ZnO 바리스터에서 첨가물이 쌍정에 미치는 영향

The Effect of Additives on Twins in ZnO Varistors

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Abstract

By comparison of the experimental results in two systems of ZnO varistors, its appear that Sb_2O_3 is the indispensable element for twinning in ZnO varistors, and the $Zn_7Sb_2O_{12}$ spinel acts as the nucleus to form twins. Al_2O_3 is not the origin of twinning in ZnO varistor, but it was found that Al_2O_3 could strengthen the twinning and form a deformation twinning by $ZnA_{12}O_4$ dragging and pinning effect. The inhibition ratios of grain growth and nonuniformity of two systems ZnO varistors increase with the increase of Al_2O_3 content. The twins affect the inhibition of grain growth, the mechanism could be explained follow as : twins increase the mobility viscosity of ZnO grain and grain boundary, and drag ZnO grain and liquid grain boundary during the sintering , then the grain growth is inhibited, and the microstructure becomes more uniform.

Key Words : Twinning, ZnO Varistor, Al_2O_3, Sb_2O_3, Dragging and Pinning Effect, Deformation Twinning

1. Introduction

Various additives are added into ZnO to improve physical properties of varistors. Bi_2O_3 is used to form the grain boundary layer, and Sb_2O_3 is added to ZnO varistor to control densification and grain growth. The inhibition of grain growth by Sb_2O_3 is considered to be dominated by a drag mechanism of $Zn_7Sb_2O_{12}$ spinel, and a reduction of grain boundary mobility due to twin formation in virtually all ZnO grain. Optimum addition of Al_2O_3 to ZnO effectively improve the nonlinearity by delaying the onset of the upturn-voltage and inhabit the grain growth.

Twinning is a common phenomena in ZnO varistors containing Sb_2O_3. Wang. *et al.* observed that grains in commercial ZnO varistors(Harris Co.) comprise twinning. Gupta noted that the grains in commercial polycrystalline ZnO varistors are always accompanied by twins. Senda and Bradt discussed the twinning mechanism in ZnO ceramics containing Sb_2O_3. However, there were no discussions about different additives on twinning in any literatures. Especially, there is no the research of effects of Al_2O_3 on twinning. The purposes of this paper is to investigate complex effects of different additives on twinning and analyze the effect of twins on grain growth in ZnO varistors.

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2. Sample Preparation

ZnO varistor samples are prepared in two different systems to analyze the effects of Al_2O_3 and Sb_2O_3 on twinning. A-series consist of 7 compositions according to Al_2O_3 contents in ZnO,

$3wt\%Bi_2O_3$, $3.6wt\%Sb_2O_3$, $1.16wt\%Co_2O_3$, $0.88wt\%NiO$, $0.71wt\%MnO_2$, $0.93wt\%Cr_2O_3$. B-series are same with A-series beside Sb_2O_3.

ZnO varistor samples are made by the conventional technique[16]. The samples are mechanially grounded by SiC papers, and then polished with 1-m Al_2O_3 powder. The polished surfaces are etched with a 2% $HClO_4$-ethanol solution and observed with a scanning electron microscope(SEM). X-ray diffraction analyser is used to analyse the crystalline phase of samples by using Al-K target at 1.5/min. scanning speed. Specimens for the transmisson electron microscope(TEM) are prepared by cutting 3 mm diameter disks with an ultrasonic cutter and grounded to less than 100 μm with SiC papers and polished with 1 μm Al_2O_3 powder. The specimens are then thinned to 1000 Å by ion milling method, and investigated at an acceleration voltage of 300 kV. The operating parameters of TEM are λ = 1.8 Å and camera length, L of 50 cm.

3. Results and Discussion

Typical SEM photo of system of ZnO varistor is given in Fig. 1. There are always twinning existing in ZnO grains of A-series, but no twnning in grains of Bi-series. This phenomon shows that the Al_2O_3 dopant is not the origin of twinning in ZnO varistor.

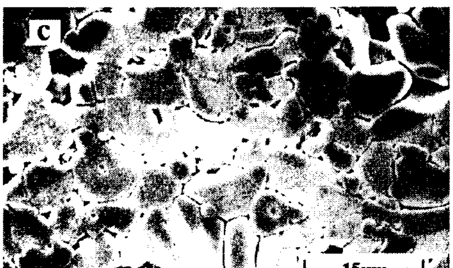

Fig. 1. SEM photos of twinning(Al_2O_3 content of 0.005 wt%)

Ordinally, commercial ZnO varistor consists of additions, such as Bi_2O_3, Co_3O_4, Cr_2O_3, MnO_2, Sb2O3, Al_2O_3, and Nb_2O_5. Gupta reported that ZnO varistor containing Bi_2O_3 and other additions, such as Co, Mn, and Sb etc., generated crystallographic twins. But there was not twinning existing in $ZnO-Pr_6O_{11}$ varistors containing Co, K, Cr, etc. additions[9,11]. Senda and Bradt and Gupta did not observe twinning in pure ZnO and $ZnO-Bi_2O_3$ varistor, but twinning was always observed in ZnO varistors with Sb_2O_3. From our observation in two different systems of ZnO varistors and results in other literatures mentioned above, it is evident that Sb_2O_3 act as the indispensable element for twinning in ZnO varistors. Similarly, in our experimental results, it was observed that all twins are single ones located at or near to the centers of ZnO grains from the SEM photo of sample A1 without Al_2O_3 in Fig. 1.

The number of twins and ZnO grains number were counted from the SEM photo and the ratio of twinning was calculated with Al_2O_3 contents, which is illustrated in Fig. 2. As discussed above, the Al_2O_3 dopant is not the origin of twinning in ZnO varistor, but the twinning ratio increases obviously with the increase of Al_2O_3 content. When Al_2O_3 content reaches 1wt%, about 50-60 percent of ZnO grains was twins. Therefore, it appears that the Al_2O_3 is not the origin of twinning in ZnO varistors, but it promotes twin formation.

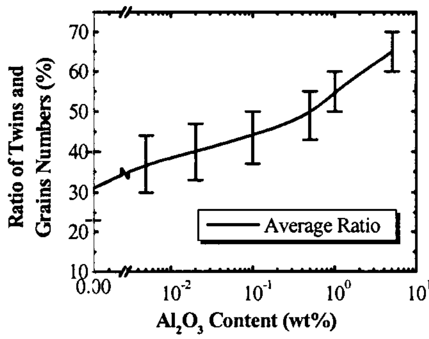

Fig. 2. The ratio of twinning with different Al_2O_3 contents.

The microstructures of twins with Al_2O_3 are not same with those in $ZnO-Sb_2O_3$ and $ZnO-Sb_2O_3-Bi_2O_3$ systems varistors. Only a part of twins with Al_2O_3 have twin grain boundary always located at or near to the center of the ZnO grain caused by grain growth mechanism. And other twin boundaries show a complicated shapes. When the Al_2O_3 content is small, a large number of twins are growth twins, and complicated twins are observed only few. But the portion of grains having complicated twin boundaries increase with the increase of Al_2O_3 content.

To estimate the inhibition effects on grain growth in ZnO varisors, the average intercept length and its respective standard deviation of ZnO varistor grains are used. The inhibition of grain growth is observed with the increase of Al_2O_3 contents in two systems as discussed in literatures. The standard deviation becomes smaller, and the microstructure of ZnO varistor becomes more uniform with the increase of Al_2O_3. In order to analyze the effect of Al_2O_3 on grain growth, the inhibition ratio of grain growth and nonuniformity inhibition ratio are calculated. Then, the inhibition ratio of grain growth *Kg* is defined as

$$K_g = (D_0 - D_i) / D_0 \quad (1)$$

here, *D*0 is the average grain size of the sample of B-series without Al_2O_3, and *Di* is the average grain size of sample of A and B-series with *i* wt% Al_2O_3. And the nonuniformity inhibition ratio *Ku* is defined as

$$K_u = (\sigma_0 - \sigma_i) / \sigma_0 \quad (2)$$

here, 0 is the standard deviation of the sample of B-series without Al_2O_3, and *i* is the standard deviation of sample in A and B-series with *i* wt% Al_2O_3. Because the grain growth of the sample of B-series without Al_2O_3 is not affected by Al_2O_3 ,Sb_2O_3 and twin, its average and standard deviation are used as the comparing criterion to calculate *Kg* and *Ku*. Therefore, higher *Kg* is, better the inhibition effect is and higher *Ku* is, more uniform the ZnO varistor is.

Fig. 3 and Fig. 4 show that the inhibition ratios of grain growth and nonuniformity of two systems ZnO varistors increase with the increase of Al_2O_3 content. As discussed by Nunes and Bradt, Quadir and Readey, Al_2O_3 reacts with ZnO to form $ZnAl_2O_4$ spinel during sintering. $ZnAl_2O_4$ spinel inhabits the grain growth by dragging and pinning effects. So, because more $ZnAl_2O_4$ spinels are formed, the inhibition effect on grain growth is stronger and the the microstructure of ZnO varistor becomes more uniform with the increase of Al_2O_3 content.

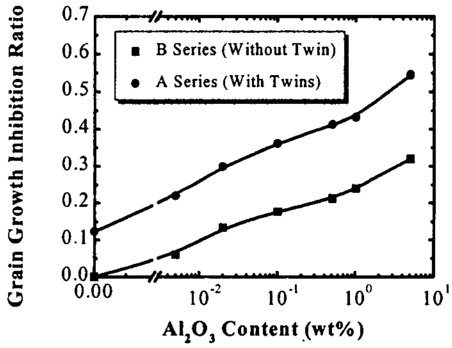

Fig. 3. The inhibition ratio of Grain growth with different Al_2O_3 contents.

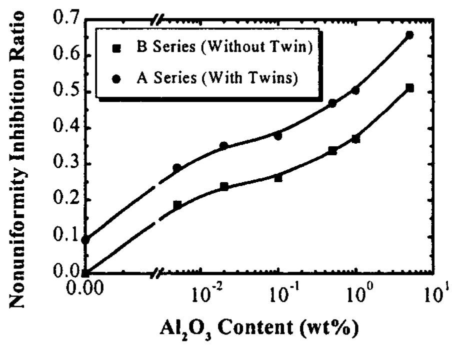

Fig. 4. Nonuniformity inhibition ratio of with different Al_2O_3 contents.

The relationship among twins ratio, Al_2O_3 content and average grain size of A-series ZnO varistors are given in Fig. 5. When Al_2O_3 is added into A-series ZnO varistors, the twin obviously increases with the increase of Al_2O_3 content. This result appears that Al_2O_3 affects the twin formation.

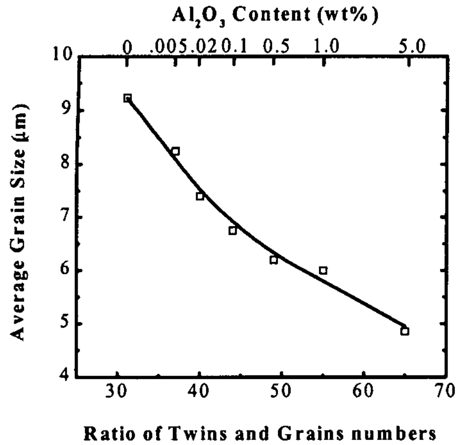

Fig. 5. The relation between the average grain size and the ratio of twins and grains numbers of ZnO varistors.

The effects of only twins on ZnO grain growths and the uniformity in microstructures of ZnO varistors are given in Fig. 6. However, the differences contain the effects of the $Zn_7Sb_2O_{12}$ spinel, which are difficult to be expelled from those differences. The inhibition ratios of grain growth and the nonuniformity increaes obviously with the increase of twins in Fig. 6.

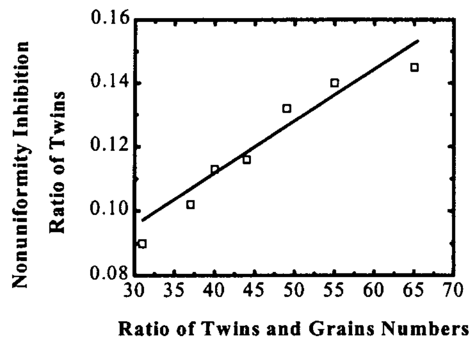

Fig. 6. Twins effect on the nonuniformity in microstructure of ZnO varistors.

4. Conclusions

By comparison of the experimental results in two different systems of ZnO varistors, it is shown that Sb_2O_3 acts as the indispensable element for twinning in ZnO varistors and the $Zn_7Sb_2O_{12}$ spinel acts as nuclei to form twins. The Al_2O_3 dopant is not the origin of twinning in ZnO varistor, but Al_2O_3 promoted the twinning and formed $ZnAl_2O_4$ which deformed twinning by dragging and pinning. The inhibition ratios of grain growth and nonuniformity of two systems ZnO varistors increase with Al_2O_3 content. The twins affects the inhibition of ZnO grain growth. Grain inhibition mechanism by twins could be explained that the twins decrease the mobility of ZnO grain and increase of viscosity of grain boundary, and drag ZnO grain and liquid grain boundary, and then the grain growth is inhibited, and the microstructure becomes more uniform.

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