

WEIWEI JIANG*, SHIMIN LIU, YING WANG, HUALIN WANG, NAN WANG, WEIPING CHAI
School of Materials Science and Engineering, Dalian Jiaotong University, Dalian 116028, China
Engineering Research Center of Optoelectronic Materials and Devices, Education Department of Liaoning Province, Dalian 116028, China

As a kind of interesting transparent conductive material which is necessary for obtaining sputtering target and photocatalyst, Ga doped ZnO (ZnO:Ga, GZO) powders were prepared by sol-gel successfully. The influence of gel calcining temperature on photoelectric of sputtering target and photocatalytic properties of powders was investigated in detail at the first time. The measurement results show GZO has a hexagonal wurtzite structure. All of GZO powders have good conductivity, absorption in UV wavelength range and photocatalytic activity. GZO which is got when the gel was calcined at 400℃ has the best photoelectric properties and photocatalytic activity under UV light radiation. These results affords research base for the application of GZO in photoelectron and environmental depollution fields.

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Keywords: ZnO:Ga, Powder, Calcining temperature, Photoelectric property, Photocatalytic property

1. Introduction

In modern society, the traditional energies will be depleted. So many new energies have been developed. Among them, solar energy is used widely already and solar cell is the typical representative. Transparent conductive oxide (TCO) layer in the structure of solar cell acts as an important role. Indium tin oxide (ITO), which is an old kind material of TCO, is of high cost although has been industrialized. Al-doped ZnO (AZO) [1-3] as the appropriate substitute for ITO are researched widely due to its low cost and nontoxic but its conductivity is not very well. Considering that Ga and Al all belong to ⅢA, Ga-doped ZnO (GZO) causes researchers' interest. According to research results, the atomic number of Ga is 31 and Al's is 30, the radiuses of Ga^{3+} and Zn^{2+} are nearly same ($R(Zn^{2+})\approx0.74$Å, $R(Ga^{3+})\approx0.62$ Å), the bong lengths of Ga-O (1.92A) and Zn-O (1.97A) are also nearly same. These three data-groups make it sure that the introduction of Ga to ZnO matrix cannot cause crystal lattice distortion obviously although high doping concentration. So Ga is a king of n-type valid dopant. Moreover, Ga atom has the higher chemical stability than Al atom. The above merits bring attention for GZO but all of researches were carried around thin films [4-9]. As we all know, thin film deposition technologies include sputtering, CVD, sol-gel, and so on. Among these, sputtering has been applied widely for film production. Its mechanism is that ions with high energy which come from gas ionization bombard target, atoms escape from surface of target and then deposited on substrate. According to this, the quality of target must affect the properties of thin films. Furthermore, considering that the target can be obtained through compacted powders and then sintered, the properties of powders influence the quality of target so that the properties of thin films maybe changed. Hence, it is important to study the properties of powders.

At the same time, another application of solar energy is the gain of environment decontamination through photocatalysis. GZO should be has photocatalytic activity due to high photocatalytic activity of ZnO [10-11].

Up to now, there is no report about studying on photoelectric and photocatalytic properties of GZO powders to the best of our knowledge. In this paper, GZO powders were prepared by sol-gel method successfully. The influence of gel calcining temperature on photoelectric and photocatalytic properties of GZO was investigated in detail at the first time.

2. Experiment

Zinc nitrate nanohydrate [$Zn(NO_3)_2 \cdot 6H_2O$] and gallium nitrate nanohydrate [$Ga(NO_3)_3$] were used as raw materials. Firstly, 9.45g $Zn(NO_3)_2 \cdot 6H_2O$ was put into deionized water and stirred until the solution became transparent. Then 0.3825g $Ga(NO_3)_3$ was weighed according to stoichiometric ratio R_{at} (Ga : Zn) =2 at% and

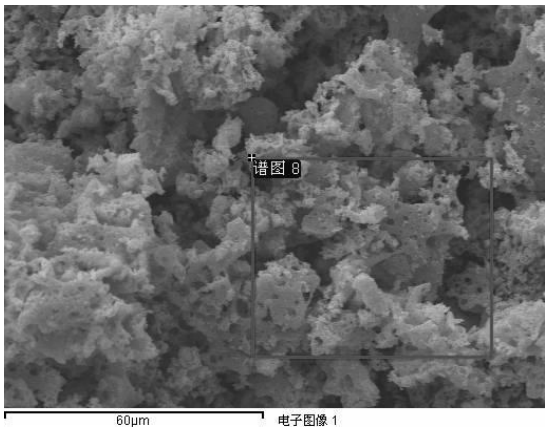
added to the front solution. Moreover, 50ml polyvinyl alcohol solution which contains 1g polyvinyl alcohol powder was added at rate of 20 drops per minute to this solution as stabilizer too. The mixed solution was stirred fully for 0.5h with heating at 80 °C to get the sol. The sol was dried at 150 °C in oven for 6h to be gel, ground and devided into three which was calcined at 400, 600, 800 °C for 2h, respectively. At last, three GZO samples were obtained.

The crystal structures of the GZO powders were analyzed by X-ray diffraction (XRD) using Empyrean X'pert diffractometer with Cu radiation (λ=0.1506 nm). The morphology of the GZO powders was observed by JEOL JSM-6360LV scanning electron microscopy (SEM). Optical properties of the GZO powders were performed using a U-3310 ultraviolet-visible spectrophotometer with an integrating sphere. To study the photoelectric properties of GZO powders, they must be pressed into tablets and then calcined at 1100℃. The square resistance ($R_{□}$) of tablets was measured at room temperature by a Loresta EP MCP-T360 four-point probe. The thickness (d) of sintered tablets was measured by vernier caliper. The resistivity (ρ) was obtained by calculation according to the formula: $\rho = R_{□} \cdot d$. To study the photocatalytic properties of GZO powders, 0.1g powder was get out from every sample, put into 20ml methyl orange solution which concentration is 0.01g/L. Then the solution was dispersed by ultrasonic for 0.5h to reach to adsorption equilibrium and radiated under UV-light source which centre wavelength is 254nm for 8h. The distance between UV lamp and containers is 10cm. After this, the absorption spectra of methyl orange solution were measured with U-3310 ultraviolet-visible spectrophotometer every two hours.

3. Results and discussion

3.1 Structural properties

The components of sample were analyzed through EDS result which is shown in Fig. 1. It shows Ga was doped into ZnO successfully. Au is from the process of gold plating for sample preparation. The XRD patterns of GZO powders prepared by sol-gel but gel calcined at different temperatures are shown in Fig. 2. All the powders show three strong diffraction peaks located at 2θ of 31.7º, 34.4º, 36.2º which correspond to the (100), (002) and (101) peak, respectively. Compared with PCPDF#65-3411, it indicates that all the GZO powders have a polycrystalline hexagonal wurtzite structure. The results reveal that the dopant Ga does not change the hexagonal wurtzite structure in the GZO powder. And no characteristic peaks related to Ga compounds phase are found. Moreover, crystal particle sizes of three samples are calculated by Scherrer equation. With increasing calcining temperature, the sizes are 30.23nm, 32.55nm, 35.53 nm orderly.



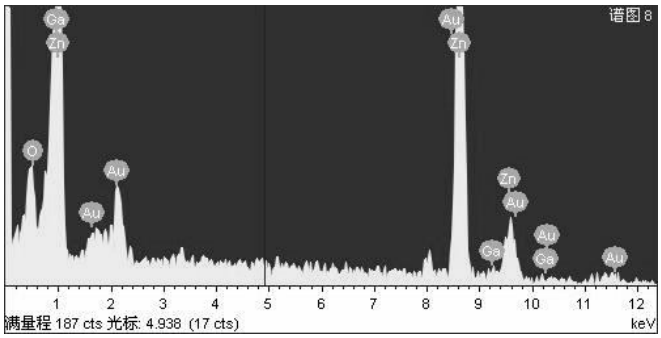


Fig. 1. EDS of GZO powder prepared by sol-gel but gel calcined at 400 ℃.

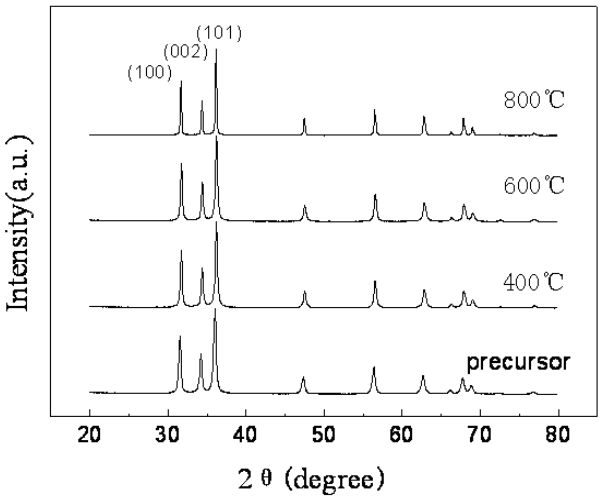
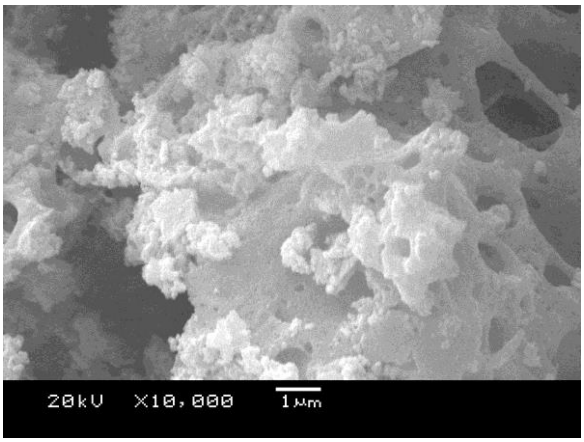


Fig. 2. XRD patterns of GZO powders prepared by sol-gel but gel calcined at different temperatures.

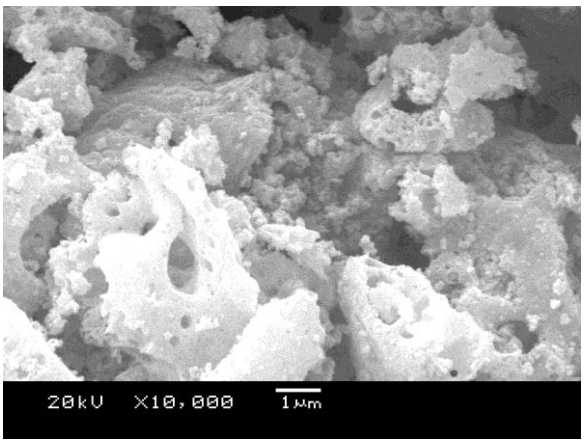
3.2 Morphology

SEM micrographs of GZO powders prepared by sol-gel but gel calcined at different temperatures are shown in Fig. 3. In Fig. 3(a), powder has gel net structure accompanied with a few of bigger secondary particles. It is told that secondary particle size is very small. In Fig.

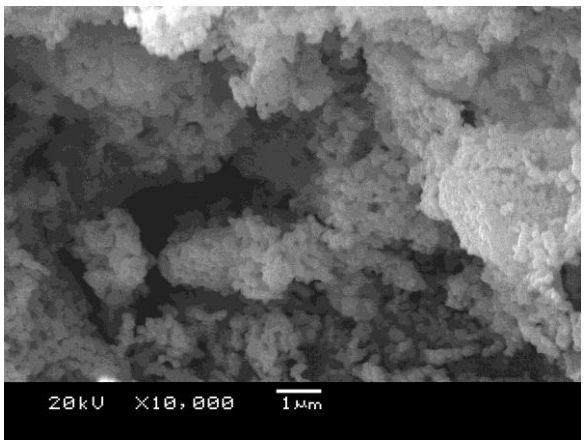
3(b), gel net structure disappears gradually and the number of big particles increases. In Fig. 3(c), there is no gel net structure but big particles. All of these show that secondary particles sizes increases with increasing of gel calcining temperature. High calcining temperature is beneficial to growth of crystal and particle aggregation.



(a) 400 °C



(b) 600 °C



(c) 800 °C

Fig. 3. SEM micrographs of GZO powders prepared by sol-gel but gel calcined at different temperatures (a)400 °C,(b)600 °C ,(c)800 °C.

3.3 Electrical properties

Sputtering target can be obtained through compacted powders and then sintered. Synthesis condition of powders must have effect on the quality of target. GZO gel was calcined at 400, 600, 800 °C for 2h, respectively, and then compact the powders to obtain tablets. At this stage, the resistivity of three tablets exceeds the measure limit of four-point probe. GZO tablets were sintered at 1100 °C for 2h. It is shown in Fig. 4 that the resistivity of samples changes with gel calcining temperatures. Under the same other synthesizing conditions, the resistivity increases with the increasing of gel calcining temperatures. GZO tablet which is got when the gel was calcined at 400℃ has the best electrical property. This is because that the secondary particles sizes are smaller than the other two seen from Fig. 3 so that the tablet is the densest one after sintering. Compact texture is beneficial to that carriers can transfer easily. Moreover, it can be found from Fig. 4 that the increasing extent of resistivity between the two samples which gel calcined at 400 °C and 600 °C is smaller than that between 600 °C and 800 °C. The growing extent of secondary particles increases with increasing of gel calcining temperature. So the secondary particles grow up more quickly when gel calcining temperature increases from 600 °C to 800 °C than that increases from 400 °C to 600 °C. The larger the secondary particles are, the worse the compactness is.

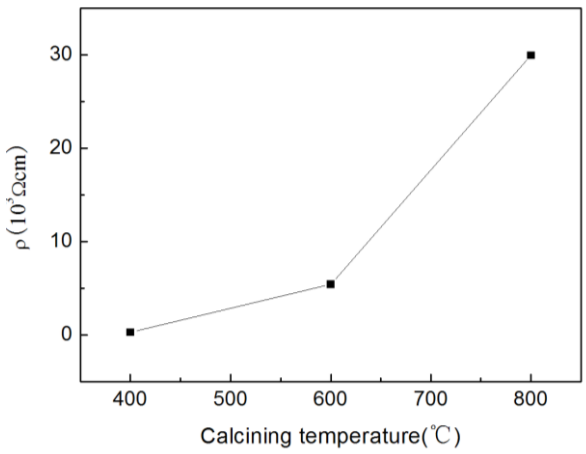


Fig. 4. Resistivity of GZO powders prepared by sol-gel but gel calcined at different temperatures.

3.4 Optical properties

The dependence of optical properties on gel calcining temperature is investigated. Fig. 5 shows the absorption spectra with different gel calcining temperatures. As for photocatalyst applications, the strong optical absorption in the UV region is essential for GZO powders. From Fig. 5, strong absorption is observed in the UV wavelength range for all GZO

powders. Although the gel calcining temperatures are different, the absorption spectra shapes of samples are same nearly.

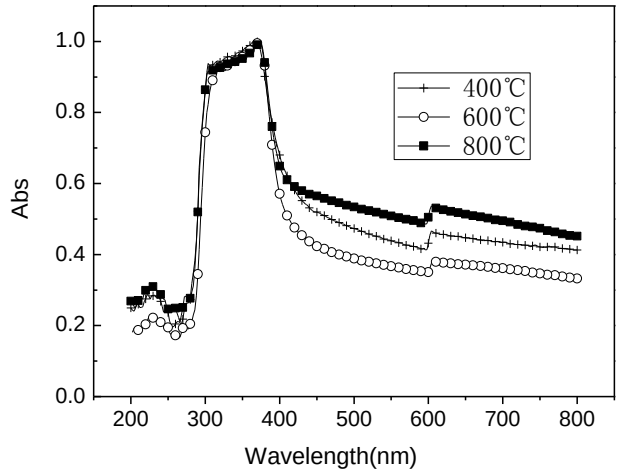


Fig. 5. Optical properties of GZO powders prepared by sol-gel but gel calcined at different temperatures.

3.5 Photocatalytic properties

The mechanism of photocatalysis is that electron-hole pairs emerge when semiconductor is radiated under light source which energy of photon is higher than that of forbidden band of semiconductor. OH free radicals are created through the reaction between holes and OH^- existing on the surface of semiconductor. OH free radicals have high oxidation activity and they can decompose pollution [12]. Photocatalytic properties of GZO powders prepared by sol-gel but gel calcined at different temperatures are shown in Fig. 6. All of powders have high photocatalytic activity under radiation of UV light source. For every sample, the degradation ratio of methyl orange increases with increasing time and it is to be nearly 100% on 8h due to electron-hole pairs emerging steadily. Furthermore, the degradation ratio of methyl orange reduces with gel calcining temperature increasing. The reason is that specific surface area of powder is large when secondary particle size is small. For photocatalysis, the number of OH free radicals which can oxide pollution is large when specific surface area of powder is large. It means degradation ratio is high. From Fig. 3 (SEM photographs), the particle size of sample obtained at 400 ^oC gel calcining temperature is smaller than the other two. So it has the strongest photocatalytic activity. Specific surface area reduces with gel calcining temperature increasing and it results to photocatalytic activity reducing with gel calcining temperature increasing.

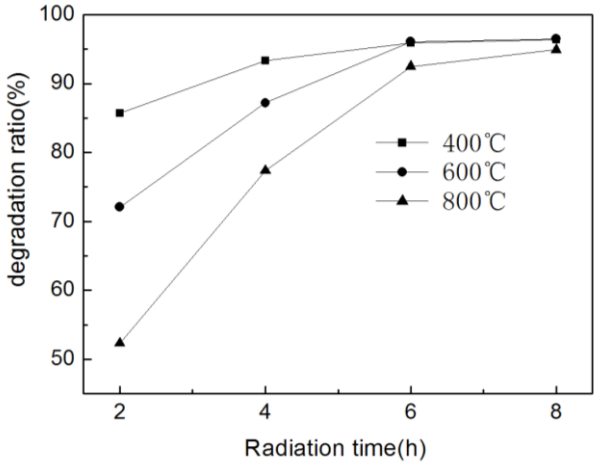


Fig. 6. Photocatalytic properties of GZO powders prepared by sol-gel but gel calcined at different temperatures.

4. Conclusions

ZnO:Ga powders with a hexagonal wurtzite structure were prepared by sol-gel method successfully. The effect of gel calcining temperature on photoelectric of target and photocatalytic properties of powders was studied at the first time. GZO which is got when the gel was calcined at 400 ^oC has the best electrical property. This is related to the compactness of tablet due to the difference of secondary particle size. Strong absorption is observed in the UV wavelength range for all GZO powders. It shows GZO powders have photocatalytic activity under UV light source. The sample obtained at 400℃gel calcining temperature has the highest photocatalytic activity because specific surface area of powder is large when secondary particle size is small. This work report is good foundation for GZO application in optoelectronic and photocatalysis fields.

Acknowledgements

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*Corresponding author: rosejiangwei@126.com