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The Effect of Additives on Twinning in ZnO Varistors

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By comparison of the experimental results in two systems of ZnO varistors, it's 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 $ZnAl_2O_4$ 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, Nonuniformity

I. 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.[1,2] 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.[1] 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.[3-6]

Twinning is a common phenomena in ZnO varistors containing Sb_2O_3.[1,7-17] Wang. *et al.*[7] observed that grains in commercial ZnO varistors (Harris Co.) comprise twinning. Gupta[8] noted that the grains in commercial polycrystalline ZnO varistors are always accompanied by twins. Senda and Bradt[14] discussed the twinning mechanism in ZnO ceramics containing Sb_2O_3. In other hand, Kim and Goo[13] researched the stacking layer of the cation and anion in the twin boundary of ZnO added with Sb_2O_3, Bi_2O_3 and CoO in detail and identified that the cation and anion are associated closely with the twin boundary and described the head-to-head configuration which results from this twinning in the ZnO structure with polar hexagonal. 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.

II. Samples 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 in Table 1. B-series are same with A-series beside Sb_2O_3.

ZnO varistor samples are made by the conventional technique.[16] The mixtures of raw materials are dried by spraying at 8000 rpm and then pressed into discs at a pressure of 600 kg/cm^2. The pressed bodies are sintered at 1200°C for 2 hrs. in air and cooled to room temperature. The final size of samples is 15 mm in diameter and 1 mm in thickness. The samples are mechanially grounded by SiC papers and then polished with 1-μm Al_2O_3 powder. The

Table 1. The Compositions of ZnO Varistor Samples

A-Series	ZnO-3.0wt%Bi2O3-3.6wt% Sb_2O_3-16wt%Co_2O_3-0.88wt% NiO-0.71wt%MnO_2-0.93wt% Cr_2O_3	A1	Al_2O_3 -None
		A2	Al_2O_3 -0.005wt%
		A3	Al_2O_3 -0.02wt%
		A4	Al_2O_3 -0.1wt%
		A5	Al_2O_3 -0.5 %
		A6	Al_2O_3 -1.0wt%
		A7	Al_2O_3 -5.0wt%
B-Series	ZnO-3.0wt%Bi_2O_3-1.16wt%Co_2O_3-0.88wt% NiO-0.71wt%MnO_2-0.93wt% Cr_2O_3	B1	Al_2O_3 -None
		B2	Al_2O_3 -0.005wt%
		B3	Al_2O_3 -0.02wt%
		B4	Al_2O_3 -0.1wt%
		B5	Al_2O_3 -0.5wt%
		B6	Al_2O_3 -1.0wt%
		B7	Al_2O_3 -5.0wt%

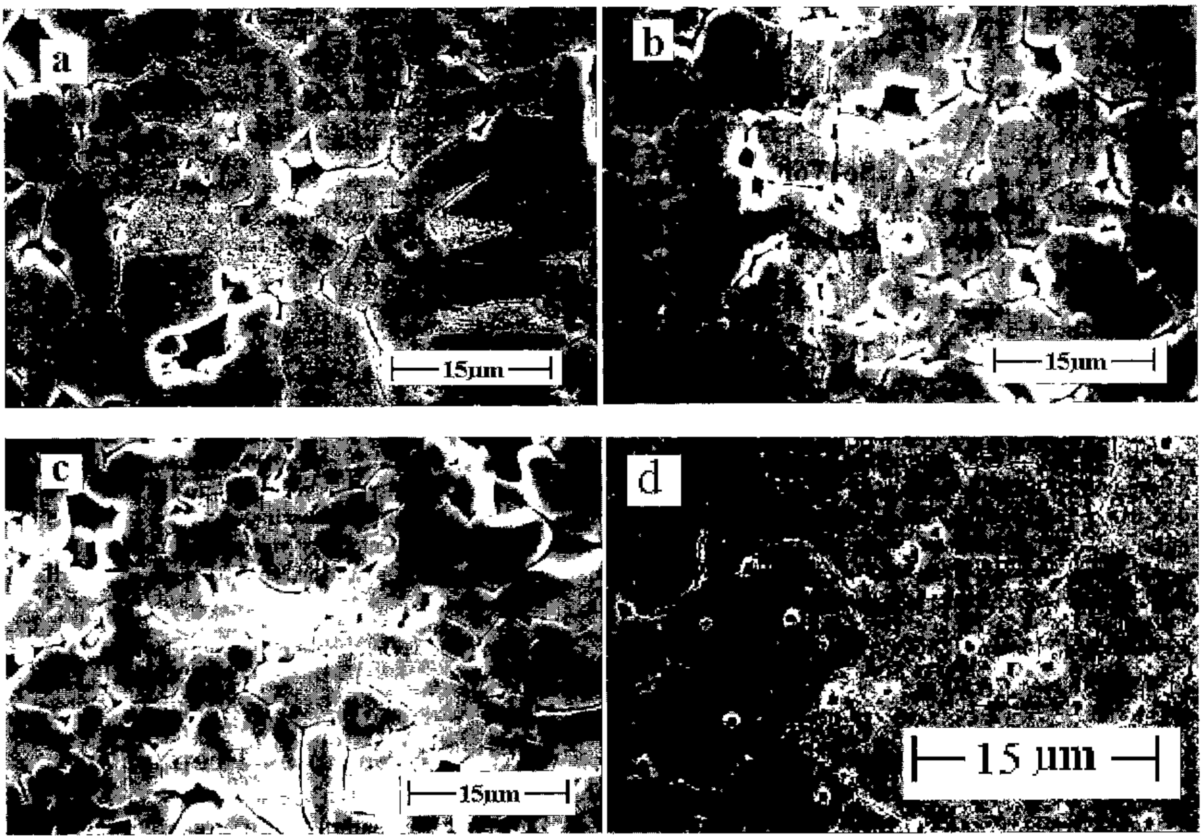

Fig. 1. SEM photos of twinning in commercial ZnO varistors with different Al_2O_3 content, (a) 0 wt%, (b) 0.005 wt%, (c) 1wt% Al_2O_3 and (d) sample of B series with 0.5 wt% Al_2O_3.

polished surfaces are etched with a 2% $HClO_4$-ethanol solution and observed with a scanning electron microscope (SEM)(Hitachi, S-2700). X-ray diffraction analyser (Phillips, PW 1830) is used to analyse the crystalline phase of samples by using Al-Kα target at 1.5°/min. scanning speed. Specimens for the transmisson electron microscope (TEM) (Hitachi, H-9000 NAR) 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 1000Å by ion milling method, and investigated at an acceleration voltage of 300 kV. The operating parameters of TEM are λ=1.8Å and camera length, L, of 50 cm.

III. Results and Discussion

1. The effect of Sb_2O_3 on twinning in ZnO varistors

SEM photos of two different systems of ZnO varistors are given in Fig. 1. There are always twinning existing in ZnO grains of A-series, but no twnning in grains of Bi-series. This phenomenon shows that the Al_2O_3 dopant is not the origin of twinning in ZnO varistor.

Ordinally, commercial ZnO varistor consists of additions, such as Bi_2O_3, Co_3O_4, Cr_2O_3, MnO_2, Sb_2O_3, Al_2O_3 and Nb_2O_5. Gupta[8] 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[17] and Gupta[8] 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.[1] 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. Senda and Bradt[1] analyzed the formation intensity of the twinning to Sb_2O_3 added to pure ZnO. They observed a single twin boundary in every ZnO, regardless of the Sb_2O_3 content, the sintering temperature or the grain size of the ZnO ceramics. It was statistically studyed by Yamamoto *et al.*[9,11] that the individual twin boundary was always located at or near to the center of the ZnO grain. 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(a).

Fig. 2(a), (b) are the TEM photos of selected-area-diffraction pattern (SADP) and the bright-image in the ZnO grain of sample A4, respectively. The bright-image in Fig. 2(b) shows a continuous thickness fringes across the ZnO grain, which are known as a typical phnomenon of twinning.[14] Then, the selected-area-diffraction pattern (SADP) at the [1-1 1] zone axis is illustrated in Fig. 2(a).

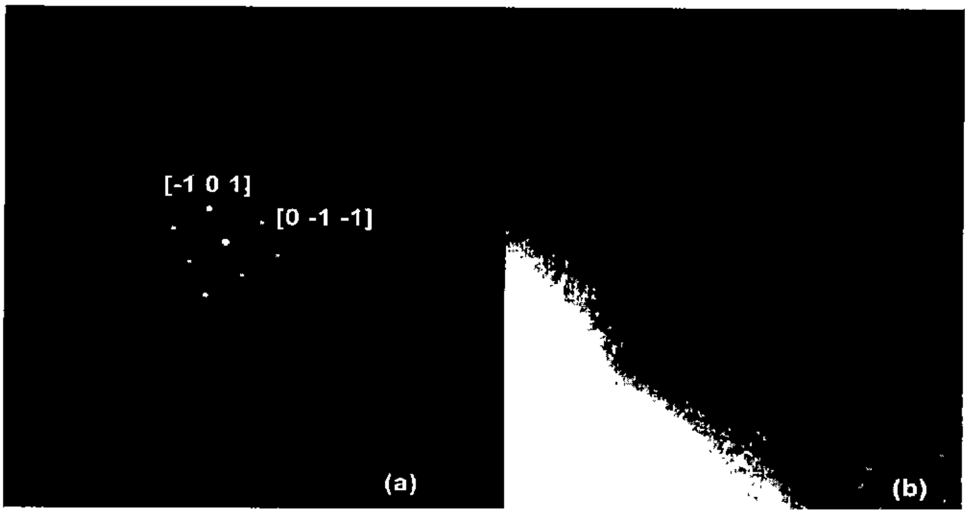

Fig. 2. TEM photos of twins in the ZnO grain of sample A4 (0.1wt% Al_2O_3 content) (a) the selected-area-diffraction pattern (SADP) and (b) the bright-image.

ZnO has the wurtzite structure and belongs to th P6$_3$mc space group which is hexagonal and polar. The wurtzite suructure of ZnO can be described as a close packed oxygen anion structure consisting of layer of oxygen anions with the smaller zinc cations located at the tetrahedral interstics. It is nesssary to consider if either the antimony oxide or the $Zn_7Sb_2O_{12}$ spinel structure may have any relationship or potential effect on the ZnO structure to twin. The spinel structure is not too different in its atomic arrangement from the wurtzite structure, as it also consists of stacked layers of colse packed oxygen anions.[13,12] This suggests that perhaps the twinning condition that is created by the addition of antimony oxide to ZnO may be similar in its fundamental nature to the traditional hexagonal/cubic/hexagonal stacking layer sequency wihich so often occurs for the twinning of hexagonal meterials.[12]

2. *Strengthening effect of Al_2O_3 on twinning and deformation*

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. 3. 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.

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.[14] 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. The typical SEM photo of complicated twins are shown in Fig. 4. We can observe No.2, No.3, No.6, No.8, No.12, No.17, No.18 grains have growth twins; No.1 and No.13 grains have zigzag twin boundaries; No. 7 and No.14 grains have "Z" shape twin boundaries; No.10, No.11, and No.16 have triangle twin boundaries. In the results, it would be said that these complicated twins are belong to a kind of deformation twins.[14]

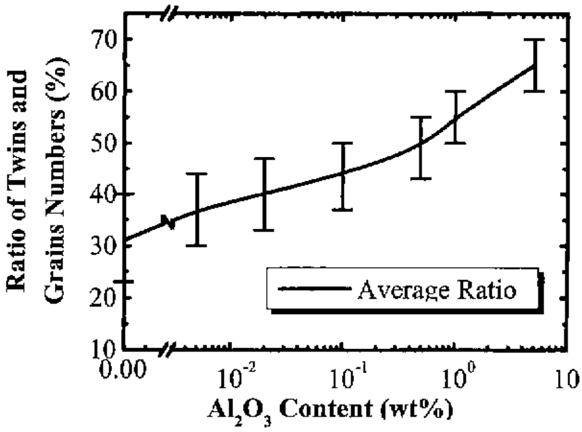

Fig. 3. The ratio of twinning with different Al_2O_3 contents.

The possible mechanism to generate deformation twinning could be explained when Al_2O_3 is added to ZnO-Bi_2O_3-Sb_2O_3 system ZnO varistors. During sintering, Al_2O_3 reacts with ZnO to form $ZnAl_2O_4$ spinel, which was observed by X-ray diffraction of ZnO varistors as given in Fig. 5. But the $ZnAl_2O_4$ spinel can not act as nucleus to form twin like $Zn_7Sb_2O_{12}$ spinel, because twinning is not

Fig. 4. The deformation twins in ZnO varistor sample of A-series with 1 wt% Al_2O_3 addition.

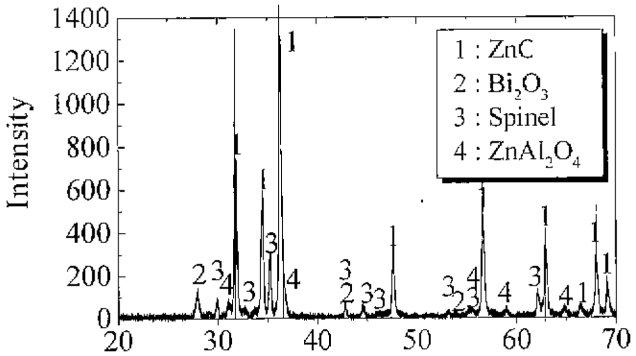

Fig. 5. X-ray diffraction pattern of commercial ZnO varistor with 5 wt% Al_2O_3.

observed in $ZnO-Bi_2O_3-Al_2O_3$ system ceramics. As discussed by other researchers,[3,6] $ZnAl_2O_4$ spinel inhibit the grain growth by dragging and pinning effect at the grain boundary. Then mechanical stress would be generated when ZnO grain collide with $ZnAl_2O_4$ spinel due to thermal motion. In the other hand, thermal stresses would be developed between the ZnO primary and the $ZnAl_2O_4$ spinel as a sequence of thermal expansion due to the mismatch of those phases. The mechanical and thermal stresses would lead to deformation twinning. Where it was known that the small thermal stress could not generate the serious deformation twin in ZnO varistors.[14]

Consequently, when the $ZnAl_2O_4$ spinel pins in the grain boundary during sintering, it blocks the motion of liquid Bi_2O_3 grain boundary by dragging and pinning effect and then its wrapping effect to $Zn_7Sb_2O_{12}$ spinel would be reduced, and more twins are generated. With the increase of Al_2O_3 content, more $ZnAl_2O_4$ spinels would be formed and then the blocking effect to liquid Bi_2O_3 grain boundary increases. This causes the wrapping effect weaken and then more $Zn_7Sb_2O_{12}$ spinels are free to form twins as nuclei. In the other hand, the mechanical stress generated by ZnO grain colliding with $ZnAl_2O_4$ spinel due to thermal motion increases, and leads to form more deformation twins.

3. Inhibiton effect of twins on grain growth in ZnO varistors

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 literature.[2,3] 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 K_g is defined as

$$K_g = (D_0 - D_i)/D_0, \qquad (1)$$

here, D_0 is the average grain size of the sample of B-series without Al_2O_3, and D_i is the average grain size of sample of A and B-series with *i* wt% Al_2O_3. And the

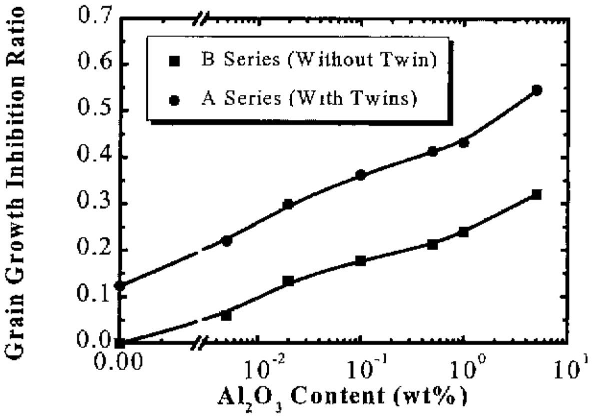

Fig. 6. The inhibition ratio of Grain growth with different Al_2O_3 contents.

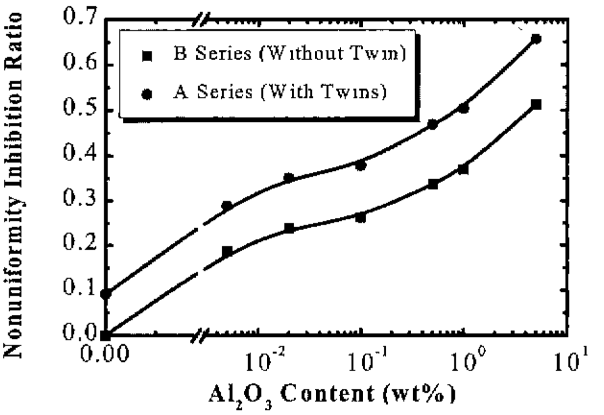

Fig. 7. Nonuniformity inhibition ratio of with different Al_2O_3 contents.

nonuniformity inhibition ratio K_u is defined as

$$K_u = (\sigma_0 - \sigma_i)/\sigma_0, \qquad (2)$$

here, σ_0 is the standard deviation of the sample of B-series without Al_2O_3 and σ_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 K_g and K_u. Therefore, higher K_g is, better the inhibition effect is and higher K_u is, more uniform the ZnO varistor is.

Fig. 6 and Fig. 7 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,[2] Quadir and Readey,[3] 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.

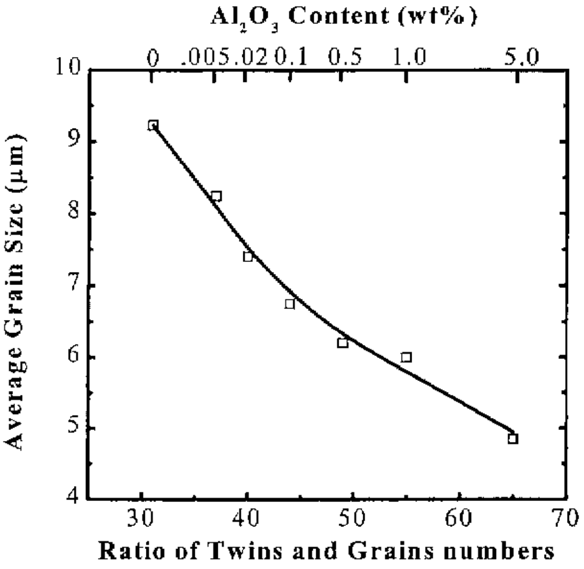

Fig. 8. The relation between the average grain size and the ratio of twins and grains numbers of ZnO varistors.

In other hand, when Sb_2O_3 is added into ZnO varistor, the $Zn_7Sb_2O_{12}$ spinel inhibits the grain growth, too. Senda and Bradt[1] suggested that Sb_2O_3 effect on grain growth inhibition in ZnO-Sb_2O_3 system varistor. They supposed that both the $Zn_7Sb_2O_{12}$ spinel and the twins are responsible for the ZnO grain growth inhibition by Sb_2O_3.

All samples in B-series do not contain any twin. So the inhibition of grain growth in B-series is the only effect of Al_2O_3. But in A-series with Sb_2O_3, all samples have twins. As a result, the inhibition ratio of grain growth in A-series is the total effect by Al_2O_3, Sb_2O_3 and twins.

The relationship among twins ratio, Al_2O_3 content and average grain size of A-series ZnO varistors are given in Fig. 8. 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.

If the twins do not affect the ZnO grain growth and the uniformity in ZnO varistors, then there should be only a constant differences between two curves in Fig. 6 and Fig. 7 for simplification, where, the constant differences is the influence of Sb_2O_3 on grain growth inhibition by the dragging effect of formed $Zn_7Sb_2O_{12}$ spinel. But according to our experimental results, it is shown that there are the difference existing in two different systems ZnO varistors and the difference becomes larger with the increase of Al_2O_3 content.

The effects of only twins on ZnO grain growths and the uniformity in microstructures of ZnO varistors are given in Fig. 9 and Fig. 10. 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. 9

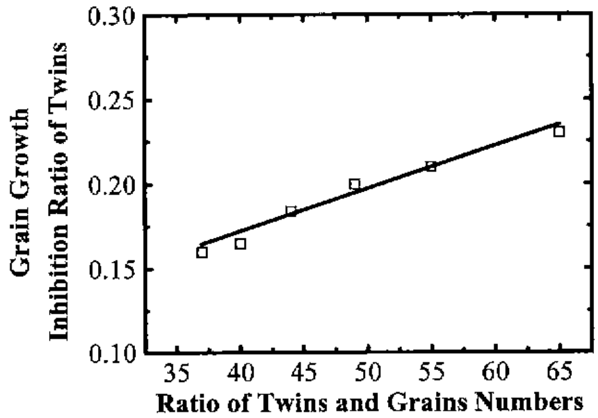

Fig. 9. Twins effect on the inhibition of ZnO grain growth in ZnO varistors.

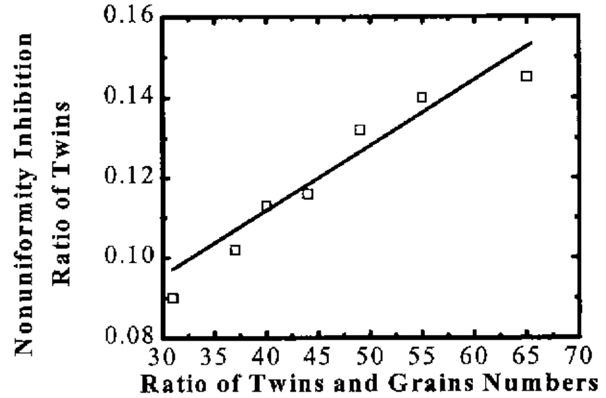

Fig. 10. Twins effect on the nonuniformity in microstructure of ZnO varistors.

and Fig. 10. Therefore, it is comfirmed that the twins have identically effects on the ZnO grain growths and the uniformity in microstructures of ZnO varistors.

IV. Conclusions

1. 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.

2. 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.

3. The inhibition ratios of grain growth and nonuniformity of two systems ZnO varistors increase with Al_2O_3 content.

4. 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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