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Effect of Cr doping on secondary phases and electrical properties of zinc oxide ceramic thick film varistors

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Abstract: In order to get high-performance low voltage varistors, Cr_2O_3 doped ZnO ceramic thick films were fabricated by modified sol-gel process. The precursors were fabricated by dispersing doped-ZnO ceramic nano-powders in the sols, which were prepared by dissolving zinc acetate dihydrate into 2-methoxyethanol and stabilized by diethanolamine and glacial acetic acid and doped with a concentrated solution of bismuth nitrate, phenylstibonic acid, cobalt nitrate, manganese acetate and chromium nitrate. The results show that $ZnCr_2O_4$ phase can form in ZnO based ceramic films doped 1.0% (mole fraction) Cr_2O_3. Three secondary phases, such as Bi_2O_3, $Zn_7Sb_2O_{12}$, and $ZnCr_2O_4$ phases, are detected in the thick films. The Raman spectra show that the intensity and the position of Raman bands of $Zn_7Sb_2O_{12}$ and $ZnCr_2O_4$ phases change obviously with increasing Cr_2O_3 doping. The nonlinearity coefficient α of ZnO thick films is 7.0, the nonlinear voltage is 6 V, and the leakage current density is 0.7 μA/mm^2.

Key words: sol-gel processs; thick films; ZnO; secondary phases; low voltage varistors

1 Introduction

ZnO ceramic thick films have great potentials and advantages of fabricating low-power low voltage varistors[1−3]. The effects of dopants on the properties of ZnO bulk ceramics and thin films have been widely studied, Bi_2O_3 and other glass materials accelerate the formation of the grain boundary, improve the density of the ceramics[4]. Sb_2O_3 can lower the leakage current density, and enhance the nonlinear coefficient α[5−7]. Al_2O_3 and Ga_2O_3 added as the donor can enhance the carrier density, decrease the resistivity, and improve the electrical properties of the film varistors in the large current rising region[8−9], while the doping of alkali metals such as K_2O, Li_2O, Na_2O can form acceptor barrier in the ZnO grain boundary, and increase the nonlinear coefficient of the films[10−11]. The transition metal such as Co, Mn, and Ni can also improve the nonlinear coefficient[12].

However, to the best of my knowledge few researchers have investigated the influences of dopants on the low voltage nonlinear I—φ characteristics of the ZnO thick films, which are different from the previous ZnO bulk ceramics. The annealing temperature of ZnO-based ceramic films by sol-gel processing is lower than 850 ℃. The formation of the grain boundaries, and the secondary phases are different from those of ZnO bulk ceramics. The differences will affect the electrical properties of ZnO ceramic thick films. The electrical properties of ZnO film varistors can be influenced by many factors such as electrode materials[13−14], dopants[15], annealing temperature and film thickness. We have studied the electrical properties of the thick films at different annealing temperatures[16].

The electrical properties are affected strongly by the secondary phases, and the types of secondary phases formed depend on the amount and the type of additives. Therefore, the present work focuses on the effects of the dopants (especially Cr_2O_3) on secondary phases and the nonlinear I—φ characteristics of low voltage ZnO-based ceramic films. This will contribute to developing high-performance low-power low voltage ZnO ceramic thick film varistors.

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2 Experimental

ZnO ceramic thick films were deposited on the Au/SiO_2/Si substrates by a modified sol-gel process. The sols were prepared by zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$)(chemical purity), dopants such as $Bi(NO_3)_3 \cdot 5H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, Sb_2O_3 and the solvents, such as 2-methoxyethanol. $Zn(CH_3COO)_2 \cdot 2H_2O$ and the dopants were first dissolved in 2-methoxyethanol by addition of diethanolamine (MEA) and glacial acetic acid at 60 ℃, respectively. The resultant solution was stirred at room temperature for more than 24 h to yield a clear, stable and homogeneous sol. The precursors were fabricated by dispersing the ZnO nano-powders in the sols. The films with 10−20 layers were deposited on Au/SiO_2/Si by spining at 2 000 r/min for 30 s, and annealed at 550−950 ℃ in air for 2 h. Then, part of the 5 μm thick films was corroded to reveal part of the lower electrodes. After the upper electrodes had been deposited by sputtering, the thick films were cut to several samples. The detailed processing has been reported in Ref.[17].

The I—φ characteristics of low voltage ZnO ceramic thick film varistors were measured by transistor characteristics tester, the nonlinear voltage ($\varphi_{1\,\mathrm{mA/cm^2}}$) and the leakage currents were measured by MY−4C varistors synthesize parameter-testing instrument. The phases of the samples were analyzed by RIGAKU D/max-3B X-ray diffractometer with Cu K_α radiation (30 kV, 30 mA). Raman spectra of the films were obtained by means of Renishaw System RM−1000. Raman spectra were excited with the 514.5 nm line of an Ar+ laser at an incident power of 20 mW and obtained in the range of 100−2 000 cm^{-1}.

3 Results and discussion

Fig.1 shows the XRD patterns of the ZnO ceramic films doped with 0.5% Cr_2O_3 annealed at 750 ℃, the α-spinel and $ZnCr_2O_4$ phase is observed. In ZnO bulk ceramics, the formation of $ZnCr_2O_4$ phase is determinated by the content of Cr_2O_3 whether Sb_2O_3 exists or not. When the amount of Cr_2O_3 is no more than 1.0%, $ZnCr_2O_4$ phase can not form in the ZnO ceramics doped with Sb_2O_3[18], and only the amount of Cr_2O_3 is more than 5.0%, the $ZnCr_2O_4$ phase can be observed[19]. In ZnO thick films, $ZnCr_2O_4$ phase can form in the condition of a little amount of Cr_2O_3 doping. This indicates that Cr^{3+} and Zn^{2+} distribute in molecular level, and lead to the formation of $ZnCr_2O_4$ phase, which distributes at the grain boundaries, inhibiting the growth of ZnO grains, and reducing the concentration of Cr^{3+} in spinel phases. This suggests that the effect of Cr_2O_3 on the carrier density and barrier height at grain boundaries of ZnO thick films are lower than that of ZnO bulk ceramics.

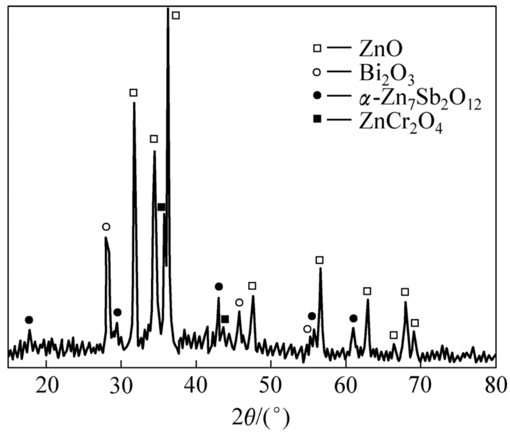

Fig.1 XRD patterns of ZnO films doped with 0.5% Cr_2O_3

Fig.2 shows the evolution nonlinear voltages nonlinear coefficient α, and the leakage current density of thick film varistors with Cr_2O_3 content. Cr_2O_3 doped in ZnO ceramic thick films plays an important role in the two ways during the annealing, one is stabilizing spinel phases, the other is inhibiting the growth of ZnO grains. β-spinel phase has a good stability during sintering but poor stability on cooling, and would transform to pyrochlore phase. Cr_2O_3 has the effect of inhibiting the formation of β-spinel phase. When ZnO thick films are sintered at high temperature, Cr^{3+} cations dissolve into Bi enrichment phases and α-spinel phases. The α-spinel phases involve with Cr^{3+}, having a good stability not only in sintering procedure, but also in the cooling procedure[18]. Therefore, Cr_2O_3 has the effect of stabilizing spinel phases. The composition and stability of spinel phases has a notable effect on the electrical properties of the film varistors. The stability of spinel

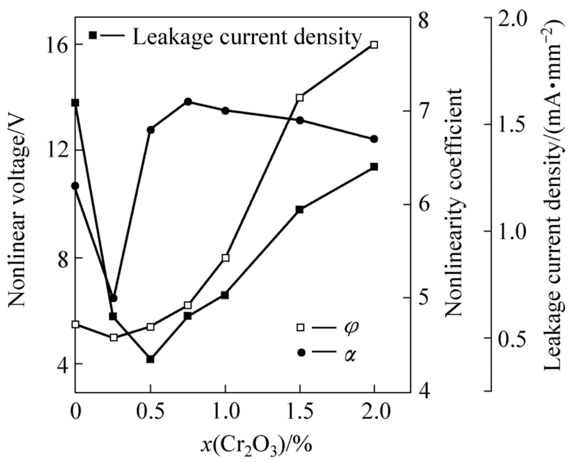

Fig.2 Nonlinear voltages, coefficient and leakage current density of film varistors changed with Cr_2O_3 Content

phases lead to the diffusion and redistribution of dopants in thick film. These could change the features of ZnO grain and intergranular phases, and finally affect the electrical properties of ZnO ceramic thick films[20]. In addition, Cr_2O_3 inhibits the growth of ZnO grains, causing the refining of the ZnO and spinel grains[18], and leading to the increase of nonlinear voltage. Cr^{3+} ion dissolving in the spinel phases partly diffuses into ZnO lattice as donor, and increases the carrier density in ZnO thick films[21], decreases the barrier height of grain boundaries, thus leading to the increase of leakage current. Consequently, when the additive Cr_2O_3 is no more than 0.5%, the leakage current of the films increases but notably decreases with the increase of Cr_2O_3.

Fig.3 shows the Raman spectra of ZnO thick films with different dopants. The proportion of spinel phase formed in the films reaches the theoretical value when the films is only doped with Bi_2O_3 and Sb_2O_3 as seen in Fig.3(a), and the broad Raman peaks, 710.7 cm^{-1} and 715 cm^{-1} appear. The spinel phase peaks become stronger and sharper but the secondary peaks disappear with increasing MnO doped into the films, as seen in Fig.3(b).With Co_2O_3 and Cr_2O_3 continually doping into ZnO films, the spectra peaks move to low wave number side. When Co_2O_3 is added in the films, the spinel peak moves to 708 cm^{-1} and a subordinate peak appears at 716 cm^{-1}. When Cr_2O_3 is added in the films, the spinel peak moves to 709 cm^{-1} and becomes stronger and sharper, indicating that the $Zn_7Sb_2O_{12}$ spinel structure is notably affected by the dopants especially the trivalent cations. Because the trivalent cations enter the spinel octahedral structure and replace Zn^{2+}, the spinel structure changes remarkably, which further proves the previous XRD results.

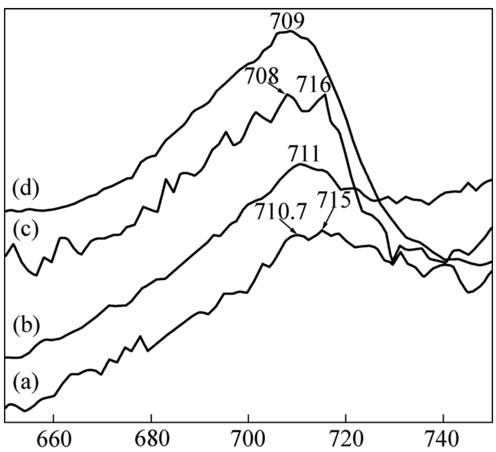

Fig.3 Raman spectra of $Zn_7Sb_2O_{12}$ phase when ZnO based films doped with Bi_2O_3 and Sb_2O_3(a); Bi_2O_3, Sb_2O_3 and MnO(b); Bi_2O_3, Sb_2O_3, MnO and Co_2O_3(c); and Bi_2O_3, Sb_2O_3, MnO and Cr_2O_3(d)

Fig.4 shows the Raman spectra of ZnO based films doped with different contents of Cr_2O_3, the primary $ZnCr_2O_4$ peaks appear at 825 cm^{-1} and 826 cm^{-1}. With increasing amount of Cr_2O_3, $ZnCr_2O_4$ peaks position shifts 1 cm^{-1}, and the peaks become stronger and sharper, which indicates that the increasing Cr_2O_3 doping leads to $ZnCr_2O_4$ phase growing larger. In all of the samples doped with different oxides, the lattice of the films doped with Cr_2O_3 is the smallest, which indicates that the ZnO films are mainly affected by Cr^{3+} cations. Because Cr^{3+} cations have higher octahedral activation energy than the other dopants cations, and are very easy to substitute Zn^{2+} cations. The peak at 709 cm^{-1} is ascribed to $Zn_7Sb_2O_{12}$ and shifts to 713 cm^{-1}.

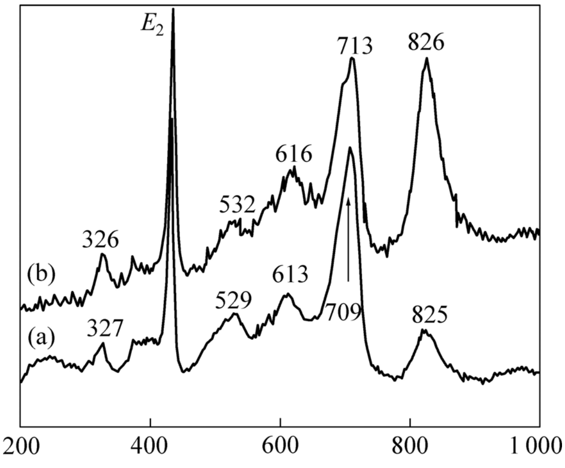

Fig.4 Raman spectra of ZnO based films doped with 0.25% Cr_2O_3(a) and 0.5% Cr_2O_3(b)

The dopant cations form intergranular phases at ZnO grain boundary and diffuse to adjacent ZnO lattice to substitute part of the Zn^{2+}. The substitution would cause the distortion of the lattice and results in increasing carrier density. Because the diffusion of additive cations almost occurs at adjacent of grain boundary, the donor density at grain boundary is much higher than that in grain. The $Zn_7Sb_2O_{12}$ and $ZnCr_2O_4$ secondary phases form quickly at lower annealing temperature, which leads to the formation of stable grain boundaries. In this procedure, the other cantions such as Mn^{2+}, Mn^{4+} and Cr^{3+} diffused into the secondary phase lattices due to substitution and diffustion, which would cause the lattice distortion. Therefore, besides the distortion of the lattice caused by the substitution of the dopant cations, the surface lattice distortion of the ZnO lattice caused by the formation of secondary phases in grains is considered to be the main origin of the properties changes of ZnO based thick films.

4 Conclusions

1) Thanks to dopants mixing in molecular level by modified sol-gel process, the formation of $ZnCr_2O_4$ phase of the films doped with little Cr_2O_3 is very easy and reduces the amount of Cr^{3+} dissolved into the spinel phases.

2) Cr^{3+} diffuses into ZnO grains and decreased the barrier height of grain boundaries, and leads to increase of leakage current, consequently, the Cr_2O_3 content is no more than 0.5%.

3) Raman spectra indicate three secondary phases, such as Bi_2O_3, $Zn_7Sb_2O_{12}$ spinel, and $ZnCr_2O_4$ phases, appear in ZnO thick films. The formation of $ZnCr_2O_4$ phase in the films at low temperature is of great advantage to stabilize the $Zn_7Sb_2O_{12}$ spinel phase, and improve ZnO grain boundary features as well. The peak of 709 cm^{-1} is ascribed to $Zn_7Sb_2O_{12}$ and shifts to 713 cm^{-1} with Cr_2O_3 doping.

4) When the amounts of additives Bi_2O_3, Sb_2O_3, MnO and Cr_2O_3 are 0.5%, 1.5%, 0.5% and 0.75%, respectively, the nonlinearity coefficient α of ZnO thick films is 7.0, the nonlinear voltage is 6 V, and the leakage current density is 0.7 $\mu A/mm^2$.

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