Preparation of low voltage ZnO Varistor using point seed

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ABSTRACT: The low pressure of ZnO varistor ceramics were prepared with 99.5 mol % ZnO +0.5 mol % $CaCO_3$. Subsequently, placed in a constant temperature conditions of 1420 ℃ for 10 h, and cooking in boiling water long enough. The microstructure of the particle size analyzed by optical microscope, the doped ZnO varistors sheet seed analyzed by field emission scanning electron microscopy, the phase structure analyzed by X- ray diffraction. The results showed that this method can be prepared the best electrical properties of low-voltage ZnO varistor ceramics. The varistor voltage is 11 V/mm, the leakage current is 0.018 mA and nonlinear coefficient it is 15.6.
KEYWORD: ZnO; varistor ceramics; low voltage; point seed

1 INTRODUCTION

Since 1968 Japanese scientist Matsuoka developed a ZnO varistors, AB Glot carry out SnO_2 varistor ceramics to research and initial success in 1974, ZnO varistor ceramics have been widely used in various types of high-voltage power system (M.Matsuoka, 1971). However, with the rapid development of computer, electronic components, electronic instruments, communication and navigation equipment and other electronic devices, ZnO varistors demand for excellent electrical properties under low pressure conditions is increasing (A. B. Glot, 2006).

The pressure-sensitive voltage (U1mA) (O. G. Gromov , 2015) The formula (U1mA = nU0 = (t / d) × U0 (where, n is the average number of ZnO grains; U0 is a single crystal boundary layer breakdown voltage, t is ZnO varistors sheet thickness, d is the average size of the ZnO grains), generally considered the current academic ZnO varistors achieve low pressure of two ways: the first is to increase the average size of the ZnO grains, second add species to induce grain growth accelerator. in fact, the most common and mature grain increased accelerator as TiO_2, but when TiO_2 and ZnO sintered, often produce continuous growth, the emergence of abnormal growth of particles (Y. L .Tsai ,1985). studies have shown that these large particles causes abnormal electrical impulses in the operation of the resistor aging, impact of current damage.

Currently, nucleation and growth from the perspective of controlling the microstructure of ZnO ceramics obtained nonlinear coefficient, leakage current, excellent electrical properties of low voltage ZnO varistors are still relatively new research topic. Based on this, the proposed introduction of point-like seed growth and low voltage ZnO varistors prepared larger particles and particle size of ZnO grains uniformly, so as to achieve low-voltage, high efficiency and low energy consumption purposes ZnO varistors for ZnO varistor low pressure of reference.

2 PREPARATION AND CHARACTERIZATION OF SEED PUNCTATE

2.1 *Basic preparation methods and principles*

Preparation of ZnO seed point, the process is as follows: Once in a ball milling, a drying process, two times of ball milling, two times of drying, sieving, granulation, pressing, sintering, boiling water dissociation, drying, particle size grading. According to preliminary orthogonal test, using test materials ZnO and $BaCO_3$, according to the formula 99.5 mol % ZnO + 0.5 mol % $BaCO_3$ expanded composition ratio test (F. L. Souza, 2003).

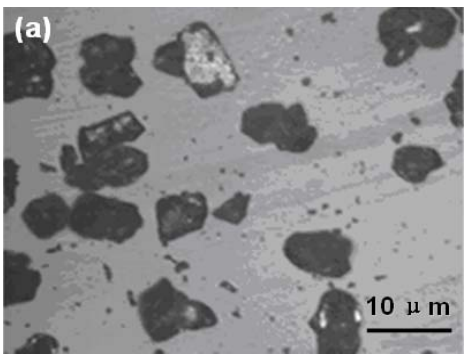
The process flow process in boiling water boiled long enough, is to get small punctate seed is very important part. The boiling water boiled in this part, you can also tap the appropriate internal crystalline substance in order to increase the dissociation rate. This is because the main component of the internal crystalline material is ZnO grains and enriched BaO, BaO main component can be dissolved in water,

boiled in boiling water can be dissociated from the grain boundary portion, the finally obtained sufficiently dispersed dot ZnO seed.

The process flow process in boiling water after boiling long enough, you can use different standards Sieve particle size grading after hydrolysis to obtain different grain sizes dot ZnO seed. As observed in the irradiation of light spots ZnO seed, the seed can be found after presenting grade sintered yellowish green, and has a certain luster, relatively tiny shiny particles. You can approximate that these tiny dot ZnO seed single crystal structure. This is because the preparation of point-like seed formulations, $BaCO_3$ after high temperature sintering will decompose into BaO, and the radius of barium ions is larger, it will be excluded from the ZnO crystal lattice. When the dosage formulation is more appropriate (using orthogonal experiment method to calculate the optimum ratio of 99.5 mol% ZnO + 0.5 mol% $BaCO_3$), can be formed in the main phase of ZnO grains at the core, the outer wrapping layer structure BaO . Subsequently, the two-layer structure in boiling water boiling process, BaO dissolved in water, ZnO will gradually break along the grain boundaries to give the dot ZnO single crystal single crystal structure similar to a seed.

2.2 *Dot ZnO seed microstructure and phase composition analysis*

Using different standards sieve particle size grading after hydrolysis to obtain different grain sizes dot ZnO seed. Figure 1 is a sub-sample screening elected 0 μm ~ 48 μm and 48 μm ~ 61 μm range of point-like ZnO seed crystal structure of an optical microscope. Figure 1 (a) is 0 μm ~ 48 μm dot ZnO seed crystal structure, Figure 1 (b) of 48 μm ~ 61 μm range of point-like ZnO seed crystal structure. Comparing Figure 1 (a), (b) can be found: ZnO crystal small particles having a crystal light, 48 μm ~ 61 μm range of point-like crystal structure ZnO seed size more uniform, and 0 μm ~ 48 μm dot crystal structure while ZnO seed crystal surface damage also appeared a lot more irregular shapes. Generally speaking, ZnO seed crystal according to the above formula and process conditions of preparation showed good form at larger grains.



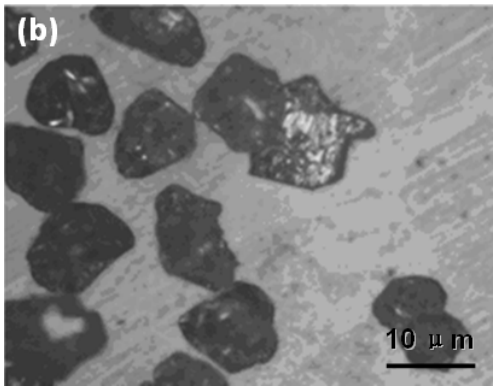


Fig1 0 nm ~ 48 μm ZnO (a) and 48 μm ~ 61 μm ZnO (b) crystal small particles of the optical microscope

Figure 2 is an X-ray diffraction pattern of ZnO crystals of small particles. Control hexagonal wurtzite structure ZnO polycrystalline standard X-ray diffraction pattern [9] can be found, completely overlap small particles of ZnO crystal X-ray diffraction peak and peak standard pattern.

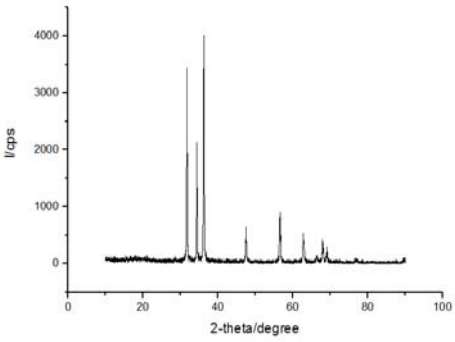


Fig.2 The XRD pattern of ZnO crystal granules

No obvious diffraction peaks containing BaO or Ba element phase appears. The results corroborated the raw material for preparing dot ZnO and $BaCO_3$ seed crystal structure of ZnO scientific. Because the diffraction characteristics grains containing no obvious BaO or Ba element phase of peak, indicating ZnO and $BaCO_3$ no chemical reaction and physical diffusion: barium ions are excluded from ZnO crystal lattice, and in boiling water boiling after hydrolysis into solution. In other words, the use of point-like ZnO seed process and methods, you can get the ideal ZnO seed.

3 PREPARATION AND CHARACTERIZATION OF MIXED SEED ZNO VARISTORS SHEET

Basic preparation methods and principles

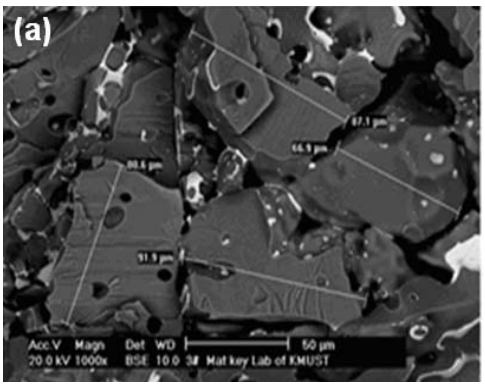
Previously prepared on the basis of corresponding mixed powder (choose the environment essentially pollution-free ZnO, Bi_2O_3, MnO_2, Co_2O_3, Sb_2O_3 as the cell, a certain proportion of the material is weighed and mixed) to complete the ingredients.

Weigh formulated composition ratio corresponding to the mixing powder and the corresponding level of grain seed, complete ingredients. In addition, since the performance of TiO2 varistor ceramic piece has an important role, so the total design of the eight group trials (including non-doped titanium group 1, group 2 Ti, Ti is not coarse seed group 3, not mixed with titanium fine seed Group 4, Ti coarse seed group 5, Ti fine seed group of six high-pressure crude Ti seed group of seven high-voltage Ti fine seed group 8), according to the following process of ZnO varistor ceramic pieces (Batching - ball milling, drying, sieving, granulation, tablet, row of plastic, sintering, grinding, thickness measurement, cleaning, manual silver coated, burning infiltration of silver electrode, electrical properties measurements). The experiment found that the electrical properties of non-doped titanium coarse seed group (varistor voltage of 11 V / mm, the leakage current of 0.018 mA, nonlinear coefficient of 15.6) better.

Mixed seed sensitive tiles will be warped and chipping cracks one side, because the incorporation of the seed and not uniformly distributed in the disc-shaped ceramic body, the side more, another less surface during the sintering process, containing more than one side of the seed grow too big too fast, while containing little seed of slower growth in the smaller side, both sides will appear between the stress. Thus, the seed should be distributed as evenly as possible incorporated in the pellet ceramic body to prepare an ideal seed-doped pressure sensitive tiles. Workaround: should pay more attention to the granulation Do not shake the mold when some plasticizer polyvinyl alcohol (PVA) and loading.

4 ZNO VARISTORS SHEET BACKSCATTERED ELECTRON ANALYSIS

Analysis test uses scanning electron microscopy, the main purpose is to analyze the grain size and distribution of the pressure-sensitive tiles inside to find out the relationship between preparation process, grain growth and electrical properties between the pressure-sensitive tiles. Figure 3 is a non-doped titanium coarse seed group (a) and Ti coarse seed group (b) test tiles fracture backscattered electron image.



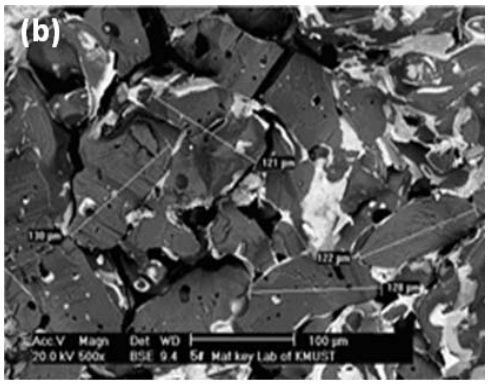


Fig.3. Ti crude seed group (a) and Ti crude seed group (b) test fracture of backscattered electron image tiles

Method may be calculated utilizing estimates of two or more pressure-sensitive internal grain size of the tiles, wherein fig. 3 (a) is 81.6 μm, Fig. 3 (b) is 125.3 μm. According to the relevant literature [8,9], the difference between these two kinds of ZnO varistor ceramics grain size can be interpreted as: Ti3 + radius of 69 pm, Ti4 + radius of 68 pm, and Zn2 + radius close, so Ti3 + or Ti4 + will substitutional into the ZnO grains caused by lattice distortion, so that Zn2 + and O2 + activated, so variable price elements Ti at a high temperature reduction results in a certain amount of oxygen vacancies around, the oxygen vacancies is very conducive to particle diffusion It will be to promote solid phase mass [10]. In addition, the sintering process will most TiO2 and Bi2O3 liquid phase reaction Bi4 (TiO4) 3 phase, ZnO material solubility in Bi4 (TiO4) 3 liquid phase than in the liquid phase in Bi2O3, which greatly accelerated the dissolution - deposition of liquid transfer process [11]. Accordingly, TiO2 on growth of ZnO grains have a certain role.

In addition, the figure can also be found, the figure appeared abnormal growth of particles [6-8], indicating that the use of seed-grown low-voltage ZnO varistor ceramics doped than simply low-voltage ZnO varistors performance is superior..

5 SUMMARY AND OUTLOOK

1) point-like seed grow best raw materials and low voltage ZnO varistors ratio is: 99.5% mol ZnO + 0.5% mol $CaCO_3$, optimum conditions: 10 hours at 1420 ℃ constant temperature conditions;

2) in boiling water boiled long enough, use different standards and sample screening level can be obtained after a more excellent electrical properties of low voltage ZnO varistor ceramics, and the optimum voltage of 11 V / mm, the leakage current of 0.018 mA, nonlinear coefficient of 15.6;

3) by means of scanning electron microscopy to obtain ceramic fracture surface of backscattered electron image, basically confirms the high sintering temperatures, contributing to the role of long holding time, TiO_2 and ZnO grains of seed.

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