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Investigation on microstructure and electrical properties of CuAl_{1-x}Y_xO_2 ceramics by electrical impedance spectroscopy

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Abstract

Y_2O_3-doped CuAlO_2 (CAO) ceramics with delafossite structure were prepared by the solid state oxide reaction method. X-ray diffraction analysis demonstrates that the most of the Y^{3+} enter into the CAO lattice to occupy Al^{3+} sites, while the second phase Al_2Y_2O_12 is formed due to the limited solubility of Y_2O_3 into CAO. The activation energies derived from the temperature dependency of bulk conductivity and dielectrically relaxation present a trend to decrease similarly as the Y_2O_3 is added. Besides, the carrier mobility rises gradually as Y_2O_3 is added, and turns to sharp augment at the Y_2O_3 addition reaching to x = 0.04. Hence, at small Y_2O_3 addition, the emergence of the insulated Al_5Y_3O_12 limits the conductivity; on the other hand, the sharp augment of carrier mobility results from the increase of the conductivity when Y_2O_3 addition is over x = 0.04.

Keywords:

CuAlO_2, Y_2O_3 doping, Impedance, Carrier mobility

1. Introduction

Transparent conducting oxides (TCOs) is of great interest because of the wide range of applications such as flat panel displays, organic light emitting diodes, thin film transistors, touch panels and optical waveguides, etc. [1]. However, the development of transparent devices basically requiring p-n junctions was hampered due to the lack of p-type transparent semiconductors with good performance. The situation didn’t change until Kawazoe et al. [2] successfully fabricated p-type CuAlO_2 (CAO) thin film in 1997. Since then, CAO has attracted a great interest for its application ranging from p-n junction to transistors.

Unfortunately, the conductivity of CAO is 2–3 orders of magnitude lower than that of commonly n-type TCOs like indium tin oxide [2,3]. Consequently, it is a very necessary and exigent task to improve the electrical conductivity of CAO. As it is well known, the electrical conductivity of a semiconductor is proportional to the concentration and mobility of its carriers [4,5]. Doping CAO with acceptors is adopted as one of the most effective ways to increase the carrier density and consequently improve the electrical conductivity [6–9]. It is believed that the acceptor doping can increase the electrical conductivity of p-type semiconductor by contributing to the hole concentration, and thus decrease the optical transmittance because more carriers could absorb more photons [8–11].

CAO is a p-type semiconductor with delafossite structure. For CuMO_2, the increase of the size of M^{3+} cation decreases distance of Cu–O and increases the Cu–Cu distance [12], which brings in the lattice distortion and the variation of the carrier mobility [13]. Jiang et al. reported that Cr doping into CAO can modify the structure of the top of valence band (VB) because Cr 3d state contributes to VB [14]. However, the coexistence of Cr^{2+} and Cr^{3+} will increase the carrier density and decrease the optical transmission. Therefore, in CAO-based solid solutions, the isovalent substitution for Al^{3+} in delafossite CAO will provide a routine to realize the variation in carrier mobility while keep the optical behaviors.

In the work, trivalent Y^{3+} is applied to occupy the Al^{3+} site of the delafossite CAO. The effect of Y_2O_3 addition on the structure and electrical properties of CAO ceramics will be investigated. By means of the electrical impedance spectroscopy (EIS), the electrical conductance and dielectric relaxation behavior are analyzed. Combined with the carrier mobility, the relation between electrical properties and microstructure is probed.

2. Experimental details

CuAl_{1-x}Y_xO_2 (x = 0–0.06) samples were produced by solid oxide reaction method using CuO, Al(OH)_3 and Y_2O_3 (purity higher than 99%) powders as raw materials. The powders were weighed
according to stoichiometric ratio and mixed through ball milling, with partially stabilized zirconia balls as media, in alcohol for 12 h. After drying, the mixture was calcined in a covered alumina crucible at 1100 °C for 10 h. The calcined powders were remilled for 12 h, and then pressed into disks of 11.5 mm in diameter at around 100 MPa using polyvinyl alcohol as binder. The green disks were debinded at 560 °C for 6 h, and then sintered at 1200 °C for 4 h in a sealed alumina crucible. After polishing, the sample for the impedance measurement was sputtered with Au electrodes on both sides while the sample for Hall measurement was sputtered with Au electrodes through a mask. The mask consists of four round pores with a diameter of 1.0 mm arranging in a rectangle form. The samples as-sputtered with Au electrodes were annealed at 450 °C for 30 min in air.

The crystal structure was examined by an x-ray diffractometer (XRD, Bruker D8 Advance, Germany) in the 0–2θ configuration using Cu Kz radiation. The electrical impedance response was recorded by an impedance analyzer (Concept 400, Novocontrol Technologies, Germany) in a frequency range between 1 Hz and 10 MHz and temperature range between −150 °C and −75 °C. Hall measurements were carried out at room temperature using the van der Pauw method by a Hall System (HL5550 LN2 CRYOSTAT, Nano metrics).

3. Results and discussion

3.1. Structural properties

All the samples show a high relative density above 95% based on the Archimedes method, indicating their good sintering behavior. Besides, Fig. 1 shows XRD patterns of the CuAl1−xY2O3 samples with different x values. When x = 0, all diffractions could be assigned to delafossite CAO (JCPDS 76-2398, R3m). With increasing Y2O3 content in CAO, there appear new diffractions located at 29.8°, 33.4°, and 35.0°, matching to those of cubic Al5Y3O12 (JCPDS 73-1370). To find out the solubility of Y2O3 into CAO lattice, indexing the XRD patterns were recorded as shown in Fig. 2. As seen in Fig. 2, the diffraction around 36.68° and (012) diffraction around 37.85° shifted toward lower angles with the increasing Y2O3 content, illustrating that the Y3+ doping leads to lattice expansion. The lattice expansion implies that Y3+ enters into the CAO structure to occupy the Al3+ sites because of the larger radius of Y3+ (0.892 Å) than that of Al3+ (0.530 Å). Besides, the gradual shift to small angle of the (101) and (012) diffractions demonstrates the increasing of the amount of Y3+ entering into the CAO lattice. However, accompanied by the increasing of the amount of Y3+ entering into CAO lattice, the intensity of the diffractions assigned to Al5Y3O12 goes up with the increasing Y2O3 content. Hence, the appearance of the second phase Al5Y3O12 is thought to be resulted from the difference of reaction activity among the raw materials, including Al(OH)3, Y2O3, and Cu2O, respectively.

3.2. Impedance analysis

EIS is the most reliable and important technique to study the electrical and dielectric properties and process of a material, and has been used to study many kinds of materials in previous works [15–17]. In our work, the impedance spectra of CAO with different Y2O3 doping are adopted to observe the effect of the Y2O3 content on the electrical properties of CAO ceramics.

The complex impedance (Nyquist) plots of CAO ceramics measured at temperatures from −125 °C to −75 °C are shown in Fig. 3. In the measuring temperature range, the Nyquist plots of the CAO present deformed semicircular arcs, which suggest that the relaxation in CAO is not an ideal Debye relaxation [18,19]. And with the temperature increase, the arcs become depressed, which

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indicates that carriers are thermally activated. Besides, the intercept of the semicircular arcs on the real Z', i.e., the bulk resistance denoted as R$_{DC}$, decreases with increasing temperature, presenting a behavior of negative temperature coefficient of resistance (NTCR). CAO with different Y$_2$O$_3$ addition also show similar phenomena in the temperature dependence of complex impedance. To compare the effects of Y$_2$O$_3$ content on the bulk resistance, the relation of Y$_2$O$_3$ content and the electrical conductivity $\sigma_{DC}$ ($=1/R_{DC}$), is shown in the insert of Fig. 3. Obviously, the electrical conductivity decreases along with Y$_2$O$_3$ doping increment until the addition reaches 0.03. While the addition x is over 0.04, the electrical conductivity turns over to increase.

The $\sigma_{DC}$ of CuAl$_{1-x}$Y$_x$O$_2$ solid solutions are plotted as function of the reciprocal temperature 1000/T as shown in Fig. 4. The $\sigma_{DC}$ shows a linear relation with the reciprocal temperature, which confirms that the temperature dependence of the electrical conductivity obeys the Arrhenius law:

$$\sigma_{DC} = \sigma_0 \exp\left(\frac{-E_{DC}}{kT}\right)$$  \hspace{1cm} (1)

where $\sigma_0$ is the pre-exponential factor; $E_{DC}$ the activation energy derived from the conductivity, and k the Boltzmann constant, respectively. And the $E_{DC}$ values of all the CuAl$_{1-x}$Y$_x$O$_2$ samples are estimated and shown in Fig. 5. For Y$_2$O$_3$-doped CAO ceramics, with the improving Y$_2$O$_3$ content, the activation energy shows a tendency to decline. However, when x = 0.03, an unusual activation energy as small as 0.15 eV is observed.

Frequency-dependent imaginary impedance Z'($\omega$) spectra of CAO measured in temperatures ranging from −150 °C to −75 °C is shown in Fig. 6. With the increase of temperature, the Z'($\omega$) spectrum is characterized by two important features: peak broadening and asymmetry enhancing. The peak broadening and shifting to high frequencies with temperature indicate the existence of temperature-dependent electrical relaxation phenomenon in the material [20]. The asymmetric broadening of the Z($\omega$) peak suggests that multiple relaxations exist in the material [15], with their own discrete relaxation time depending on the temperature. And the enhanced asymmetry may be due to the existence of multiple relaxation phenomena. But what kinds of relaxation mechanisms play the dominant role in the electrical properties in CAO may need to be verified by further work. Other CAO samples with different Y$^{3+}$ content show similar phenomena in the frequency-dependent

![Fig. 5. Activation energy $E_a$ for CuAl$_{1-x}$Y$_x$O$_2$ ceramics at different Y$_2$O$_3$ addition.](image)

![Fig. 6. Frequency dependence of the Z' of CuAl$_{1-x}$Y$_x$O$_2$ ceramics at different temperatures.](image)

![Fig. 4. Variation of bulk conductivity ln$\sigma_{DC}$ as a function of the reciprocal temperature 10$^3$/T of CuAl$_{1-x}$Y$_x$O$_2$ ceramics.](image)

![Fig. 7. Variation of relaxation time ln\tau as a function of the reciprocal temperature 10$^3$/T of CuAl$_{1-x}$Y$_x$O$_2$ ceramics.](image)
In the relaxation system, one can determine the most probable relaxation time (\(\tau\)) from the frequency of the Z\(\prime\) peak according to the relation: \(\tau = 1/(2\pi f)\). The variation of \(\ln\tau\) of CuAl\(_1\)xY\(_2\)O\(_3\) solid solutions with reciprocal temperature is shown in Fig. 7. Obviously, the value of \(\ln\tau\) presents a linear relation with the reciprocal temperature, suggesting that the temperature-dependence of electrical relaxation process follows the Arrhenius relation:

\[
\tau = \tau_0 \exp\left(-\frac{E_r}{RT}\right)
\]

(2)

where, \(\tau\) is the relaxation time; \(\tau_0\) the pre-exponential factor, and \(E_r\) the activation energy derived from the relaxation time, respectively. \(E_r\) is estimated and also presented in Fig. 5. As seen from Fig. 5, the \(E_r\) and \(E_{BC}\) of CuAl\(_1\)xY\(_2\)O\(_3\) solid solutions show the same tendency to decrease with the increase of Y\(_2\)O\(_3\) content. Our result falls in the range reported by the previous works. It was reported that the activation energy of CAO-based solid solutions be in the range of 0.08–0.30 eV \[8,9,14,21–27\]. Furthermore, the decline of the activation energies for CuAl\(_1\)xY\(_2\)O\(_3\) solid solutions may be correlated with the effect of Y\(_2\)O\(_3\) on the bandgap of CAO due to the difference between the band gaps between CAO (3.50 eV) \[2\] and CuYO\(_2\) (2.63 eV) \[28\].

4. Carrier mobility

Carrier mobility is an important parameter to measure the performance of semiconductor conductivity. Table 1 shows the carrier mobility of CuAl\(_1\)xY\(_2\)O\(_3\) solid solutions as a function of Y\(_2\)O\(_3\) content. It is seen that the mobility presents an increased trend with increase of Y\(_2\)O\(_3\) content. When the Y\(_2\)O\(_3\) addition is small, the carrier mobility increases slowly. While the Y\(_2\)O\(_3\) addition reaches over about \(x = 0.03\), the carrier mobility grows sharply. It is suggested that the variation of carrier mobility with the Y\(_2\)O\(_3\) content is related to lattice distortion. Due to the difference of the radius of Y\(_3\)\(^{3+}\) and Al\(^{3+}\), Y\(_3\)\(^{3+}\) doping leads to the lattice distortion of ALO\(_6\) octahedrons, broadening Cu–Cu distance in ab planes, and causing the reduction of the overlap of electronic wave function between neighboring Cu\(^{3+}\) ions. The overlap has always been considered a highly significant factor in carrier hopping \[14\]. On the other hand, the lattice distortion induced by Y\(_3\)\(^{3+}\) doping influences the band structure of CAO, and leads to the top of VB modified because of the contribution Y\(_3\)\(^{3+}\)4d state to the hybridization of O 2p state \[14\]. The change in the band structure would contribute to the carrier mobility, and results in the rapid increase of the carrier mobility as more Y\(_2\)O\(_3\) content is added.

The variation of conductivity on the Y\(_2\)O\(_3\) content could be interpreted by carrier mobility and microstructure. As seen in Fig. 4, the value of electrical conductivity decreases with Y\(_2\)O\(_3\) content from \(x = 0\) to \(x = 0.03\), followed by an increase of \(x = 0.04\). This phenomenon implies that the two mechanisms affecting conductivity coexist and compete each other. As seen from the XRD patterns, the Y\(_2\)O\(_3\) addition causes the emergence of Al\(_5\)Y\(_3\)O\(_{12}\). The existence of insulated Al\(_5\)Y\(_3\)O\(_{12}\) decreases the electrical conductivity of the material. In other hand, the increase of the carrier mobility improves the conductivity of the material. When the \(x\) is small, the existence of Al\(_5\)Y\(_3\)O\(_{12}\) is the main factor dominating the conduction behavior and thus decreases electrical conductivity. When \(x\) achieves a certain value, the carrier mobility grows sharply and becomes the dominant factor. The high carrier mobility compensates the effect of the Al\(_5\)Y\(_3\)O\(_{12}\) and leads to the increase of conductivity.

5. Conclusions

Y\(_2\)O\(_3\)-doped CAO with the delafossite structure were prepared by a solid-state oxide reaction method. XRD analysis demonstrated that Y\(_3\)\(^{3+}\) entered into the CAO structure to occupy Al\(^{3+}\) sites, even though the second phase Al\(_5\)Y\(_3\)O\(_{12}\) was formed due to the limited solubility of Y\(_2\)O\(_3\). The impedance spectra of CuAl\(_1\)xY\(_2\)O\(_3\) samples shows that the temperature-dependent electrical conductivity and dielectrically relaxation follow the Arrhenius relation, and the activation energies estimated from bulk conductivity and electrical relaxation are in good match with the previous works. In addition, with increase of Y\(_2\)O\(_3\) content, the electrical conductivity decreases from \(x = 0\) to \(x = 0.03\), followed by an increase at \(x = 0.04\). Besides, the Hall Effect measurement reveals the increase of the carrier mobility with the Y\(_2\)O\(_3\) added, which is attributed to the lattice distortion and the contribution of Y\(_3\)\(^{3+}\)4d state on the hybridization of O 2p state. The variation of the carrier mobility and microstructure could exactly explain the dependence of electrical conductivity of CAO with Y\(_2\)O\(_3\) increase: the insulated Al\(_5\)Y\(_3\)O\(_{12}\) controls the conductivity when small Y\(_2\)O\(_3\) is added, and the rapid growth of carrier mobility becomes the predominant when Y\(_2\)O\(_3\) addition exceeds over \(x = 0.04\).

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