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Nonlinear current–voltage characteristics of sintered tungsten–vanadium oxide

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We have studied the densification behaviour, microstructure and electrical properties of WO_3 ceramics with V_2O_5 as the additive ranging from 0.5 to 15mol%. Scanning electron microscopic photos indicated that the grain size of WO_3–V_2O_5 specimens is smaller than that of pure WO_3. The addition of V_2O_5 to WO_3 showed a tendency to enhance the densification rate and to restrict the grain growth. Electrical properties of all specimens were measured for different electrodes at different temperatures. The formation of the grain boundary barrier layer was confirmed by the non-ohmic I–V behaviour. The nonlinear coefficient was obtained at the current density J=0.01, 0.1 and 1mA/cm^2 for a series of WO_3–V_2O_5 samples. The V0.5mol% specimen showed an abnormal phenomenon that the nonlinear characteristics appeared at 350°C and disappeared at lower and higher temperatures. This implies that it could be applied as a high-temperature varistor. The double Schottky barrier model was adopted to explain the phenomena for the WO_3-V_2O_5 varistors.

Keywords: V_2O_5-WO_3 ceramics, current–voltage characteristics, microstructure
PACC: 7300, 6150K

1. Introduction

Voltage-dependent resistors or varistors are widely used for surge protection, both in electronic circuits and in power systems. Non-ohmic oxide ceramics based on ZnO containing small quantities of other metal oxides dominate the production of the best varistors for voltages higher than about 10V.[1] Because the request of autocontrol circuitry for semiconducting circuitry design becomes stricter and stricter for the properties of varistors, it is necessary to explore new functional materials with a very low breakdown voltage. It is known that the traditional additives are mainly Bi, Pr, Pb, and Ba etc,[2–4] which are large ions. Tsai and Wu [5,6] studied the effect of relatively light element vanadium doped ZnO ceramics. Varistors for lower voltages are available, which are made of titanium oxide;[7,8] however, varistors based on other ceramic systems, such as tungsten trioxide, are under investigation.

WO_3 is a nonstoichiometric n-type semiconductor due to oxygen loss, labelled as WO_{3-y}, and the electrical transport mechanism in tungsten trioxide has not been completely clarified yet. A lot of studies have shown that the electrical properties of tungsten trioxide depend on fabricating and measuring conditions.[9] Makarov and Trontelj [10] found that Na_2CO_3 and MnO_2-doped WO_3 ceramics exhibited nonlinear current–voltage characteristics with a low breakdown voltage; Wang *et al*[11,12] reported the nonlinear current-voltage characteristics of Na_2CO_3 and other oxide doped WO_3. The non-ohmic behaviour of WO_3–V_2O_5 ceramics has not been investigated yet. In this paper, the microstructure and non-ohmic behaviour of WO_3–V_2O_5 ceramics are reported.

2. Experimental details

Pure (99%) WO_3 and (99.95%) V_2O_5 powders were used to fabricate the ceramic specimen by a conventional method. The compositions investigated were $(100-x)$mol%WO_3+xmol%V_2O_5, where x=0.5, 3.5, 5, 8, and 15. The oxides were mixed and ball-

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milled in polypropylene jars with alcohol for 24h. After drying, the powders with binder were pressed at 20MPa into disks with 16mm in diameter and thickness of 3mm. The specimens were sintered at 900°C, 1000°C and 1100°C in air for 2h, respectively, and slowly cooled to room temperature. The as-sintered specimens were polished with 1200-grit SiC paper on both sides.

The crystalline phases in typical sintered WO_3–V_2O_5 ceramic specimens were identified by x-ray diffraction (XRD, ARLX'TRA, Switzerland) analysis. Their microstructures were examined by scanning electron microscope (SEM, HITACHI X-650, Japan); they were also characterized by an energy-dispersive spectroscopy (EDS) stage attached to the SEM. On both polished surfaces of samples, In–Ga and Ag liquid electrodes were painted for electrical measurement. In the following, the specimens with painted In–Ga electrode are called the In–Ga specimens, and the specimens with painted Ag electrode are called the Ag specimens. The specimens with different V_2O_5 contents are labelled as the Vmol% specimens. The nonlinear coefficient α was obtained using

$$\alpha = \frac{1}{\log(E_2/E_1)}, \qquad (1)$$

where α is the nonlinear coefficient, E_2 is the electric field corresponding to J_2=10J_1, and E_1 is the electric field corresponding to J_1=0.01, 0.1 and 1mA/cm^2. The conductivity of the samples was measured at E=0.1V/cm. The relative density of the samples was measured by the Archimedes method.

3. Results and discussion

3.1. Microstructure and densification

The XRD patterns of typical WO_3-V_2O_5 (V0.5, 3.5, 15mol%) specimens sintered at 1000°C are shown in Fig.1(a). It is known that the two phases of tungsten trioxide, i.e. monoclinic WO_3 (γ–WO_3) and triclinic WO_3 (δ–WO_3), coexist in the sintered WO_3 ceramics.[13,14] However, Fig.1(a) reveals the existence of the matrix phase of γ–WO_3 and the second phase—V_2WO_6 phase without δ–WO_3 phase. This indicates that the grain phase of WO_3 ceramic sintered at 1000°C is stabilized in γ-phase by V_2O_5 dopant. Figure 1(b) shows the phase WO_3–V_2O_5 (V3.5mol%) at different sintering temperatures. The grain phase of WO_3=-V_2O_5 sintered at 900°C is similar to the phase in the specimen sintered at 1000°C. When the phase of WO_3=-V_2O_5 is sintered at 1100°C, the δ-=WO_3 peaks can be observed.

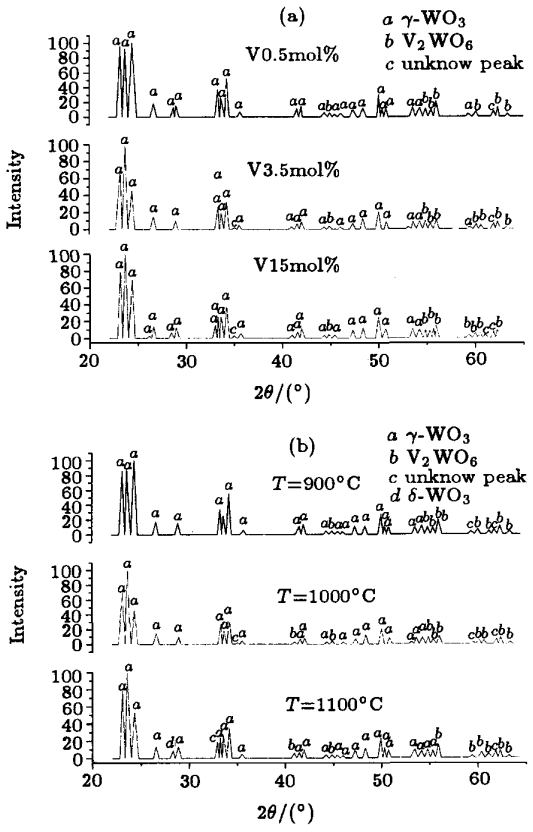


Fig.1. XRD patterns of typical WO_3–V_2O_5 specimens: (a) the V0.5, 3.5, 15mol% specimens sintered at 1000°C, (b) the V 3.5mol% specimens sintered at 900°C, 1000°C, and 1100°C, respectively.

Figures 2(a), (b) and (c) show the SEM microstructures of the V0.5, 3.5, 15mol% specimens sintered at 1000°C, respectively. It is found that the grain size is about 0.4–1.5μm. Compared with undoped WO_3 ceramics with a size of about 10μm,[12] it is clear that the doping of V_2O_5 restricts the growth of WO_3 grain. A conclusion can be drawn that the slight doping of V_2O_5 can strongly restrict the growth of grain. Figures 2(d) and (e) show the micrographs of the V3.5mol% specimen sintered at 900°C, 1100°C, respectively. It can be seen that the grain size of the V3.5mol% specimen sintered at 1100°C is 1–3μm, which is bigger than that sintered at 900°C and 1000°C. The sintering temperature has remarkable effect on the grain size.

The EDS results reveal that the vanadium element is absent within the grains, but segregated to the grain boundaries. Figure 3 shows the EDS spectrum of the grain phase and the grain boundary re-

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gion in the V15mol% specimen sintered at 1000°C. This result indicates that the V ions dissolved only slightly in the WO_3 grains during sintering, forming an intergranular vanadium-rich phase between WO_3 grains. This phenomenon has been also observed in ZnO–V_2O_5 ceramics by Tsai and Wu.[5]

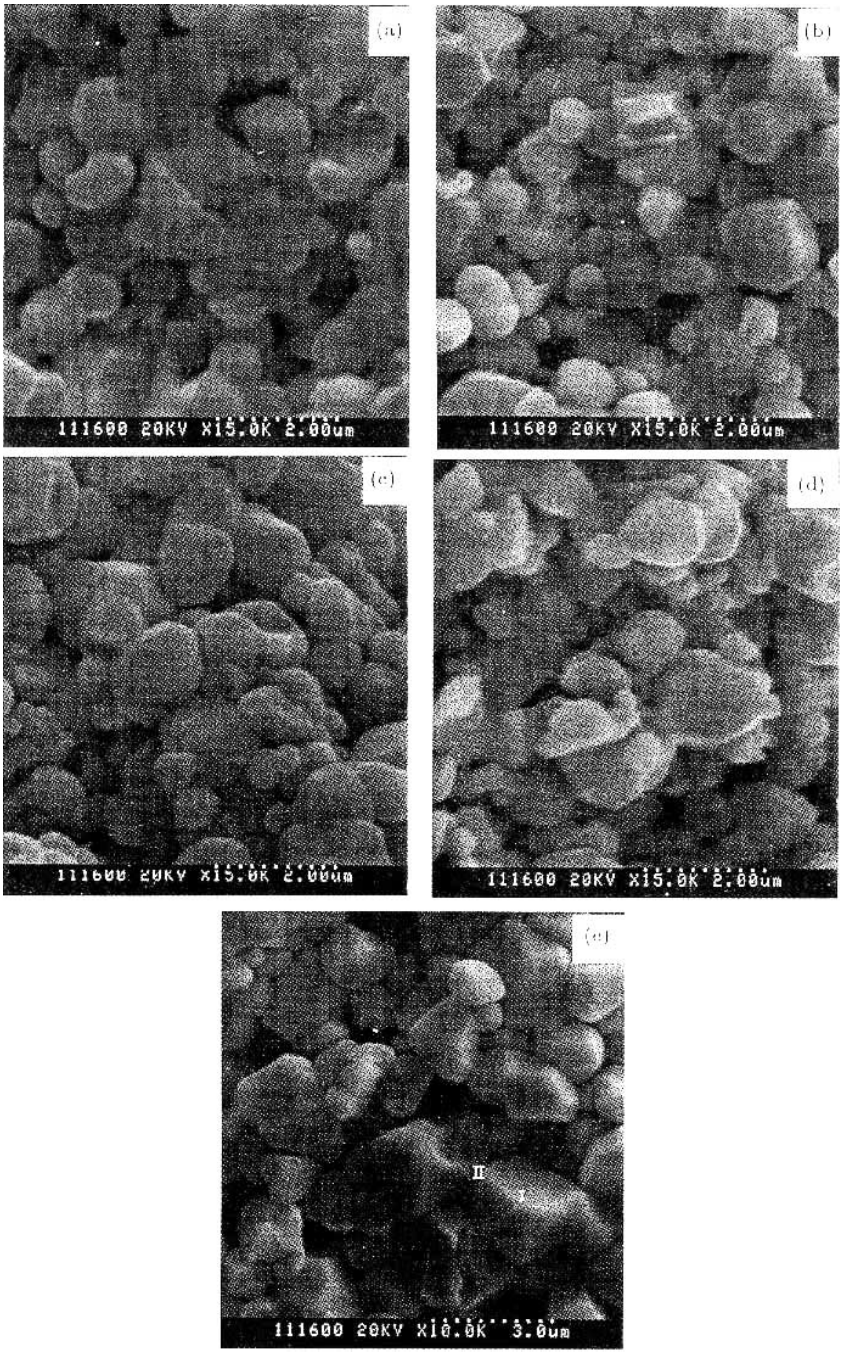


Fig.2. The microstructure of typical WO_3–V_2O_5 specimens: (a) the V0.5mol% specimen, (b) the 3.5mol% specimen, (c) the V15mol% specimen, sintered at 1000°C; (d) and (e) the V3.5mol% specimens sintered at 900°C and 1100°C, respectively.

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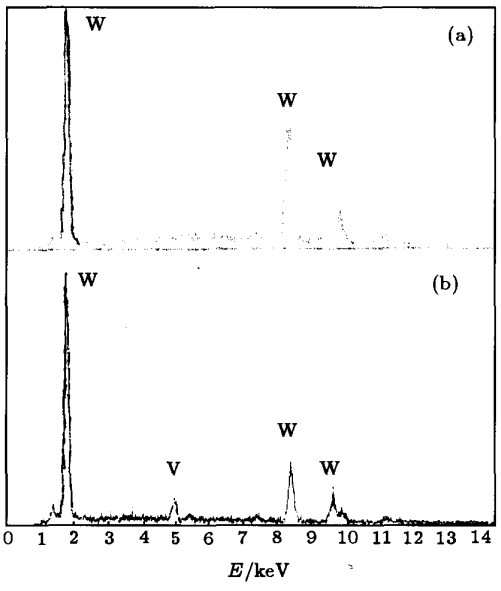


Fig.3. EDS spectra of the V15mol% specimen: (a) intra-grain region (marked 'I' in Fig.2(e)), (b) grain boundary region (marked 'II' in Fig.2(e)).

The radial shrink rate and relative density of the WO_3–V_2O_5 ceramics sintered at 1000°C are functions of the V_2O_5 content, as can be seen from Fig.4. The radial shrink rate and relative density of the specimens increase with increasing V_2O_5 content. Since V_2O_5 has a low melting point 690°C and the melting point of WO_3 is 1473°C, it is believed that the addition of V_2O_5 must have acted as a liquid phase sintering (LPS) agent in the specimens sintered at 900°C, 1000°C and 1100°C. With the increase of the V_2O_5 content, the liquid phase increases, which is in favour of the densification process, so that the radial shrink rate and the relative density of specimens increase.

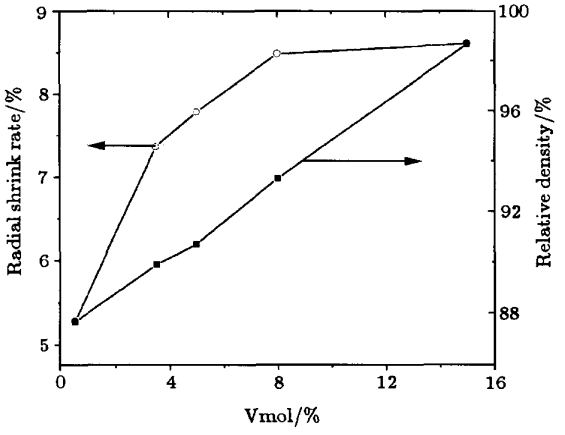


Fig.4. The radical shrink rate and relative density of WO_3 ceramics doped with different V_2O_5 contents.

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3.2. Electrical properties

3.2.1. Room temperature measuring

As can be seen from Table 1, the dc conductivity σ of the specimens increases with increasing V_2O_5 content. It is noticed that when the V_2O_5 content is below 5mol%, σ increases relatively smoothly with the increase of the V_2O_5 content, but once the content exceeds 5mol%, σ increases sharply. This suggests that a large number of carriers are introduced by V_2O_5 dopant, especially when the concentration of the dopant exceeds 5mol%.

The nonlinear characteristic curves for a series of WO_3–V_2O_5 specimens sintered at 1000°C and measured at room temperature (RT) are shown in Fig.5. Figures 5(a) and (b) show the current–voltage characteristic curves for the In–Ga specimens and the Ag specimens respectively. The corresponding α is shown in Table 1. From Fig.5(a) and Table 1, we can see that the nonlinear characteristic of the V0.5mol% In–Ga specimen is very weak. Further addition of V_2O_5 increases the nonlinear coefficient until it reaches the

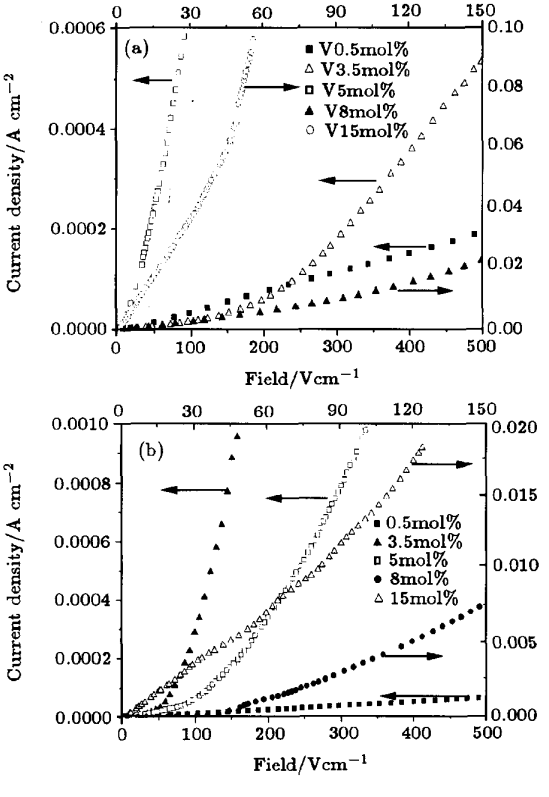


Fig.5. The current–voltage characteristics of various WO_3–V_2O_5 specimens sintered at 1000°C: (a) the In–Ga specimens, (b) the Ag specimens.

maximum value around 2.4 for the V3.5mol% specimen. Then with further increase of the concentration of V_2O_5, the nonlinear coefficient α decreases gradually. Comparing Figs.5(a) and (b), the nonlinear characteristics of the In–Ga specimens and the Ag specimens have similar trend with the change of the V_2O_5 content. This implies that the non-ohmic behaviour is a bulk intrinsic property of WO_3–V_2O_5 ceramics. But it is noticed that there are some differences, indicating that the electrodes have some effects on the nonlinear characteristics of the specimens. It is important that the V0.5mol% specimen has almost no nonlinear characteristic, and the V3.5mol% specimen has the biggest nonlinear characteristic among all the samples. Table 2 shows the effect of sintering temperature on the nonlinear coefficient of the V3.5mol% and V5mol% In–Ga specimens. The maximum α is obtained when the sample is sintered at 1000°C.

Table 1. The α value (J_1=0.1mA/cm^2) and dc conductivity (E=0.1V/cm) of various WO_3–V_2O_5 specimens sintered at 1000°C.

V(mol%)	0.5%	3.5%	5%	8%	15%
α (In–Ga)	1.1	2.38	1.48	0.99	1.04
α (Ag)	0.99	3.44	2.3	2.1	1.1
σ (10^{-9}Scm^{-1})	3.3	10.4	22.9	616.9	11481.5

Table 2. The α value of the In–Ga specimens sintered at different temperatures.

T/°C	900		1000		1100	
J_1/(mA/cm^2)	0.01	0.1	0.01	0.1	0.01	0.1
α (V3.5mol%)	1.46	–	1.5	2.38	0.91	1.03
α (V5mol%)	1.45	–	1.62	1.48	–	1.08

3.2.2. Measurement at various ambient temperatures

Figure 6(a) shows the current–voltage curves of the V3.5mol% Ag specimen at different ambient temperatures. The α of the V3.5mol% Ag specimen is given in Table 3. It can be seen that α decreases with the increase of the ambient temperature when it exceeds 100°C. From Fig.6(b), the current–voltage characteristic of the V0.5mol% Ag specimen is almost linear when the ambient temperature is below 300°C. But when the ambient temperature is 350°C, the V0.5mol% Ag specimen reaches the biggest nonlinear characteristic with α=1.42 (J_1=0.1mA/cm^2), as seen from Table 4. This is an abnormal phenomenon because usually the electrical nonlinearity of a material would degrade quickly as temperature increases: so called thermal runaway.[11] When the ambient temperature further increases, the nonlinear characteristic disappears.

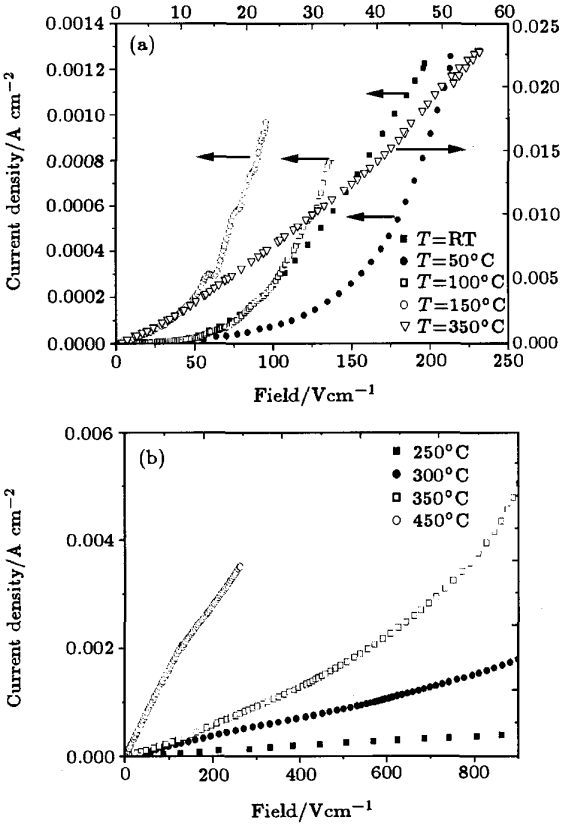


Fig.6. The nonlinear characteristic curve of WO_3–V_2O_5 specimens measured at various ambient temperatures: (a) the V 3.5mol% specimen, (b) the V0.5mol% specimen.

Table 3. The α value of the V3.5mol% specimen measured at various ambient temperatures.

T/°C	RT	50	100	150	350
J_1=0.01mA/cm^2	2.34	2.37	1.96	1.05	–
J_1=0.1mA/cm^2	3.41	2.87	3.38	1.82	0.83

Table 4. The α value of the V0.5mol% specimen measured at various ambient temperatures.

T/°C	200	250	300	350	450
J_1=0.1mA/cm^2	0.92	0.96	1.01	1.12	–
J_1=1mA/cm^2	–	0.98	1.16	1.42	1.01

Figure 7 shows the variation of conductivity lnσ with the inverse of the temperature for the V3.5mol% specimen at 1V/cm in linear region of the current–voltage curves: that is, the Arrhenius plot. As temperature rises, the conductivity increases; the sample

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exhibits a semiconductive behaviour. The activation energy E_α is calculated using the formula

$$\sigma = \sigma_0 e^{-E_\alpha/kT}, \quad (2)$$

where σ_0 is the pre-exponential factor, k is the Boltzmann constant and T is the temperature. The activation energy is about 0.24eV, which is less than that of pure WO_3 [9].

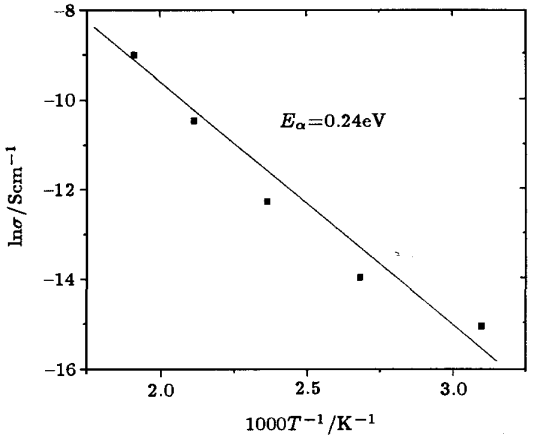


Fig.7. Arrhenius plot of the V 3.5mol% specimen.

3.3. Discussion

It is believed that part of the vanadium element is dissolved into the WO_3 lattice; even the V_2O_5 content is quite low. This phenomenon also exists in ZnO ceramics doped with V_2O_5.[5] The ion radius of V^{5+} is 0.059nm, which is close to that of W^{6+} ion, 0.065nm. Therefore, a substitution reaction occurs as

$$V_2O_5 \xrightarrow{WO_3} 2V_W^- + V_O^{2+} + \frac{5}{2}O_2. \quad (3)$$

When two V^{5+} ions diffuse into the WO_3 lattice and occupy two W^{6+} sites forming V_W^-, there will be two negative charges. To obtain the electric charge balance, one free oxygen vacancy (V_O^{2+}) is created. This is a defect compensation reaction.

By an analogy to the grain boundary defect model used to explain the formation of electrical Schottky barrier for ZnO varistors developed by Gupta and Carlson,[15] the nonlinear behaviour of V_2O_5-doped WO_3 ceramics can be explained. The positive charges (W_j^{6+}, V_O^{2+}) are located on both sides of the grain boundary, and the negative charges (V_W^-, V_W^{6-}, e^-) are distributed at the grain boundary interface. Due to the charge compensation between the positive and the negative charges, a depletion layer is created at the grain boundary.[16] As a result, a Schottky barrier is formed, leading to the nonlinear electrical behaviour of V_2O_5-doped WO_3 ceramics.

When the V_2O_5 content is about 0.5mol%, the entire additive segregates in the grain boundary regions so that the substitution reaction would not happen and the Schottky barrier is not formed. As a result, the electrical property is almost linear. This means that the resistance under either low electric field or high electric field is almost the same. So, the resistance of the V0.5mol% specimen is the largest among all the samples without showing the nonlinear electric properties. If the content of V_2O_5 increases up to 3.5mol%, part of vanadium ions enters into WO_3 lattice so that the substitution reaction happens and the Schottky barrier forms. In this case the resistance of the grain boundary increases, because electrical properties of varistors under low electrical field are mainly controlled by grain boundary as pointed out by Gupta.[1] The resistance of the V3.5mol% specimen under low electric field and high electric field are different so that it exhibits nonlinear electric properties. With further increase of V_2O_5 concentration, vanadium ions, which are mainly segregated at grain boundaries, will diffuse into the grains, and the barrier height decreases with the V_2O_5 content, hence α will decrease accordingly. It can be understood why dc conductivity increases sharply with the increase of V_2O_5 addition when V_2O_5 addition exceeds 5mol% if the diffusion of vanadium ions is taken into consideration.

It is well known that tungsten trioxide γ–β shows a phase transition at 330°C. Many authors [14] have observed the coexistence in a rather large temperature range. For the V0.5mol% Ag specimen the biggest nonlinear coefficient is obtained at 350°C, because of the coexistence of γ-WO_3 and β-WO_3.

4. Conclusions

The densification behaviour, microstructure, and electrical properties of WO_3 ceramics have been studied with V_2O_5 as the additive ranging from 0.5 to 15mol%. The grain growth of WO_3 is restricted strongly by the addition of V_2O_5. At room temperature, the V3.5mol% specimen sintered at 1000°C exhibits the best nonlinear characteristics. The nonlinear electrical behaviour can be explained using the Schottky barrier model. The nonlinear characteristic of the V0.5mol% specimen appeared at 350°C because of the coexistence of γ–WO_3 and β–WO_3, indicating that it can be used as a high temperature varistor.

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