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# Non-ohmic properties and impulse aging behavior of quaternary ZnO–$V_2O_5$–$Mn_3O_4$–$Er_2O_3$ semiconducting varistors with sintering processing

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ABSTRACT

This paper focuses on the effect of sintering process on the varistor properties and impulse aging behavior of ZnO–$V_2O_5$–$Mn_3O_4$–$Er_2O_3$ semiconducting varistors. The average grain size increased (5.7–8.1 μm) and the sintered density decreased (5.55–5.45 g/cm$^3$) with an increase in the sintering temperature. The breakdown field decreased with an increase in the sintering temperature up to 925 °C, whereas a further increase increased it. The non-ohmic coefficient increased noticeably from 3.8 to 40.8 with an increase in the sintering temperature. The sample sintered at 925 °C exhibited the best clamping characteristics, in which the clamp voltage ratio is in the range of 1.96–3.19 for impulse current of 1–50 A. Furthermore, this sample exhibited the strongest stability, with $\%\Delta E_{1\ mA/cm^2} = -9.8\%$ applying the multi-impulse current of 25 A.



## 1. Introduction

Today, modern electronic systems are ceaselessly pursuing advanced multi-function with so-called microminiaturization composed of smaller size, thinner film, lighter weight, and shorter length. IT systems such as smart TV, smartphone, smart tablet PC, notebook, smart camera, etc. surround us and play an important role in our daily lives. The core components in these systems are based on almost semiconductor devices. The progress in the development of denser integrated circuits has been accompanied by an increase in system vulnerability because the semiconductor devices are very susceptible to abnormal voltage, called transient overvoltage. Circuit protection from transient overvoltage is highly desirable to assure system survival. Therefore, it should be necessarily used for surge protection devices (SPD) to all electronic systems. Typical SPD is a varsitor called non-ohmic resistor or voltage dependent resistor. Among varistors, ZnO-based ceramic varistors have much higher surge handling capability than back-to-back Zener diode possessing a single p–n junction [1–3]. Sintered ZnO ceramics are polycrystalline oxide semiconductors with numerous oriented grains and exhibit different microstructures and electrical properties in accordance with additives and semiconductor processing.

It is impossible to co-sinter with only Ag (melting point, 961 °C) as an inner-electrode in multilayered chip varistors because commercial $Bi_2O_3$-doped and $Pr_6O_{11}$-doped ZnO varistors are sintered at temperature as high as 1000 °C. However, $V_2O_5$-doped ZnO varistors can be sintered at temperature as low as 900 °C [4,5]. This is more attractive to multilayered chip varistors, because it can be co-sintered with only Ag as an inner-electrode instead of expensive Pd or Pt [6,7]. Therefore, it is very important to investigate the effects of sintering process on varistor properties for specified composition. The $V_2O_5$-doped ZnO varistors are modified with Mn to improve non-ohmic properties [8–12]. Most studies are limited to $MnO_2$ because the $MnO_2$ induces superior non-ohmic properties to $Mn_3O_4$ [8–10,13]. However, $MnO_2$ is expensive compared with $Mn_3O_4$. Therefore, $V_2O_5$-doped ZnO varistors modified with $Mn_3O_4$ are being studied [14–16]. In this study, the effect of sintering process

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on microstructure, non-ohmic properties, dielectric characteristics, and impulse aging behavior of ZnO–$V_2O_5$–$Mn_3O_4$–$Er_2O_3$ semiconducting varistors was investigated, and it was addressed that good non-ohmic coefficient and impulse aging characteristics were attained by proper sintering.

## 2. Experimental details

Reagent-grade raw materials were prepared in the proportion of 98.95% ZnO, 0.5% $V_2O_5$, 0.5% $Mn_3O_4$, and 0.05% $Er_2O_3$ (all in mol%). Raw materials were mixed by ball milling with zirconia balls and acetone in a polypropylene bottle for 24 h. The dried mixture was mixed into a beaker with acetone and 0.8 wt% polyvinyl butyral (PVB) binder of powder weight. After drying the slurry containing PVB, the mixture was granulated by sieving through a 100-mesh screen to produce starting powder. The powder was uniaxially pressed into disk-shaped pellets of 10 mm in diameter and 1.5 mm in thickness at a pressure of 100 MPa. The pellets were set on MgO plate into alumina sagger and sintered at four fixed sintering temperatures (850°, 875°, 900°, and 925 °C) in air for 3 h, and furnace-cooled to room temperature. The heating and cooling rates were 4 °C/min. The final pellets were about 8 mm in diameter and 1.0 mm in thickness using a lapping/polishing machine. Conductive silver paste was coated on both faces of the pellets and the electrodes were formed by heating at 550 °C for 10 min. The electrodes were 5 mm in diameter. Finally, after soldering the lead wire to both electrodes, the samples were packaged by dipping them into a thermoplastic resin powder.

The sintered pellets were lapped with SiC paper and polished with $Al_2O_3$ powder to a mirror-like surface. The polished samples were chemically etched with 1 $HClO_4$:1000$H_2O$ for 25 s at 25 °C. The surface microstructure was examined by a scanning electron microscope (FESEM, Quanta 200, FEI, Brno, Czech). The average grain size ($d$) was determined by the lineal intercept method using the following expression [17]:

$$d = \frac{1.56L}{MN} \tag{1}$$

where $L$ is the random line length on the micrograph, $M$ is the magnification of the micrograph, and $N$ is the number of the grain boundaries intercepted by the lines. The crystalline phases were identified by powder X-ray diffractometer (XRD, X′pert-PRO MPD, Panalytical, Almelo, Netherlands) with Ni filtered CuKα radiation. The densities ($\rho$) of sintered pellets were measured using a density determination kit (238490) attached to balance (AG 245, Mettler Toledo International Inc., Greifensee, Switzerland).

The electric field–current density ($E$–$J$) characteristics were measured using a high voltage source-measure unit (Keithley 237, Keithley Instruments Inc., Cleveland, OH, USA). The breakdown field ($E_{1\ mA/cm^2}$) was measured at 1.0 mA/cm$^2$ and the leakage current density ($J_L$) was measured at 0.8 $E_{1\ mA/cm^2}$. In addition, the non-ohmic coefficient ($\alpha$) is defined by the following expression:

$$J = KE^{\alpha} \tag{2}$$

where $J$ is the current density, $E$ is the applied electric field, and $K$ is a constant. $\alpha$ is determined in the current density range $J_1$ = 1.0 mA/cm$^2$ to $J_2$ = 10 mA/cm$^2$ using the following expression:

$$\alpha = \frac{\log J_2 - \log J_1}{\log E_2 - \log E_1} \tag{3}$$

where $E_1$ and $E_2$ are the electric fields corresponding to $J_1$ and $J_2$, respectively.

The dielectric characteristics, such as the apparent dielectric constant ($\varepsilon_{APP'}$) and dissipation factor (tan $\delta$) of the samples were measured in the range of 100 Hz to2 MHz using a RLC meter (QuadTech 7600, Marlborough, MA, USA).

The clamping voltage ($V_c$) was measured at an impulse current ($I_p$) of 1, 5, 10, 25, and 50 A using a surge generator (Tae-yang Engineering, Busan, Korea) and an oscilloscope (TeK 3020B, Beaverton, Oregon, USA). The impulse current waveform had a width of 20 μs and a rise time of 8 μs. The clamp voltage ratio ($K = V_c/V_{1\ mA}$) is defined by the ratio of clamping voltage to breakdown voltage. The breakdown voltage ($V_{1\ mA}$) was measured at a current of 1.0 mA DC. The impulse aging test was performed at a multi-impulse current of 10, 25, and 50 A (continuously 3 times for each impulse current) using a surge generator. After applying the impulse current, the $V$–$I$ characteristics were measured at room temperature.

## 3. Results and discussion

### 3.1. Microstructure analysis

Fig. 1 shows the SEM micrographs of the samples for different sintering temperatures. On the whole, it can be seen that the grain size is inhomogeneous despite clear grain boundaries. The sample sintered at 850 °C exhibited the most uniform grain size. The increase of sintering temperature caused an abnormal grain growth rather than the improvement in the uniformity of grain size [12]. The detailed microstructure parameters are summarized in Table 1. The average grain size of the samples increased exponentially from 5.7 to 8.1 μm with an increase in the sintering temperature (see Fig. 4 in advance). The densities of sintered pellets decreased linearly from 5.55 to 5.45 g/cm$^3$ corresponding to 96.0–94.3% of the theoretical density (TD) (pure ZnO, TD = 5.78 g/cm$^3$) with increasing sintering temperature (see Fig.4 in advance). It is assumed that the decrease of sintered density is ascribed to the volatility of the V-species for $V_2O_5$ with low melting point [12].

The XRD patterns of the samples for different sintering temperatures are shown in Fig. 2. It can be seen that many minor phases such as $Zn_3(VO_4)_2$, $ZnV_2O_4$, $ErVO_4$, and $VO_2$ were produced. This is attributed to the liquid phase of $V_2O_5$ with low melting point (690 °C). Among minor phases, the $ZnV_2O_4$ and $VO_2$ were found to be the most greatly affected by sintering temperature. The $ZnV_2O_4$ ($2\theta$ = 30.0933° and 35.4420°) exhibited the greatest peak at 850 °C and almost disappeared at 925 °C. On the other hand, the $VO_2$ exhibited the greatest peak at 900 °C and almost disappeared at 925 °C. The minor phase $ErVO_4$ was not almost affected by sintering process in the light of the