Materials Letters 164 (2016) 80–83

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

High nonlinearity and low residual-voltage ZnO varistor ceramics by synchronously doping Ga_2O_3 and Al_2O_3

Hongfeng Zhao [a], Jinliang He [a,*], Jun Hu [a], Shuiming Chen [a], Qingyun Xie [b]

[a] State Key laboratory of Power Systems, Department of Electrical Engineering, Tsinghua University, Beijing 100084, China
[b] Xidian Surge Arrester Co., Ltd., Xi'an, Shaanxi 710200, China

ARTICLE INFO

Article history:
Received 7 September 2015
Received in revised form
13 October 2015
Accepted 14 October 2015
Available online 23 October 2015

Keywords:
Varistors
Electrical properties
Electroceramics

ABSTRACT

The present study examined the electrical properties of ZnO varistor ceramics co-doped with Ga_2O_3 and Al_2O_3, in particular, the current–voltage characteristics under small and intermediate currents and up-turn characteristics under a large current. With increasing amounts of Ga_2O_3 dopant at a given Al_2O_3 concentration, both the threshold voltage in the small-current region and nonlinear coefficient of the varistor ceramics increased and then decreased; in contrast, the leakage current decreased and then increased. Moreover, ZnO varistor ceramics with low residual voltage ratio, high nonlinearity, and low leakage current were obtained under an optimal Ga concentration of 0.72 mol% while the Al additive content was fixed at 0.1 mol%. This novel finding will be helpful towards the manufacture of high-quality ZnO varistors.

1. Introduction

ZnO varistors are a type of polycrystalline ceramic obtained by sintering ZnO powder with minor primary additives, such as Bi_2O_3 and Sb_2O_3, and secondary additives such as Co_2O_3, MnO_2, and Cr_2O_3 [1]. ZnO varistors play significant roles as surge protection devices, which are widely applied in electronic and electrical systems to limit overvoltage [2]. Voltage gradient is typically used as an important parameter for evaluating the performance of ZnO varistors. The voltage gradient can be improved by reducing the sintering temperature and time. However, such approaches often lead to poor nonlinearity [3]. In relative study fields, the ferromagnetic ZnO nanograined films were studied by the properties of ZnO grain boundaries, whose emphasis on the dopant solubility and ferromagnetism [4,5]. In ZnO varistor ceramics, the electrical properties induced by dopants are focused on.

Alternatively, dopants, such as Al^{3+} or Ga^{3+}, have been employed to enhance the electrical conductivity of ZnO grains [6,7]. The effect of aluminum oxide on the residual voltage of ZnO varistors had been studied [8,9], and the associated mechanism was reported [9]. The optimal effect of Al additive on the conductivity of ZnO grains was observed at an Al ionic additive concentration of 0.25 mol%. Concurrently, as reported, the presence of Al dopant increases the leakage current of varistors [7], which leads to the instability of the varistor during operation. Though progress has been achieved by doping with either Ga or Al [6,9,10], few studies have reported on improving the properties of ZnO varistors by simultaneous doping of multiple donors dopants. Following on from our previous study [7], herein, the effects of simultaneous incorporation of aluminum and gallium on the electrical properties of ZnO varisor ceramics are investigated. Specifically, the effects of varying the concentration of Ga dopant, at a given Al dopant concentration, on the electrical properties of the varistor samples were examined to subsequently establish the optimal dopant composition that would afford optimal electrical properties.

2. Experimental

The ZnO varistor samples were fabricated using analytical-grade raw materials in the proportions: $(94.55-x)$ mol% ZnO, 1.0 mol% Bi_2O_3, 0.75 mol% MnO_2, 1.0 mol% Co_2O_3, 0.5 mol% Cr_2O_3, 1.0 mol% Sb_2O_3, 1.2 mol% SiO_2, 0.1 mol% Al_2O_3, x mol% Ga_2O_3 (x=0.18, 0.36, 0.72, 1.44). As discussed in our previous study [7], the influence of Al ionic additive on the residual voltage under high current and the leakage current in the pre-breakdown region is very important. Hence, in the present study, the content of Al was fixed at 0.1 mol% in all samples. This afforded a balanced effect between the leakage current and residual voltage.

Reagent-grade oxides were mixed in proper ratios homogenized in alcohol using a planetary mill. The mixture was dried at 90 °C and pressed with 400 kg/cm^2 into discs 30 mm in diameters and 2.0 mm thick. The disks were sintered at 1200 °C for 2 h using

* Corresponding author. Fax: +86 10 62784709.
E-mail address: hejl@tsinghua.edu.cn (J.L. He).

http://dx.doi.org/10.1016/j.matlet.2015.10.070
0167-577X/

a heating rate of 5 °C/min and a cooling rate of 2 °C/min in a furnace (Nabertherm LH60/14, Germany) in air. Finally, the surfaces of the sintered samples were ground and covered with silver paste to obtain electrodes that were heated at 550 °C for 2 h.

The surface microstructure was examined by scanning electron microscopy (Jeol JSM-6700F, Japan). The average grain size (*d*) was determined by the lineal intercept method [11]. The electric field–current density (*E*–*J*) property of the samples in the pre-breakdown region were measured using a source meter (Keithley 2410, USA). The nonlinear coefficient α was determined as follows: $\alpha = 1/(\log E_2 - \log E_1)$, the residual voltage ratio *K* is calculated as: $K = U_n/U_{1\,mA}$, the impulse current (current wave form of 8/20 μs) was produced by a generator (Keytek EMC Pro, USA), the capacitance–voltage (*C*–*V*) characteristics were measured by a broadband dielectric device (Novocontrol Concept 80, Germany) at 1 kHz to calculate the donor concentration N_d and the barrier height $\varnothing_b$ [12]. The phase constitution of the samples was analyzed by X-ray diffraction analysis (Rigaku H/max 2500, Japan).

3. Results and discussion

Representative scanning electron microscopy images of the samples prepared with different Ga dopant concentrations are presented in Fig. 1. The average grain size (d) of the samples determined by the lineal intercept method are listed in Table 1; as observed, *d* decreased slightly with increasing Ga dopant concentrations. Hence, the dopant concentration minimally influenced the ZnO grain size. Fig. 2(a) shows the *C*–*V* plots $(1/C_b - 1/2C_{b0})^2$ as a function of on U_{gb} [12]. As observed, the curves gradually shifted downward with increasing Ga dopant contents. The parameters determined from the *C*–*V* plots are summarized in Table 1. Increasing the concentration of Ga to 0.72 mol% resulted in an increase in N_d and $\varnothing_b$. However, further doping led to a reduction in these parameters. Accordingly, the effect of Ga dopant on the surface state (N_i) on the grain boundary was significant. Fig. 2(b) shows the *E*–*J* plots of the samples doped with different concentrations of Ga. The electrical parameters of the samples deduced from the *E*–*J* plots are summarized in Table 1, where E_{1mA}, J_L, and α represent the breakdown voltage, leakage current, and nonlinear coefficient, respectively.

As mentioned previously, both N_d and N_i increased with increasing Ga dopant amounts (Table 1). According to the formula $\varnothing_b = eN_i^2/2\varepsilon\varepsilon_0 N_d$ [13], the higher N_i, the higher $\varnothing_b$ is. Furthermore, $E_{1\,mA}$ of ZnO varistor was enhanced, and the leakage current decreased. The value of N_d could further reduce the grain resistance based on the effect of Al additive, subsequently reducing the residual voltage in the upturn region. The residual voltage ratio decrease was attributed to the synergy effects associated with the higher N_d and N_i values.

A nonlinear coefficient of 27 was obtained at the lowest Ga dopant concentration of 0.18 mol%. Parameter α increased to 73 with increasing Ga additive amounts up to 0.72 mol%, where a transition state of donor or acceptor exists; the transition state changes the conduction characteristics of the grain boundary [6]. The process may be described by the following defect reactions:

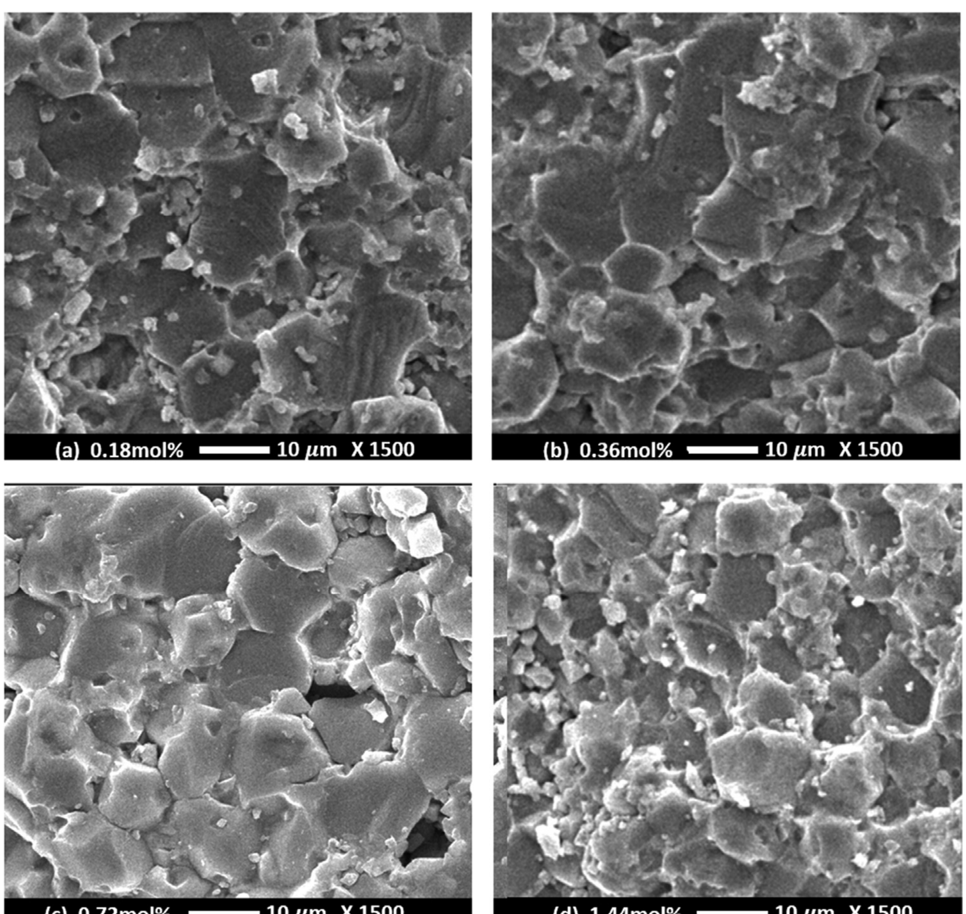

Fig. 1. Scanning electron microscopy images of ZnO varistors prepared with a fixed concentration of Al (0.1 mol%) and different concentrations of Ga co-dopant ((a) 0.18, (b) 0.36, (c) 0.72, and (d) 1.44 mol%).