Structure and Infrared Optical Properties Research on Fe-Doped CuAlO_2 Semiconductor

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Abstract. Samples of pure phase CuAlO_2 and transition metal element Fe doped were synthesized by solid phase sintered method. The phase structure, optical properties and miscellaneous phase formation mechanism were characterized by X-ray diffraction (XRD) and Infrared Spectroscopy (IR) respectively. The results of XRD show that the product was really pure p-type transparent conductive oxide CuAlO_2 . Samples containing a small amount of CuO mixed phase may be caused by block reaction environment. IR spectroscopy results show that the transmittance of the sample was declined with the increasing of the iron-doped concentration. Doped samples have more than one absorption peak is the result of mixed substitution.

Introduction

Transparent conductive oxide (TCO) are widely used in field of photoelectric devices such as solar cells, flat-panel display, electroluminescent devices and special features window coating for its features such as good electrical conductivity, high transmittance of visible light and infrared reflectivity and the stronger microwave attenuation^[1-5]. But the actual application of TCO mostly is n-type semiconductor and p type content is less. This hinders the research and development of transparent photoelectric device TCO to set up on the basis of the p-n knot semiconductor. So far, the electrical conductivity of p-type CuAlO_2 materials is still low contrast with common n TCO and it gives a bigger challenge in research and development of p type CuAlO_2 ^[6-8].

So far, many researchers used different methods to prepare CuAlO_2 polycrystalline materials. Using Al_2O_3 and Cu_2O as raw material, Ishiguro^[9] ultimately prepared CuAlO_2 polycrystalline at 1200 °C in air. Gao^[10] obtained CuAlO_2 polycrystalline by solid phase reaction of Cu_2O and Al_2O_3 at 1100 °C in nitrogen atmosphere. Ma Tao^[11] prepared low infrared absorption CuAlO_2 polycrystalline under 1200 °C by sol gel method. Doped-Fe CuAlO_2 were prepared by solid-phase and the infrared spectral characteristics of the sample were studied in the article.

Experimental

$\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$ semiconductors were synthesized by solid state reaction. Reactant materials Cu_2O , Al_2O_3 and Fe_2O_3 were weighed according to standard stoichiometric ratio. Then the reactants were put into the anhydrous ethanol. The mixed solutions were fully milled by using ball mill for 24 h. After that, the samples were put in high temperature furnace for pre-sintering after dried. Sintered powders were ball milled again. All powders were sintered at 1200 °C for 10 h after dried. The $\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$ powders of different doping proportion were obtained after cooled. The phase composition of powders samples were characterized by using DX-2000 X-ray diffraction. To research optical property of powders samples, the Infrared Spectroscopy were carried on the NEXUS670 type infrared spectrometer.

Results and Discussion

The result of CuAlO_2 powder sintered at 1200°C for 10 h is shown in the Fig.1. It can be found that the sample is CuAlO_2 by the comparison and analysis of XRD patterns of the sample and CuAlO_2 (PDF 35-1401) standard spectrum. It can be seen that the sample has CuAlO_2 and CuO two crystalline phases from the Fig.1. CuAlO_2 is the main phase which the diffraction intensity is stronger and content is more. CuO is an intermediate product which the diffraction intensity is weak and content is less. The emergence of a small amount of CuO mixed phase may be the result of the reaction between Cu_2O and oxygen, or intermediate part decomposed into Cu_2O at high temperature, and then Cu_2O combined with residual oxygen in the process of cooling crystallization^[12]. This is a foundation for the production of Fe- doped CuAlO_2 powders.

Fig.1. XRD patterns of CuAlO_2

Fig.2. Infrared spectrum of CuAlO_2

The infrared spectrum test results of CuAlO_2 powder is shown in the Fig.2. There are three relatively strong absorption peaks A, B and C located at the wave number of 933.55 cm^{-1} , 711.53 cm^{-1} and 513.07 cm^{-1} place as apparent from Fig.3. The absorption peaks intensity of B and C are unusually strong. The absorption peaks are caused by a bond between the vibration of Al^{3+} and O^{2-} which can be known that the sample contains the structure of AlO_6 . The strength value of A is weaker than those of B and C. The vibration absorption peak is caused by a bond between Cu^+ and Al^{3+} , from which can be known a sample that each O^{2-} ions associated with 4 cation around it (3 Fe^{3+} and 1 Cu^+) constituting a quasi-tetrahedral structure. In addition, the strongest infrared transmittance of sample can reached 65%.

Fig.3. Infrared spectrum of CuAlO_2 (2.5% Fe)

Fig.4. Infrared spectrum of CuAlO_2 (5% Fe)

The measured infrared spectrum is shown in Fig.3~6 where the concentration of the mixed Fe were 2.5%, 5%, 7.5% and 10% respectively. Comparing with the infrared spectrum of pure CuAlO_2 , the

wavelength of characteristic peak of mixed iron has a downward trend. The number of absorption peaks is one more than the pure sample. The absorption peak is caused by a bond between the vibration of Fe^{3+} and O^{2-} (Fe^{3+} partially substituted Al^{3+}), which a sample that each O^{2-} ions associated with four cations around it constituting a quasi-tetrahedral structure. The characteristic peak wavelengths of doped samples with concentration increasing are showed different trends. This shows that absorption of CuAlO_2 in the infrared region will have been affected by doping. In addition, from the four pair of infrared spectra can be seen that infrared light transmittance of samples has a downward trend with the concentration increasing of Fe. Therefore, the influence of Fe-doped concentration on transmittance is negative.

Fig.5. Infrared spectrum of CuAlO_2 (7.5% Fe)

Fig.6. Infrared spectrum of CuAlO_2 (10% Fe)

Conclusions

Using Al_2O_3 , Cu_2O and Fe_2O_3 as reactive material, delafossite structure of high purity $\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$ polycrystalline material, were prepared by the solid phase. It is shown that the product is really CuAlO_2 polycrystalline by XRD test. The emergence of a small amount of CuO mixed phase may be produced by the reaction of Cu_2O and oxygen. It is shown that $\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$ containing AlO_6 functional groups and a quasi-tetrahedral structure constituting by O^{2-} ions and it was surrounded four cationic in the sample by IR spectra, which have a major contribution on the optical properties of $\text{CuAl}_{1-x}\text{Fe}_x\text{O}_2$ samples. CuAlO_2 has a high transmittance in infrared light, but the transmittance of samples was declined with the doping concentration increasing.

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References

- [1] Craciun,V, Craciun,D, Wang, X, Highly conducting indium tin oxide films grown by ultraviolet-assisted pulsed laser deposition at low temperatures. *Thin Solid Film*, (2004) 256–261.
- [2] Tian-hui Zhang, Ling-yu Piao, Su-ling Zhao, New Progress in study of organic solar cell, Materials. *Chinese Journal of Organic Chemistry*, 31(2011) 260-272.
- [3] Fu-rong Zhu, Ke-ran Zhang, Low B L, Morphological and electrical properties of indium tin oxide films prepared at a low processing temperature for flexible organic light-emitting devices. *Materials Science and Engineering B*, 85(2-3) (2001) 114–117.
- [4] Fu-rong Zhu, Ke-ran Zhang, Optimized indium tin oxide contact for organic light emitting diode applications. *Thin Solid Film*, 363(1-2) (2000) 314–317.

- [5] Huai-ying Ye, Wen Li, Wei-shi Li, Progress in Polymeric electron-donating materials for organic solar cells. *Chinese Journal of Organic Chemistry*, 32(2) (2012) 266-283.
- [6] Craciun,V, Craciun,D, Wang,X, Highly conducting indium tin oxide films grown by ultraviolet-assisted pulsed laser deposition at low temperatures. *Thin Solid Film*, 453(2004) 256–261.
- [7] Kawazoe,H, Yangagi,H, Kazushige U, Transparent p-type Conducting Oxides: Design and Fabrication of P-N Heterojunctions.*MRS Bulletin*,25(8), pp.28-362,2000.
- [8] Kim,D.S, Choi,S.Y, Wet-oxidation effect on P-type transparent conducting CuAlO_2 thin film.*physica status solidi (a)*, 202(15) (2005) 167-169.
- [9] Ishiguro,T, Kitazawa.A, Mizutani,N, Kato,M, Single-crystal growth and crystal structure refinement of CuAlO_2 . *Journal of Solid State Chemistry*, 40(2) (2004) 170–174.
- [10] Gao,S, Zhang,J, Wang,Q. Preparation and Formation Mechanism of the CuAlO_2 Nanocrystals by Hydrothermal-Decomposition Method. *Journal of Functional Materials*, 37(1) (2006) 117-119.
- [11] Tao Ma, Yi Huang, Jian Ma, Properties of CuAlO_2 Polycrystal Synthesized by Sol-gel Method. *Journal of Synthetic Crystals*, 41 (2012) 1386-1390.
- [12] Guo-bo Dong, Ming Zhang, Wei Lan, Electrical transport properties of Cu_xAlO_2 ceramics.*The Chinese Journal of Nonferrous Metals*, 9(17) (2007) 1470-1474.