

Chapter 2

Sol-Gel Materials for Varistor Devices

S. Anas, K.V. Mahesh, M. Jeen Maria and S. Ananthakumar

“Struck by lightning! Struck by lightning!”

— J.R.R. Tolkien

“Somewhere, something incredible is waiting to be known”

— Carl Sagan

2.1 Varistors—An Introduction

Varistors are known in academic, research and industrial sectors as, ‘lightning arresters/surge suppressers/nonlinear resistors/voltage sensors/voltage arrestors/voltage regulators’. A varistor is a device which functions mainly by sensing and limiting the transient voltage during online operation [1]. Varistors protect circuits over a very wide range of voltages, from a few volts in semiconductor circuits to tens of kilovolts in electrical power distribution networks [2, 3]. They are also defined as nonlinear resistors due to their non-ohmic behaviour [4, 5]. The images of real varistors are provided in Fig. 2.1

Varistors are used from domestic appliances to industrial devices in both AC or DC power lines. They need only a very less response time of the order of less than 20 ns for clamping the transient surges. So, they are widely used to control the variable voltages in all modern electric or electronic devices like cell phones, laptops, tablets, notebooks, computers, cameras, watches, television, LCD and LED devices, multimedia devices, etc. [6–9]. Varistors can be connected directly across main supplies and across semiconductor switches for protecting transistors, MOSFET’s and thyristor bridges. Unlike transient suppressor diodes, they absorb much higher transient energies and suppress both positive and negative transients.

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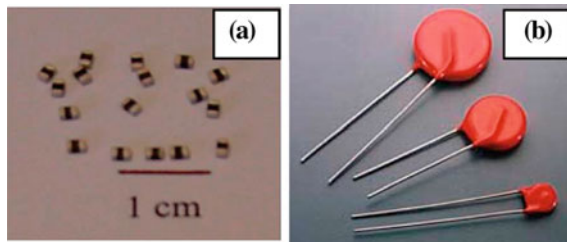
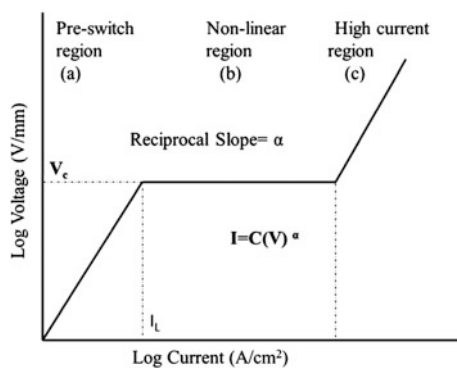


Fig. 2.1 Various types of ZnO varistors fabricated for different uses **a** varistors used in electronic circuits for ESD (electro static discharge) low-voltage suppression and protection **b** varistors used in industrial/AC line protection (reproduced with permission from [5])

Their energy absorption capability can also be tuned with respect to size of the component [10, 11]. They have wide range of voltage selection which allows for the easy selection of the correct component for any specific application. They exhibit low capacitance values, which makes them suitable even for the protection of the digital switching circuitry.

Varistors normally possess excellent surge withstanding capability because, unlike Zener diode which operates through a single junction, they generally functions as multijunction devices [12]. Furthermore, their special electrical properties are dominated by grain–boundary interface state [13]. A varistor consists of conductive grains and intergranular non-conductive layers. Existence of a potential barrier at grain boundaries results in nonlinear response of the varistor [14, 15]. This potential barrier, called Schottky barrier, blocks charge carriers by reducing the mobility of the carriers and increasing the effective resistivity of the grains. In fact, the Schottky barrier is formed due to trapping of electrons at grain boundaries. In other words, thin insulating intergranular layer between two ZnO grains creates back-to-back Zener diodes at grain boundaries. The typical property of a varistor can be better understood from the characteristic current–voltage (I/V) plot. The curve representing the current carrying capacity of a varistor as a function of the applied voltage is given as Fig. 2.2 [9].

Fig. 2.2 Schematic I–V characteristic curve of an idealized varistor **a** leakage or pre-switch region, I_L leakage current; V_c , breakdown voltage **b** non-ohmic or varistor operation region **c** high current or upturn region (reproduced with permission from [9])



As illustrated in the figure, three major regions were identified for the varistors [4, 7]. The region 1 is the low-current region ($<10^{-4}$ A/cm²). It is termed as ‘pre-switch’ or ‘ohmic region’. Here, the applied current is a linear function of the voltage. The resistivity of the varistor is very high here (greater than 10^{10} Ω cm for a normal ZnO varistor). For a given varistor device, capacitance remains constant over a wide range of voltage and frequency in the pre-switch region and its dielectric characteristics are governed by the impedance of the ZnO grain boundaries. For AC applications, the total leakage current (IL) in the pre-breakdown region is composed of resistive (IR) and capacitive (IC) currents. In the design of a surge suppresser from a ZnO varistor, it is the resistive current (IR), which is of importance since this is responsible for Joule heating within the elements. The second region is associated with a nonlinear behaviour. This particular ‘non-ohmic region’, termed as the heart of the varistor device, decides the performance of a varistor. The I–V curve is nonlinear in this region wherein the varistor voltage remains approximately constant for a large change in current. This specific nonlinear response is due to its polycrystalline microstructure, which is primarily governed by the grain–grain interface architecture. The current (*I*)–voltage (*V*) relation of a varistor in this region can be expressed in power law as

$$I = C(V)^\alpha \quad (2.1)$$

or

$$J = (E/C)^\alpha, \quad (2.2)$$

where ‘*C*’ the proportionality constant corresponding to the resistance of an ohmic resistor (a material constant), ‘ α ’ is the nonlinearity coefficient, ‘*J*’ is the current density, ‘*E*’ the applied electric field.

The third region is the high-current region. Here, the varistor becomes highly conducting and draws the current through it. In this region, the current changes by many orders of magnitude for a small change in voltage. In the high-current region (>100 A cm^{−2}), the varistor approximates to a short circuit and the I–V curve exhibits linear characteristics similar to those in the low-current region. The dielectric characteristics of this upturn region are governed by the impedance of the grain in the ZnO microstructure.

There are three significant parameters that determine the varistor properties; the breakdown voltage ‘*V_b*’, the non-linear coefficient ‘ α ’, and the leakage current ‘*I_f*’ [2, 4, 16]. In detail, the breakdown voltage ‘*V_b*’ is defined as the voltage at which the device switches from resistive behaviour to conductive behaviour. The breakdown field is usually taken as the field applied when the current flowing through the varistor is 1 mA cm^{−2}. The breakdown field ‘*V_b*’ and the sample grain size ‘*D*’ are proportionally connected by the following relation:

$$V_b = V_{gb}/D, \quad (2.3)$$

where ' V_{gb} ' is the barrier voltage. From the measured values of ' V_b ' and ' D ', ' V_{gb} ' could be obtained.

The nonlinearity coefficient, α , is defined as

$$\alpha = \log[I_2/I_1]/\log[V_2/V_1], \quad (2.4)$$

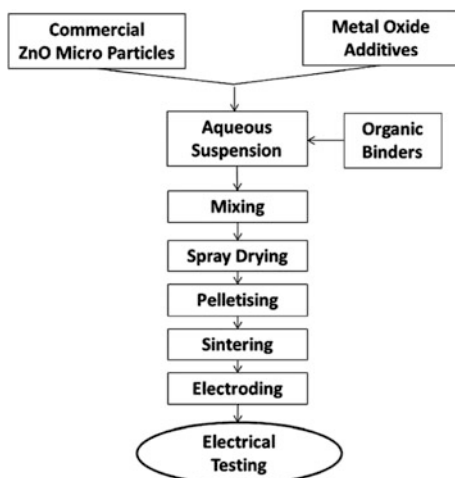
where I_1 and I_2 are the currents corresponding to the voltages V_1 and V_2 , respectively. It is practically measured from the reciprocal of the slope in the breakdown region. The nonlinearity coefficient represents protective power of a varistor device. The higher the value of nonlinearity or ' α ', the better will be the protection power of the device. Because of its variation with current, ' α ' values were taken in the range from 0.1 to 1 mA cm⁻², 1 to 10 mA cm⁻² or in specific cases up to 100 mA cm⁻². Typical reported ' α ' values for ZnO varistors varied from 20 to 100 over the current ranges mentioned above. The leakage current (I_L) is defined as the current flow at the steady operating voltage. The parameters, which are known to influence the leakage current, are (a) formulation of the materials (b) voltage applied and (c) time interval of the voltage applied. The most desirable characteristics of a varistor thus identified are, a high value of nonlinear coefficient (α), an acceptable rating of nonlinear voltage (V_b), a low value of leakage current (I_L), a long varistor life and a high-energy absorption capability.

2.2 Conventional Preparation of Varistors

The first work on varistor ceramics was reported on silicon carbide (SiC) and germanium (Ge) semiconductors [17, 18]. The strontium- and calcium-based titanates (CaTiO₃, SrTiO₃) are evolved later [19, 20]. However, these materials are outdated for the reason of poor nonlinear coefficients. For example, the nonlinear coefficient of only 10 was achieved in SiC varistor. In the 70s, Japanese physicist Matsuoka developed polycrystalline ZnO-based material as varistors [1]. Till today, his work is acknowledged as a great success in varistor ceramics. Based on the process identified by Matsuoka, the company Meidensha Corporation, a pioneer, developed ZnO surge arrestors commercially for the first time termed 'metal oxide varistors'. Now, ZnO varistors have become a commodity item and mass produced in several countries for applications ranging from power switching in electrical transmission systems to surge protection in automobile and semiconductor electronics.

Industrially, the ZnO varistors are produced in large quantities through a solid-state preparation method. The widely adopted solid-state preparation method for the varistors is provided as Fig. 2.3. Here, ZnO with the major additives and

Fig. 2.3 Stages in conventional industrial processing of varistor ceramics (reproduced with permission from [9])



minor dopants were wet mixed and the resultant powder is mixed with an organic binder (e.g. polyvinyl alcohol) and plasticiser (e.g. polyethylene glycol) [9].

The selection of the dopants and additives in varistor is extremely important [21, 22]. In addition to Bi_2O_3 , the various major additives and minor dopants used for preparing varistor compositions and their role, as seen from the literature, were summarized as Table 2.1. Typical varistor formulations consist of varistor former (oxides of elements of large ionic size Bi, Pr, La or Ba) [23, 24], performance enhancer (MnO_2 , CoO) [25, 26] and performance highlighter (Na_2O , K_2O , CuO , etc.) [27].

The varistor powder containing more than 90% of high-purity ZnO powder, with the major additives and minor dopants, were initially spray dried to obtain a granulated powder. The resultant powder in the form of microspheres was then pressed uniaxially to form cylindrical blocks. Industrially, ZnO varistors were manufactured through a high-temperature reaction called sintering. Sintering involves a heat treatment of the ceramic powder compact at a temperature below the melting point of the main ceramic constituent. By means of sintering, a dense varistor product was normally obtained. Since the varistor performance depends on the final sintered microstructures, the sintering process must be carefully carried out. Liquid-phase sintering, the technique commonly employed for varistor processing was achieved by adding Bi_2O_3 [28, 29]. At ambient temperatures, Bi_2O_3 forms insoluble layers in ZnO and segregates at the grain boundaries. They behave as electrostatic barriers and increase the low-voltage resistivity.

For sintering, the varistor powder needs to be hard-pressed to ceramic discs/pellets and should be heated at a temperature in the range of 1100–1250 °C [8, 30]. Varistor sintering was normally achieved in three stages. The low-melting eutectic reaction between ZnO and Bi_2O_3 occurring at temperature 735 °C leading to the formation of a liquid phase was the first stage. The dissolution of the dopants occurs at this stage. The liquid-phase sintering associated with the diffusion and the

Table 2.1 Role of minor additives and dopants on the properties of varistors

Additives	Role	Additives	Role
Sb ₂ O ₃	Inhibits ZnO grain growth, serves as pinning centres and retard ZnO grain boundary mobility [48, 100]	αλCoO, Cr ₂ O ₃	Enhance powder sinterability, Improve electrical properties, prevent Bi ₂ O ₃ evaporation [103, 114]
MnO ₂ , NiO	Decreases the average grain size, prevent the Bi ₂ O ₃ evaporation and increase the non-ohmic properties [101, 102]	Al ³⁺ , Ga ³⁺ , In ³⁺ , etc. WO ₃ , Nb ₂ O ₅	Behave as donors and their addition (<0.1%) causes increase in the electrical and electronic conductivity of ZnO [35, 40, 104]
Y ₂ O ₃ , SiO ₂	Grain growth inhibitors, increases the nonlinearity [34, 35, 105]	Li ⁺ , Cu ²⁺	Doping of acceptors decrease the conductivity [102, 106]
Ag ⁺	Decrease the nonlinearity but increase the resistance to degradation [107]	Na ⁺ , K ⁺	Improves the degradation resistance and controls the grain size of varistors [108]
αλTiO ₂ , SnO ₂	Forms spinel phase and controls the grain size by triggering the formation of inversion boundaries (IBs) in ZnO grains [35, 109, 110, 113, 115]	Ta ₂ O ₅	Small concentration results high grain conductivity. Excess Ta ₂ O ₅ decreases both bulk conductivity and grain size [111]
La ₂ O ₃ , Er ₂ O ₃ , Dy ₂ O ₃	Improves the nonlinearity and electrical stability [60, 112]	Pr ₆ O ₁₁ , V ₂ O ₅ , BaO, CeO ₂	Varistor-forming oxides, mainly for low-voltage varistors [23, 103]

homogeneous distribution of the dopants and initiation of the grain growth are followed in the second stage. At the end of the second stage and also in the beginning of the third stage, the grain growth, crystallization of the secondary phases such as pyrochlore (Zn₂Bi₃Sb₃O₁₄) and spinel (Zn₇Sb₂O₁₂) phases, formation of the potential barriers, and retraction of the liquid phase from the two grain boundaries to the triple junctions are taking place [5, 16]. The new phases which are formed at elevated temperatures can be readily observed through the SEM (Fig. 2.4), EDAX (Fig. 2.5) and XRD (Fig. 2.6) analyses.

Finally, at the end of the sintering process, the varistor ceramics attain a microstructure-containing electrically conducting grains and insulating grain boundaries. The resultant sintered varistor discs were then silver electroded and leads were attached prior to encapsulating the disc in an epoxy-based polymer. This type of processing route is still the preferred method in varistor industries. Cost effectiveness, processing viability, needs of only basic instrumentation tools for powder preparation and varistor disc production, less risks and hazards associated are the main commercial attraction of this route.

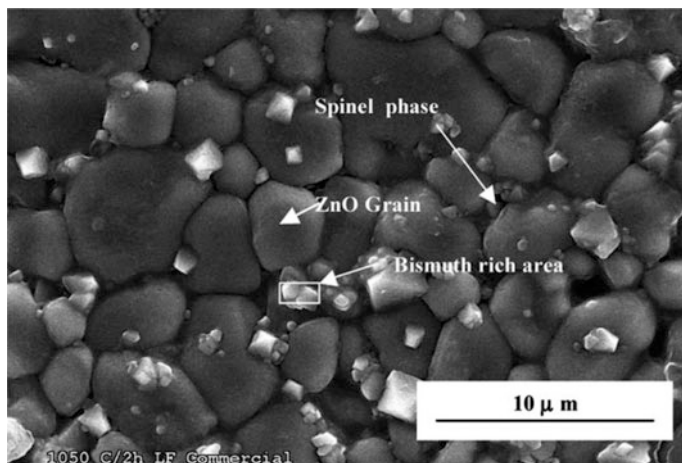


Fig. 2.4 FESEM image of a ZnO grain, spinel ($\text{Zn}_7\text{Sb}_2\text{O}_{12}$) phase and bismuth-rich phases of a commercial varistor sample (reproduced with permission from [5])

2.3 Chemical Synthesis Strategies for Varistor Particles

Even though the solid-state preparative methods are commercially attractive, a major disadvantage of the solid-state route is the difficulty in obtaining a compositionally homogeneous microstructure, which is particularly important for the fabrication of the miniaturized devices required for modern electronic and communication equipments. Varistors prepared through the solid-state method requires high sintering temperature and extended sintering schedules. They also have the limitations like exaggerated grain growth, volatility of Bi_2O_3 liquid phase, formation of undesired reactive phases and poor stability [31–35]. Moreover, a typical solid-state-derived varistor component has the dimensions of 40 mm diameter; 40 mm height and ~ 450 gm weight (medium voltage varistors). As shown in Fig. 2.7, since ZnO undergoes excessive grain growth, the varistors will normally have an average sintered grain size of 10–20 μm [16]. For a miniaturized varistor, this has to be controlled well below 5 μm for achieving many-fold increase in energy handling capability.

In order to overcome the problems associated with solid-state varistor processing, researchers mainly suggest the development of various solution-based approaches for high-energy field varistors. Chemical techniques such as amine processing [36, 37], chemical combustion [38], citrate gel [31, 39–41], microemulsion [42], precipitation [43–46], microwave [47, 48]; precipitation and reflux [16, 49, 50], organometallic [51], polymeric [10, 36, 52–56], tape casting [57], thermal oxidation [58], templated grain growth [59], urea decomposition [33, 40, 60], and sol-gel [4, 26, 16, 49, 50, 61–78], methods are used for the synthesis of doped varistor grade multicomponent powders. Most of these precursor

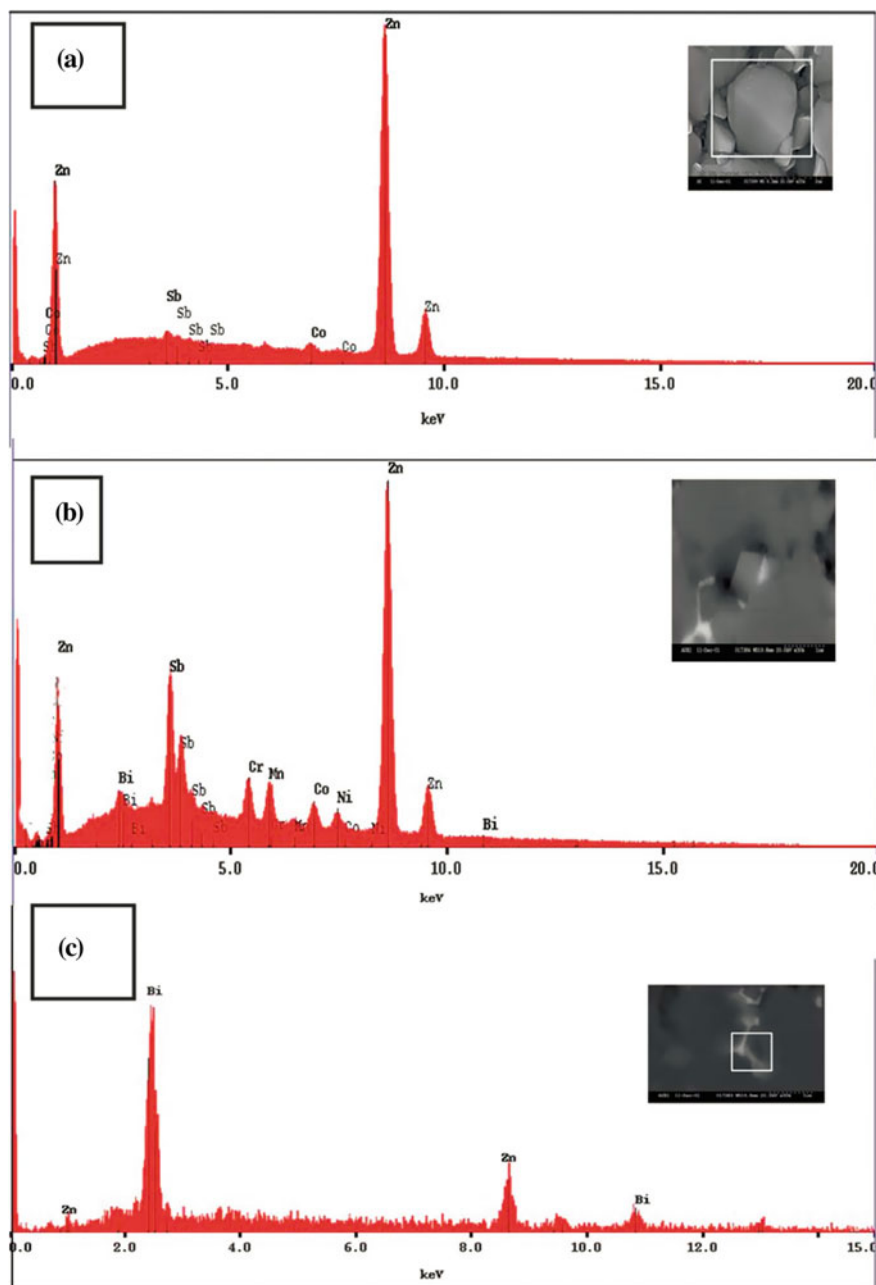


Fig. 2.5 EDAX images of **a** ZnO grains **b** spinel ($\text{Zn}_7\text{Sb}_2\text{O}_{12}$) phase **c** bismuth-rich phase (white areas in the microstructure) (reproduced with permission from [5])

Fig. 2.6 X-ray pattern of a sintered ZnO varistor which contain various phases such as Z = ZnO; S = $\text{Zn}_7\text{Sb}_2\text{O}_{12}$; B = Bi_2O_3 (reproduced with permission from [16])

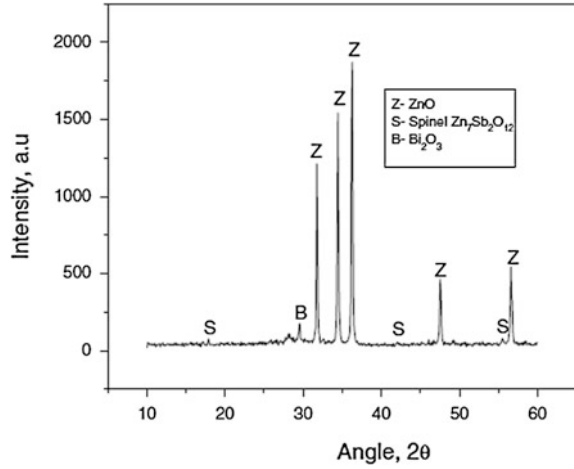
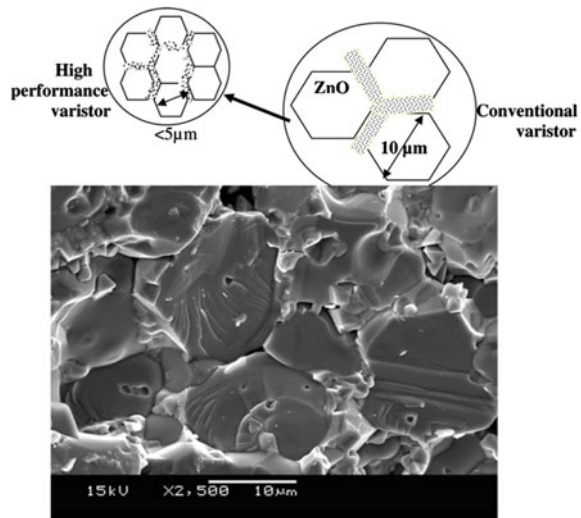


Fig. 2.7 Typical microstructure of a commercially available ZnO varistor (reproduced with permission from [16])



development methods are accompanied by a secondary sample heat treatment process like conventional, microwave, reflux and plasma methods for the conversion of sample hydroxides to corresponding oxides.

The advantages of wet chemical processing are primarily the higher purity, homogeneity and the lower processing temperature. Multicomponent dopant oxides can also be readily prepared by mixing relevant salt solutions of metal salts. By wet chemical methods homogeneity of the dopant ions among the ZnO grains can also be achieved at the atomic level. A number of liquid-phase approaches have been followed, are outlined in Table 2.2.

Table 2.2 Various wet chemical approaches for the syntheses of ZnO varistor powders and comparison of their electrical properties

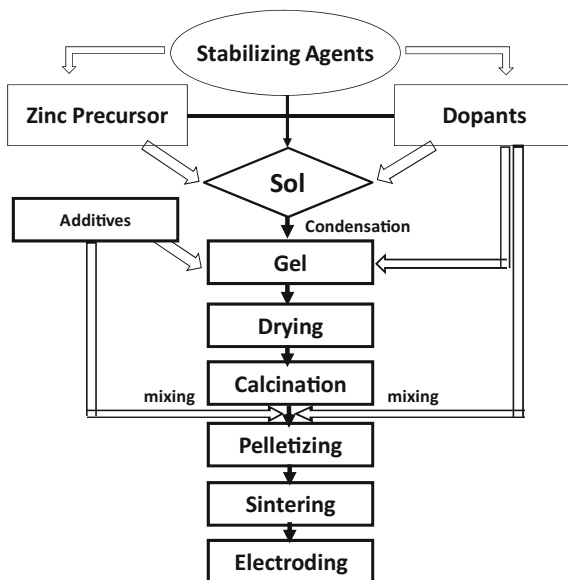
Chemical process	Reported by	Sintering ($^{\circ}\text{C}$)	V_b (V/mm)	α
Amine process	Hishita	1050	711	50
		1200	339	52
		1300	256	36
Citrate gel	Sinha	1150	515	35
	Lorenz	1000	460	72
		1000	510	75
Colloidal	Viswanath	750	3000	50
Emulsion	Hingorani	1200	450	83
Organometallic	Macary	550	1900	—
		600	1066	5.8
Pechini (polymeric complexation)	Duran	850	1500	70
	Duran	825	2000	270
	Lin	950	924	32
	Lin	950	895	48
Precipitation	Haile	1200	180	44
	Viswanath	750	3000	50
	Yang	1200	492	56
	Li	1050	540	50
	Shi	1060	218	55
	Cheng	1060	1610	15
Precipitation and reflux	Anas	1050	277	48
	Anas	1100	532	7.7
	Anas	1100	875	31
Sol-gel	Pillai	1050	786	34
	Pillai	1050	859	33
	Pillai	900	1192	—
	Westin	1100	249	37
	Tomandl	1100	375	60
	Ya	950	1000	45
	Lauf	1000	980	30
	Nobrega	1100	800	26
	Wang	1100	438	16.5
	Anas	950	557	34
	Hohenberger	1100	375	55
	Liu	1150	310	27.2
	Sedghi	1200	475	43
Sol-gel mixed route	Pillai	1050	941	33
Spray pyrolysis	Subasri	1100	960	70

2.4 Advantages of Sol-Gel Technology for Varistors

Among the various wet chemical methods, the sol-gel methods have definite advantages over other chemical methods in the production of varistor powders [9, 63, 79, 71]. Atomic level mixing of reactants, homogeneous distribution of low-level dopants and additives, hydrolysis and polycondensation reactions at room/low temperatures, preparation of particles with interaction through weak forces such as van der Waals/hydrogen bonded forces, formation of stable oxide network, size controlled particle formation through pH and concentration controls were the benefits realized through the sol-gel methods. Studies confirm that the sol-gel method yields the controlled production of ‘varistor nanoparticles’. Unlike other solution-based approaches, the sol-gel methods exhibit specific control in the production of nanosized varistor particles. The control in the nanoparticle synthesis is reported to be difficult with other techniques such as chemical decomposition [48], thermal evolution [16, 41, 49, 50], solution growth [59, 79] and precipitation methods [55]. Most of these methods needed secondary heating of the precursor materials at elevated temperatures. They resulted in particles from nano-micro-macro ranges. Many of the thermal decomposition routes release unwanted byproducts such as CO, CO₂, NO, NO₂ gases which are hazardous to the safe environment. But, on the other hand, the sol-gel methods are reported to be environmentally safe. Most of the sol-gel syntheses adopt green chemical pathway. Multicomponent compounds can be prepared through sol-gel methods with a strict control in the stoichiometry by mere mixing sols of different compounds. There are several reports available in the literature, where sol-gel techniques have been utilized for varistor applications [9, 66, 67, 75]. In general two different approaches have been taken, the first involving, the sol-gel preparation of ZnO and the subsequent addition of solid dopant metal oxides and second, the preparation of the gel from the precursor solutions of the zinc and metal additives. On summarizing the processes involved, the currently adopted sol-gel methods for the production of varistors can be briefly represented as shown in Fig. 2.8.

It has been confirmed that the sol-gel processes result in the generation of mainly ‘nanoparticles’ [9, 68, 75]. Recent literature strongly supports the use of nanopowder in varistor industries to solve many limitations associated with this field [80, 51]. Due to the high surface area, nanopowders show benefits such as low-temperature sintering. They results in increased numbers of grains and grain boundaries per unit varistor volume. It has been confirmed that nanocrystalline varistor grain has large grain boundary volume that can generate more active grain boundaries per unit varistor volume [26, 36]. This is an important understanding about varistors which can be effectively utilized for controlling the varistor dimensions. Low-temperature densification, reduction in ZnO grain size and three to four times increase in the varistors performance were the main advantages realized when nanosized powders were used [26, 81–83].

Fig. 2.8 Sol-gel synthesis of varistors with zinc oxide as the matrix



2.5 Sol-Gel Varistors

Many successful reports on the wet chemical sol-gel synthesis of varistor powders were addressed from early 1980s. The base work on the sol-gel varistors were acknowledged as the contribution from Lauf and Bond [67]. By following their processing methodology, Gert Hohenberger and Gerhard Tomandl prepared ZnO varistor powders using inexpensive source materials such as acetates and nitrates [64]. They prepared two sets of precursor solutions of ratio <3:1. The first one involved hot (90 °C) water solution containing the acetates of Zn, Co, and Mn, and H_3BO_3 and the second one contained Sb-acetate, Cr-nitrate, Bi-nitrate, Al-nitrate in ethylene glycol. By mixing and cooling these two solutions, a microcrystalline gel of the precursor material was resulted. As a result of the more homogeneous distribution of dopants, the sol-gel samples exhibited a higher breakdown field (375 V mm⁻¹) and nonlinear properties ($\alpha = 55$). By adopting similar processing strategies, improvement in the varistor properties were also achieved by Nobrega and his team [45].

Westin and co-workers [73, 84] have tried different sol-gel methods to obtain the varistor precursors. They used typical sol-gel precursors such as $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}_3(\text{OAc})_7(\text{OH})_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Sb}(\text{OBun})_3$ and $\text{bi}(2\text{-ethylhexanoate})_3$. A breakdown voltage of 249 V mm⁻¹ and $\alpha = 37$ were successfully achieved in these varistor compositions. Puyane and his team [71, 72] reported the production of ZnO powders by a sol-gel route and showed that these powders were sintered at lower temperatures compared to the conventional varistor materials. In other studies, Ya and co-workers [75, 85] reported the preparation of

varistors using sol-gel prepared ZnO nanopowders (20 nm). These materials displayed superior electrical properties with a high value of the nonlinear coefficient ($\alpha = 45$) and lower leakage current ($I_L < 1$ mA).

Sinha and Sharma [41] explained a most viable method for the preparation of varistor precursor gel by adding citric acid to nitrate solutions (pechini process) of varistor constituents. The gel on calcination resulted submicron-sized reactive varistor powder that exhibited homogeneity and stoichiometric control. The citrate gel derived varistor exhibited better varistor properties ($V_b = 515$ V/mm and $\alpha = 35$) than the varistor derived from a urea route ($V_b = 280$ V/mm and $\alpha = 21$). Duran and his team [10, 36] introduced a metallorganic polymeric method for preparing homogeneous and nanosized (28 nm crystallite size) doped ZnO ceramic powders. Dense ceramic bodies (>99% of theoretical) were fabricated by normal liquid-phase sintering at 850 and 940 °C for 1–5 h. Ceramics so-fabricated showed a nonlinear coefficient, α , of >70, and a breakdown voltage, V_b (1 mA/cm²), of >1500 V/mm.

Lorenz and co-authors [40] reported a modified citrate gel synthesis for the production of ZnO-based varistor powder. Doped ZnO powder was initially prepared by coating ZnO powder with a layer of citrates of the dopants using the citrate gel technique. Then, the doped ZnO powder was coated with a layer of the additives. ZnO-based varistors prepared by this modified citrate gel route showed higher values of characteristic field strengths [$V_b < 450$ V/mm and first nonlinear coefficient ($\alpha = 70$)]. Chu and his colleagues [86] proposed a new sol-gel processing method to prepare ZnO-based varistor powders, using inexpensive zinc acetate dihydrate, ethylene glycol, n-propyl alcohol and glycerol as starting materials. The procedure of the powder preparation is shown in Fig. 2.9. Compared to conventional oxide-mixing techniques, by adopting this route, the sintering temperature could be lowered by about 200 K to 1000 °C and the grain size as smaller as <2 nm. This proves very helpful for achieving high breakdown strength.

Huang and his team [65] illustrated the preparation of ZnO-based ceramic films, with thickness close to 2–4 μ m. These films were deposited on Au/Si substrates by novel sol-gel process. The precursors were developed by dispersing doped ZnO ceramic nanopowders into the sols, which were prepared by dissolving zinc acetate dihydrate into 2-methoxyethanol and stabilized by diethanolamine and glacial acetic acid and doped with a concentrated solution of bismuth nitrate, phenylstibonic acid, cobalt nitrate, manganese acetate and chromium nitrate. The doped ZnO ceramic nanopowders were prepared by sol-gel processing. The samples were dried and calcined in air at 150 and 800 °C, respectively. The nonlinear V – I characteristics of the films for use as varistors were studied by transistor characteristics testing instrument. The studies confirm the production of varistor with nonlinear voltage as 2–10 V and the nonlinear coefficient (α) as 3–22. The highest nonlinearity coefficient with nonlinear voltage of 4 V was achieved at 750 °C by the films with a thickness of 2 μ m.

Pillai and co-workers, the pioneers in the sol-gel high-energy field varistors [9], reported the production of zinc oxide precursor gels by the reaction of an ethanolic solution of zinc acetate and oxalic acid [69]. The gels were initially dried at 80 °C

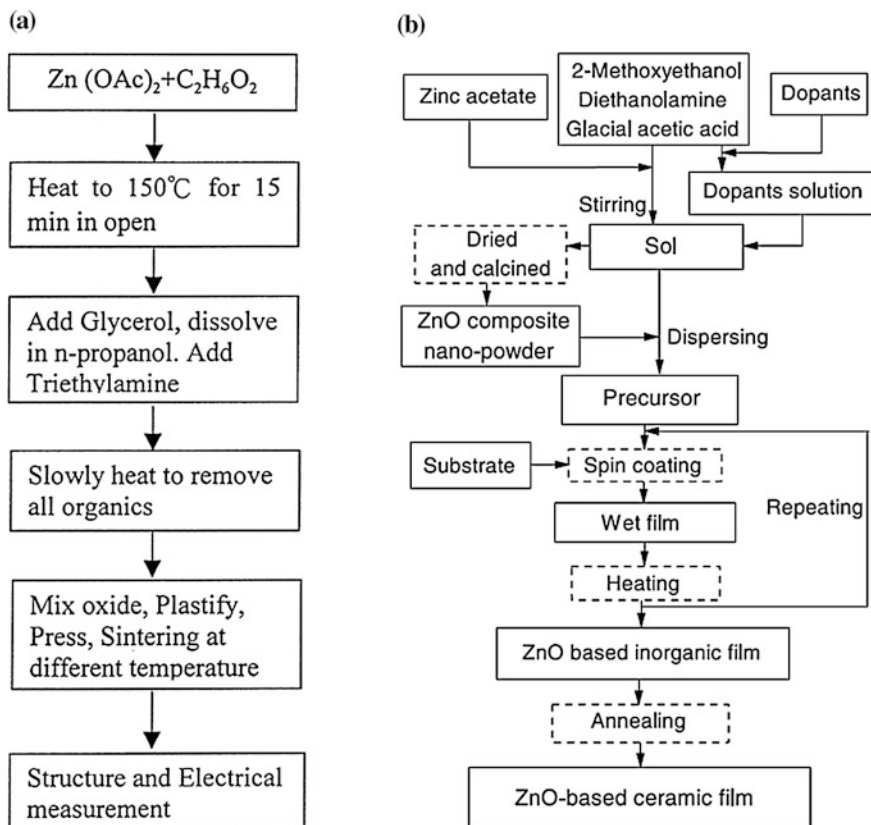


Fig. 2.9 **a** Flow diagram for the sol-gel preparation method of ZnO-based varistor powder (reproduced with permission from [86]). **b** Flowchart showing the procedure for preparing ZnO-based ceramic films (reproduced with permission from [65])

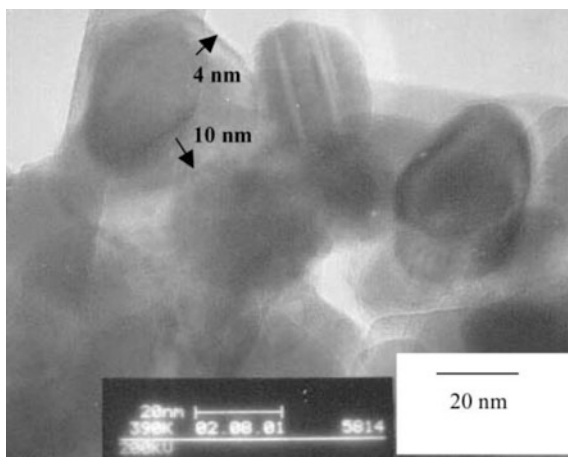
and calcined at 500 °C for 2 hours. This resulted ZnO nanoparticles with size of 30 nm. Subsequently, varistor materials were fabricated from this nanoparticulate ZnO via two separate routes: (a) from a “core shell” material using metal salts as additives; (b) using a conventional solid-state mixing of metal oxides. As shown in Fig. 2.10, “Core shell” type varistor powders were prepared by coating the nano-ZnO with additive metal salts. To achieve a homogeneous coating of oxides (Sb, Bi and Co) around the ZnO particle, solutions of chloride salts of these elements were mixed with a dispersion of nano-ZnO (as prepared above) and reacted with ammonium carbonate. Sintering (1050 °C) and subsequent electrical studies were carried out for each of these samples and they were compared with commercial varistor samples prepared under similar conditions. “Core shell” type varistor material showed considerably higher breakdown voltage ($V_c = 850 \pm 30 \text{ V mm}^{-1}$) as compared to a sample prepared by mixing with metal oxides ($V_c = 683 \pm 30 \text{ V mm}^{-1}$) and commercial

varistor discs ($V_c = 507 \pm 30 \text{ V mm}^{-1}$). The high breakdown voltage obtained is attributed to the formation of more varistor-active grain boundaries per unit area.

In a further experiment [26], linear arrays of ZnO nanoparticles have been successfully prepared by a simple sol-gel condensation reaction involving chemical modifiers [1,2-ethanediol (EG) and diethanolamine (DEA)]. The modifiers were added to the ethanolic solution of zinc acetate before the addition of the ethanolic solution of oxalic acid. The gel formed was subsequently treated and the powders were characterized. As shown in Fig. 2.11, the FESEM and TEM analyses revealed that the calcined material were composed of approximately spherical nanoparticles having average diameter $21 \pm 3 \text{ nm}$, self-assembled to form arrays extending in length up to 2–4 μm . The morphology of the ZnO is found to depend sensitively on the amounts of chemical modifiers present. In their absence, the ZnO produced (nano-ZnO) is an unstructured agglomerate of nanoparticles. Varistors prepared from the nanoarray ZnO by sintering (1050°C) with appropriate mixtures of metal oxides showed a breakdown voltage of $786 \pm 30 \text{ V mm}^{-1}$, which is substantially higher than that of samples prepared under similar conditions from either micron-sized commercial ZnO ($507 \pm 30 \text{ V mm}^{-1}$) and from nano-ZnO ($683 \pm 30 \text{ V mm}^{-1}$).

Through a more sophisticated preparative method, high-performance varistor precursor gels were prepared from the precursor solution containing ethanol and diethanolamine solutions of zinc, cobalt, manganese, nickel, aluminium and ethylene glycol solution of bismuth, antimony and chromium salts, by adding with oxalic acid [5]. The obtained gels were dried at 80°C and calcined at 500°C . Ultrafine ($\sim 15 \text{ nm}$) doped ZnO nanoparticles were resulted. The obtained varistor powders were sintered at 1050°C for 2 h. The xerogels, calcined powders and sintered materials were characterized. Full densification, high breakdown voltage ($941 \pm 30 \text{ V mm}^{-1}$; which is 85% higher than the commercial varistor at 1050°C) and a good nonlinear coefficient ($\alpha = 33 \pm 3$) were observed for samples sintered

Fig. 2.10 HRTEM of ZnO nanoparticles coated with oxides of Sb, Bi and Co precursors (reproduced with permission from [69])



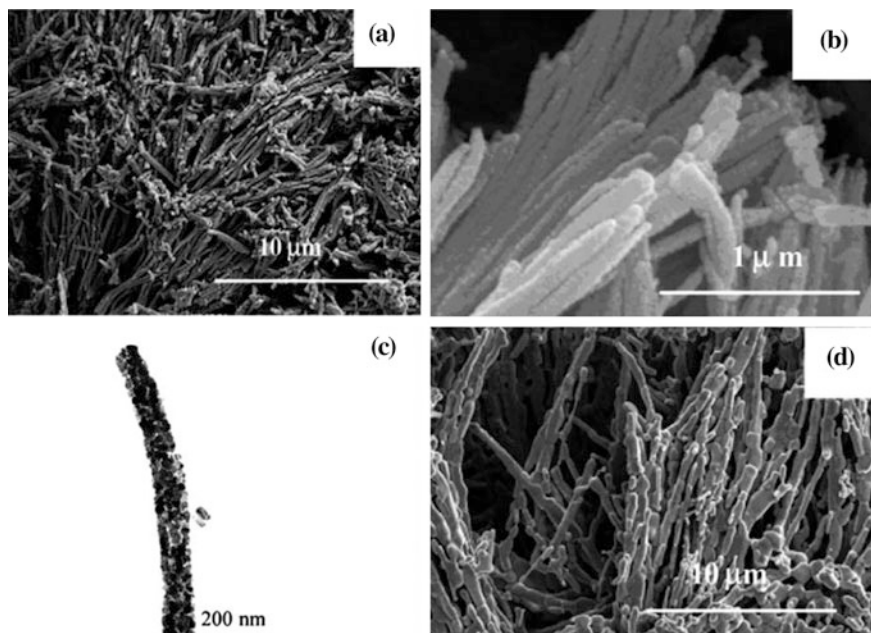


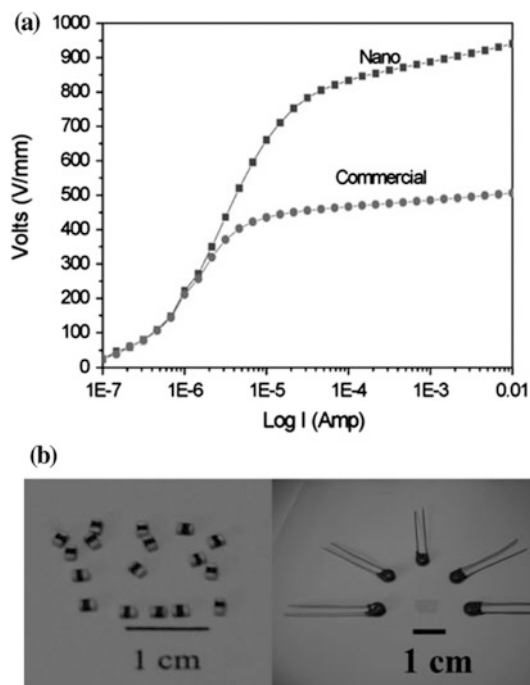
Fig. 2.11 Electron microscopy images of nanowire ZnO for varistor applications prepared by a sol-gel route. **a** and **b** FESEM images of samples calcined at 500 °C. **c** TEM image of a single array of ZnO nanoparticle separated by ultrasonication in ethanol. **d** FESEM image of ZnO nanoarray at 1000 °C (reproduced with permission from [26])

at 1050 °C for 2 h, Fig. 2.12. Highly dense varistor discs were prepared from the sintered material, with a breakdown voltage 85% higher than that of commercial varistors, making them suitable for use in miniaturized electronic circuitry. Improved performance of these materials has been attributed to the small grain size and better dispersion of additives on ZnO grains.

Zhang and his group [78] reported the preparation of a polycrystalline nanograin-boundary multi-doping ZnO-based nonlinear varistors with higher concentration additives, through a sol-gel method. The results showed the merit of sol-gel method in terms of high threshold voltage, at a lower sintering temperature, than the varistor prepared by a solid-state reaction method. The major conclusions are depicted in Fig. 2.13. The results showed that the grain size and the homogeneity of the material are the important factors which directly affect the characteristic of the varistor.

Anas and his team [50] reported the synthesis of varistor grade zinc oxide nanopowders through a non-hydrolytic sol-gel method. Thermo-gelation, using diethylene glycol and triethanolamine, was the method adopted for making varistor precursor gel. Hexagonal nanocrystalline varistor grade ZnO particles of size 50 nm were achieved by heating the sample precursors at 270 °C for 2 h and at 500 °C for 2 h. The varistor properties of the samples, from 850–1150 °C, revealed that the

Fig. 2.12 Varistor samples prepared by sintering at 1050 °C: **a** I–V curve, **b** varistors fabricated using mixed precursor route (reproduced with permission from [5])



samples have narrow grain size distribution with higher breakdown voltage and nonlinearity, than any commercial varistor. As evident from the studies, Table 2.3, the breakdown voltage was found to be decreasing with an increase in the sintering temperature and grain size.

In another study, Cheng and co-workers [61] reported the preparation of Al_2O_3 -doped ZnO varistors through sol-gel methods. Citric acid (CA) was added to ethylene glycol (EG) in a 3:2 CA/EG molar ratio, and this mixture was stirred at about 80 °C to form a transparent solution. This solution was added with the aqueous solution of the additive salt to form the sol. The resultant mixed oxide sols were subsequently evaporated. The obtained powder was calcined at 500 °C for 2 h and sintered at 900 °C for 2 h. Figure 2.14 shows the typical characteristics of the xerogels (a) and the powder (b) obtained by this method. The xerogels showed typical porous structure. The powder was loosely agglomerated with the particle size in the range of 30–40 nm. The studies confirms that the average grain size of the varistor decreased from 4.4 to 3.0 μm and the breakdown voltage increased from 720 to 1160 V/mm, as the amount of Al_2O_3 increased from 0.0 to 0.40 wt% which are incorporated in the varistor matrix through sol-gel pathway.

Very recently, Liu and his group [68] introduced xanthan gum, a polymerization agent, for preparing ZnO– Co_2O_3 – Bi_2O_3 nanocomposites through sol-gel methods. As illustrated through Fig. 2.15, spherical- and hexagonal-doped nanocrystalline ZnO powders with particle size of about 20–45 nm were easily obtained in the

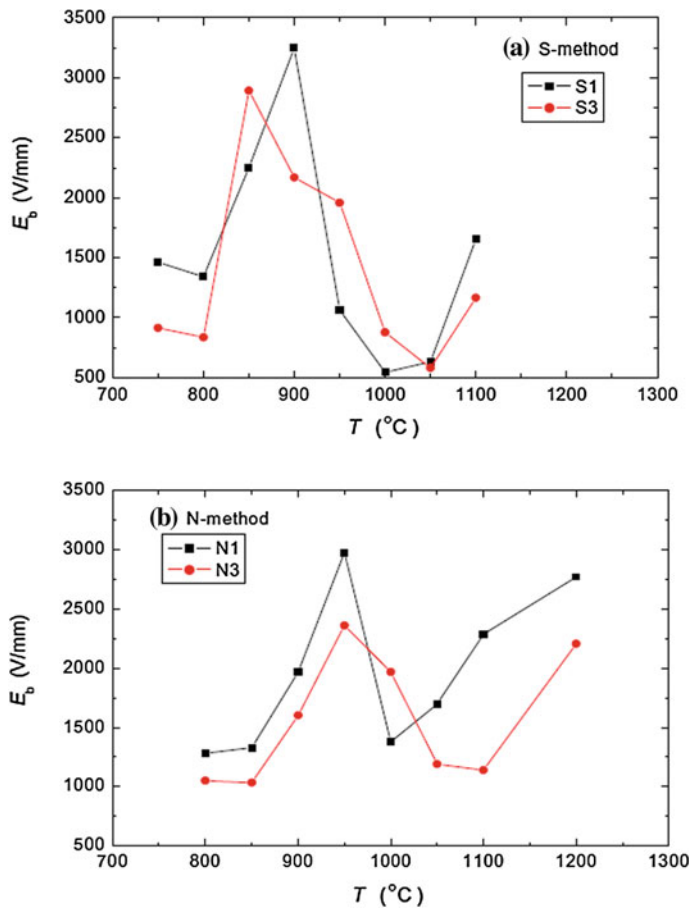


Fig. 2.13 Threshold voltage E_b versus sintering temperature: **a** sol-gel method; **b** solid-state reaction method (reproduced with permission from [78])

Table 2.3 Densification and electrical property studies on gel-derived varistors [50]

Sintering temperature	Grain size (μm)	Density (g/m^3)	Breakdown voltage (V_b)	Nonlinearity index, α
950 °C/2 h	<2	5.0	557	34
1050 °C/2 h	<4	5.1	493	36
1150 °C/2 h	<8	5.4	323	16

presence of xanthan gum. Xanthan gum was used as a polymerization agent to avoid hard agglomeration and then control the growth of the nanopowders. The metal elements (Co and Bi) were evenly distributed in the ZnO grain after calcination at 1150 °C for 2 h. The varistor ceramics sintered at 1150 °C for 2 h in air

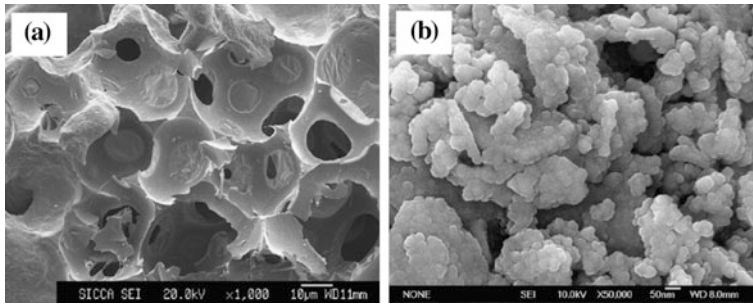


Fig. 2.14 SEM micrograph of the gel **a** and ZnO powder **b** prepared by sol-gel method (reproduced with permission from [61])

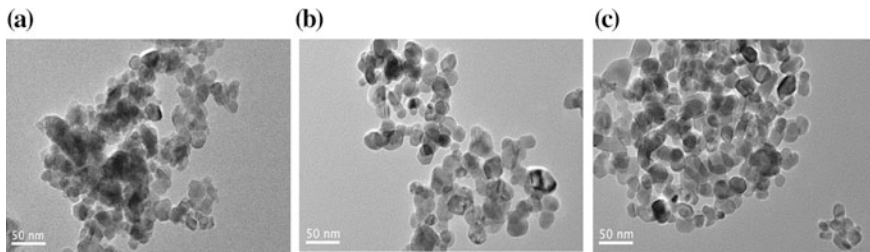


Fig. 2.15 TEM images for doped nanocrystalline ZnO powders with **a** 0.5% Xanthan gum, **b** 1% Xanthan gum, **c** 1.5% Xanthan gum (reproduced with permission from [68])

have a density of 5.52 g/cm^3 corresponding to 95.5% of the theoretical density with breakdown voltage of 310 V/mm and nonlinear coefficient of ~ 27.19 . The experimental results showed the advantage of addition of the xanthan gum for avoiding hard agglomeration and improving electrical performance of the varistors.

Of late, the effect of transition metals and rare earth ions on sol-gel derived varistors has also been studied. Dong and his colleagues [62] published Y_2O_3 -doped ZnO- Bi_2O_3 thin films on silicon substrates by sol-gel process and annealing in air at 750°C for 1 h. The article confirms the development of thin-film varistors having nonlinear V - I characteristics with the leakage current of 0.46 mA, the threshold field of 110 V/mm and the nonlinear coefficient of 3.1, with the films contain 0.2% (mole fraction) yttrium ion. With increasing Y_2O_3 content, the grain size of ZnO was found to be decreased. In a similar way, Wang and co-workers [77] reported pure and Pr-doped ZnO (0.5 at.%, 1 at.%, 1.5 at.% and 2 at.%) nanoparticles synthesized through a sol-gel method. The samples exhibited hexagonal ZnO lattice structure and another Pr_6O_{11} phase was detected in the 2 at.% Pr-doped ZnO nanoparticles. The calculated average crystalline size decreases from 29.73 to 25.5 nm when Pr content increased from 0 to 2 at.%. The energy dispersive X-ray spectroscopy (EDS) analysis for 2 at.% Pr-doped ZnO confirms the evidence of Pr

in ZnO nanoparticles, and the varistor ceramics has a sintered density of 5.42 g/cm^3 corresponding to 96.8% of its theoretical density, with breakdown voltage of 438 V/mm and nonlinear coefficient of 16.5.

2.6 High-Performance Varistors: Through Nanoinclusions

High-performance varistors are miniaturized varistors, which generally possess high breakdown field, high nonlinearity and low leakage currents, that can be commonly used for the purpose of arresting high voltages in high-energy fields and for smoothening variable voltages in modern electric and electronic devices such as laptops, mobile phones, etc. In the current scenario, the major thrust in the varistor field is the production of this miniaturized lightweight varistors via a safer and much economic processing route [5, 9, 39, 87]. This greatly demands novel approaches and strategies which requires large number of conducting grains and higher fractions of insulating grain boundaries within a small varistor volume [10, 51]. It is evident from the scientific journals/reports that the ‘sol-gel derived nanopowders’ can be effectively utilized as the raw material for the production of miniaturized varistors. Detailed information on this and the fabrication of high-performance varistors using nanopowders were provided in the earlier section (see Sect. 2.5). However, toxicity problems, handling and packing difficulties are the drawbacks involved in the use of only the nanopowders. At the same time, the industries also call up on new developments in the varistor field for attaining miniaturized devices at low production cost. These issues received most attention in the design and development of state-of-the-art processes or smart techniques for the development of miniaturized varistors.

2.6.1 Grain Size Reduction and Grain Boundary Area Improvement

2.6.1.1 Addition of Nanofillers

High-performance varistor blocks can be achieved by effective grain size reduction [9, 34, 51, 83, 88, 89]. This can be achieved by the inclusion of nanosized varistor powder to the commercial micron-sized varistor powder [16, 87]. Rather than using nanopowder as a single source for varistor manufacture, scientific reports authenticate the use of nanopowder as ‘nanofiller’ for improving the varistor properties. The microstructure modifications as expected in the nanofiller-based composite varistor approach can be depicted schematically as Fig. 2.16.

As shown in Fig. 2.16, before sintering, the average diameter of an industrially processed spherical varistor powder granule is in the range of $<50 \text{ }\mu\text{m}$. This varistor

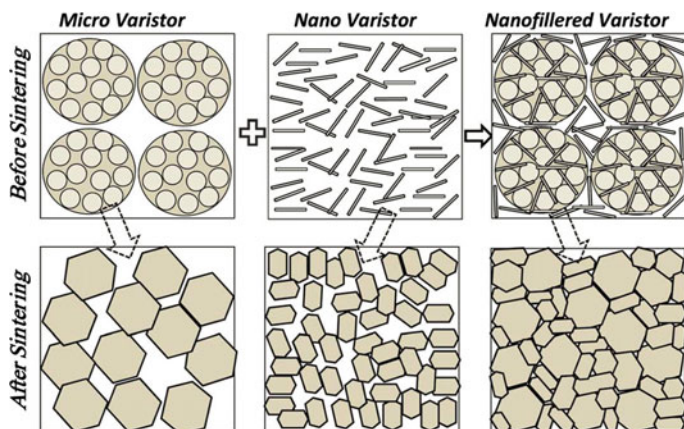


Fig. 2.16 Schematic representation of the ‘nanofiller’ approach for the high-energy field varistors (reproduced with permission from [87])

granule contains loosely adhered spherical particles having average size 3–5 μm , with distributions of nano- to micro-scale interstitial porosities. The large amounts of nano- and micropores on the powder granule and the interstitial macropores produced during compaction cause sintering problems in varistors and hence they need to be eliminated. Usually varistors require high sintering temperatures to remove these pores. But high sintering temperatures causes excessive grain growth in ZnO varistors. By the use of nanopowders as nanoadditives or nanofillers to the commercially available spray-dried micron-sized granules, the nanopowder enters into the pores of the micropowder and fills the varistor interstitial voids. This will not only increase the particle packing but also yields high particle contact area which favours accelerated densification at comparatively low temperatures. The resultant composite varistor powder produces sintered varistor ceramics with significant grain size reduction and possesses sintered microstructures with distributions of nano- and micrograins, say a bimodal grain size distribution. In either case, an effective increase in the number of ZnO grains within a specific varistor volume can be achieved.

In addition to the grain size reduction, the nanofiller addition also helps the varistor industries to have many practical advantages. The blending of nanofillers with a commercial micron-sized varistor powder simply by dry or wet milling can easily be introduced as an intermediate unit operation during varistor manufacturing. Varistors made out of such nanofillers not only promises high-energy field varistors but also provide a huge potential to miniaturize varistors at low production cost. Hence, this method can be taken as a ‘smart technique’ for the manufacturing of varistors. Reports on the nanofiller varistor studies shows that only a 5 wt% addition of the nanofiller resulted a varistor with theoretical density = 99%, average sintered grain size = 1 μm , $V_b = 875 \pm 30 \text{ V mm}^{-1}$ and $\alpha = 31 \pm 3$, when compared to the

commercial sample with average grain size = 6 μm , $V_b = 421 \pm 30 \text{ V mm}^{-1}$ and $\alpha = 17 \pm 3$, which were processed under similar sintering conditions at $\leq 1100^\circ\text{C}$.

2.6.1.2 Adopting Controlled Sintering Methods

High-performance varistors can also be achieved from nano- or micro-sized varistor powder through a control in the sintering method. This can be possible either through reducing the grain size or through improving the varistor grain boundary area. These can be accomplished via following different sintering processes like multistage sintering/step sintering, spark plasma sintering, microwave sintering, constrained sintering, etc. [16, 47, 49–51, 57, 70, 82, 90].

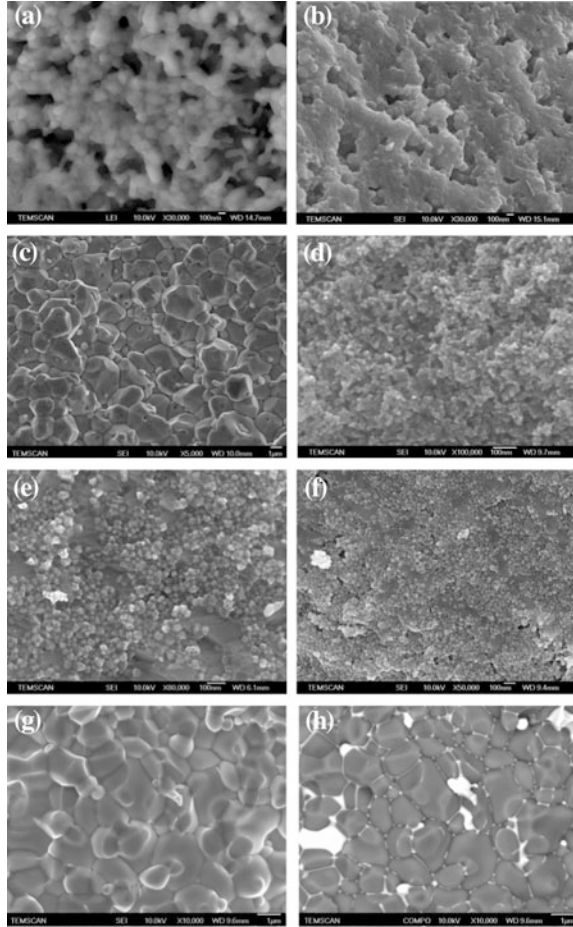
High-performance ZnO varistors with submicrometre grain size can be achieved through a strategic two-stage, one-cycle, pressureless thermal processing method at temperatures as low as 825°C in air [10]. Densification in a two-stage sintering is believed to be based on a rapid rearrangement of the solid ZnO nanoparticles in the presence of a liquid phase at the first stage up to 900°C . In the second stage, on cooling to 825°C , the liquid-phase recedes, thus, improving the ZnO–ZnO direct contacts and suppressing the grain boundary migration while maintaining densification by very active grain boundary diffusion. Full density with a close-packed arrangement of the grains was obtained at the second stage without additional grain growth. The nonlinear coefficients ‘ α ’ of such fully dense varistors were as high as 270, and the breakdown field ‘ V_b ’ of about 20 kV/cm at 1 mA/cm^2 can be achieved. Recently, Pillai and co-workers [70] reported the production of nano-zinc oxide varistor material by a sol-gel route. Varistor discs fabricated from these materials were subjected to a two-step sintering schedule. In a typical experiment, the samples were heated to 1000°C , then allowed to cool for over 30 min to 900°C and held there for 6 h. As evident from Table 2.4, the studies showed that the nanovaristor samples prepared through the stepwise sintering conditions would normally exhibit higher breakdown voltages ($1192 \pm 30 \text{ V mm}^{-1}$) than any commercially available varistor.

Spark plasma sintering (SPS) is another method preferred for the preparation of high-performance nanostructured varistors. Through SPS, grain size reduction can be achieved by sintering the sample at very low temperatures. An enhancement in the varistor property can thus be expected at low-sintering temperatures. For example, Macary and his team [51] used 8-nm-sized zinc oxide nanoparticles, which were synthesized through an organometallic approach, for SPS. As seen in Fig. 2.17, nanostructured varistors were obtained by SPS by sintering the sample at

Table 2.4 Breakdown voltages of varistor samples sintered at different temperatures [70]

Sample	V_b (V/mm)
Commercial varistor (1000 $^\circ\text{C}/0 \text{ h}$; 900 $^\circ\text{C}/6 \text{ h}$)	723
Nanovaristor (1000 $^\circ\text{C}/0 \text{ h}$; 900 $^\circ\text{C}/6 \text{ h}$)	1192
Commercial varistor (1000 $^\circ\text{C}/2 \text{ h}$)	584
Nanovaristor (1000 $^\circ\text{C}/2 \text{ h}$)	951

Fig. 2.17 SEM SEI micrographs of fracture surface of: **a** Sample 1 sintered at 1000 °C in a furnace; **b** Pellet 2, Sample 1 sintered by SPS at 800 °C; **c** Pellet 3, Sample 1 sintered by SPS at 900 °C; **d** Pellet 1, Sample 1 sintered by SPS at 600 °C; **e** Pellet 5, Sample 2 sintered by SPS at 550 °C for 15 min; **f** Pellet 6, Sample 2 sintered by SPS at 600 °C for 4 min; **g** Pellet 10, Sample 2 sintered by SPS at 800 °C; **h** SEM BEI micrograph of the same image as **g** (reproduced with permission from [51])



sintering temperatures as low as 550–650 °C. At 600 and 650 °C, the grain size was evaluated for these varistors and it was found to be equal to 300–500 nm and to 1 μ m, respectively, with the breakdown field values above 1000 V/mm.

Microwave sintering is another promising method for obtaining varistors with smaller and uniform grain size distribution [16, 47–50, 83]. When compared to the conventionally sintered samples which exhibit non-homogeneous Bi_2O_3 vaporization, the microwave-sintered samples can be produced with homogenous Bi_2O_3 vaporization. Thus more uniform microstructures can be resulted with this method. Also, the time required for the microwave sintering was only less than half the time that required for conventional sintering. For example, Cong [91] and Subasri [83] prepared microwave-sintered samples and compared their properties with respect to the conventional ones. The study proves that microwave-sintered samples hold good varistor properties that can be even modulated for developing miniaturized varistors at a very low cost.

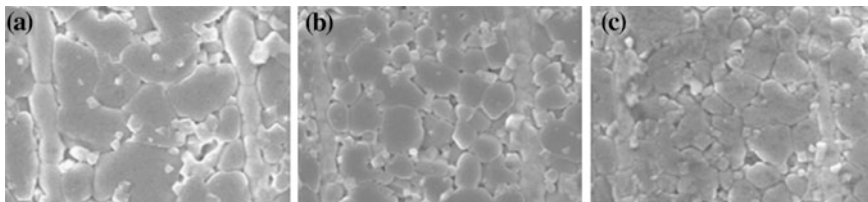


Fig. 2.18 Microstructure of ZnO-based MLV obtained by free sintering (a) at 925 °C for 2 h (b), and (c) microstructure of ZnO-based MLV obtained by constrained sintering with a constraining layer thickness of 24 and 44 mm at 925 °C for 2 h (reproduced with permission from [80])

Another promising approach for the fabrication of ZnO-based high-performance varistor is the preparation of multilayer varistor by constrained sintering [80, 90]. Here, nonreactive borosilicate glass and alumina (Al_2O_3) can be used as the constraining layer, which is laminated on both sides of the multilayer varistor (MLV). It is obvious from Fig. 2.18 that the mean grain size and the distribution of grain size of ZnO-based MLVs are greatly reduced because of constrained sintering. A sandwich structure of borosilicate glass + alumina/ZnO-based MLV/borosilicate glass + alumina can be fabricated. The in-plane shrinkage of the ZnO-based MLV tape can be reduced using a nonreactive borosilicate glass + alumina (Al_2O_3) tape, which densifies in a different temperature region than the ZnO-based MLV tape. The nonreactive borosilicate glass + alumina (Al_2O_3) tape will densifies at low temperature, where it is constrained by the non-shrinkage green ZnO-based MLV tape. At higher temperature, the ZnO-based MLV tape densifies and the shrinkage is inhibited by the already dense nonreactive borosilicate glass + alumina (Al_2O_3) tape. Hence, a self-constrained sintering can be accomplished, because each tape acts beside its functional performance as a constraining layer. It is clear from the studies performed by Lee and co-workers [80] that the mean grain size and the distribution of the grain size of ZnO-based MLVs can be remarkably reduced when constrained sintering is used instead of free sintering. The mean grain size of ZnO-based MLVs decreases with increase in the thickness of the constraining layer. Thus the property of a multilayer varistor can be effectively tuned with respect to the thickness of the constraining layer.

2.6.2 *Homogeneous Dopants Distribution at the Grain Boundaries*

2.6.2.1 *Conducting Wet Chemical Syntheses*

High-performance varistors can also be accomplished by performing wet chemical syntheses. Detailed discussion on the synthesis of nanoparticles through wet chemical methods and the resultant varistor with homogeneous distribution of

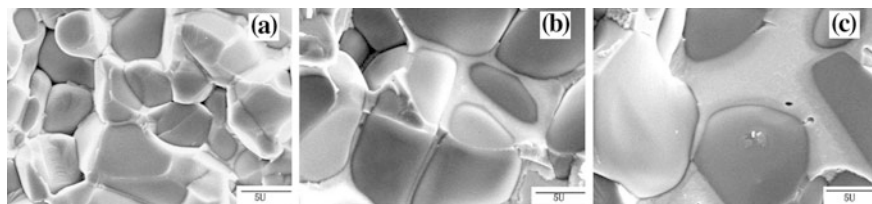


Fig. 2.19 SEM photographs of microstructure of ZnO ceramics for **a** 1 wt% Bi_2O_3 , **b** 3 wt% Bi_2O_3 and **c** 5 wt% Bi_2O_3 sintered at 1150 °C (reproduced with permission from [92])

dopants are given in earlier sections (please refer Sects. 2.3, 2.4 and 2.5). Among the many methods employed, the solution coating methods stands out as the best one for the effective distribution of dopants at the varistor grain boundaries [34, 35, 44]. In this method, the ZnO particles were coated with dopants such as Bi_2O_3 , Sb_2O_3 , Co_2O_3 , Cr_2O_3 and other minor additives via liquid nanocoating technique. For example, Li and his team [44] suggests the preparation of an additive solutions in alcohol media (ethylene glycol and ethanol in the volume ratio is 5:3) as the initial step for developing a nanolayer-coated ZnO grains. The method involves the ultrasonic treatment of the pure ZnO, which is dispersed in the additive solution, for about 1 h. The solution was then heated up to 90 °C and stirred until it changed into slurry. The slurry was dried in an oven at 150 °C for 8 h. It was then pulverized into powder and heated at 450 °C. The microscopic analyses of the resultant powder showed that the ZnO composite powder was homogeneously coated and ultrafine. The resultant varistors prepared through the nanocoating method showed higher threshold voltage (540 V/mm) and the nonlinear coefficient ($\alpha = 50$). Likewise, different solution coating methods were reported by many researchers to coat various minor additives and dopants over ZnO surfaces. For example, Yuan and his collaborator [92] tried to deposit a homogeneous layer of Bi_2O_3 over ZnO through nanocoating. As seen in Fig. 2.19, through solution coating methods, effective distribution of dopants at the grain boundaries were achieved.

2.6.2.2 Performing Temperature Controlled Step-Sintering Processes

Another method to control the distribution of dopants at the varistor grain boundaries is to sinter the material at temperatures near the liquid-phase formation or the varistor key-phase formation steps [5, 10, 28]. By performing the liquid-phase sintering, dopants and minor additives can be uniformly distributed along the varistor grain boundaries. In fact many researchers have reported that in ZnO– Bi_2O_3 varistor systems, the Bi_2O_3 additive forms the liquid phase at 850 °C, which is actually the driving force for grain boundary diffusion and rapid densification. For example, the effect of microstructure modification by step-sintering of varistor discs was studied by Anas and co-workers [16]. As illustrated through Fig. 2.20, by step-sintering (heating the sample to a higher temperature and cooling

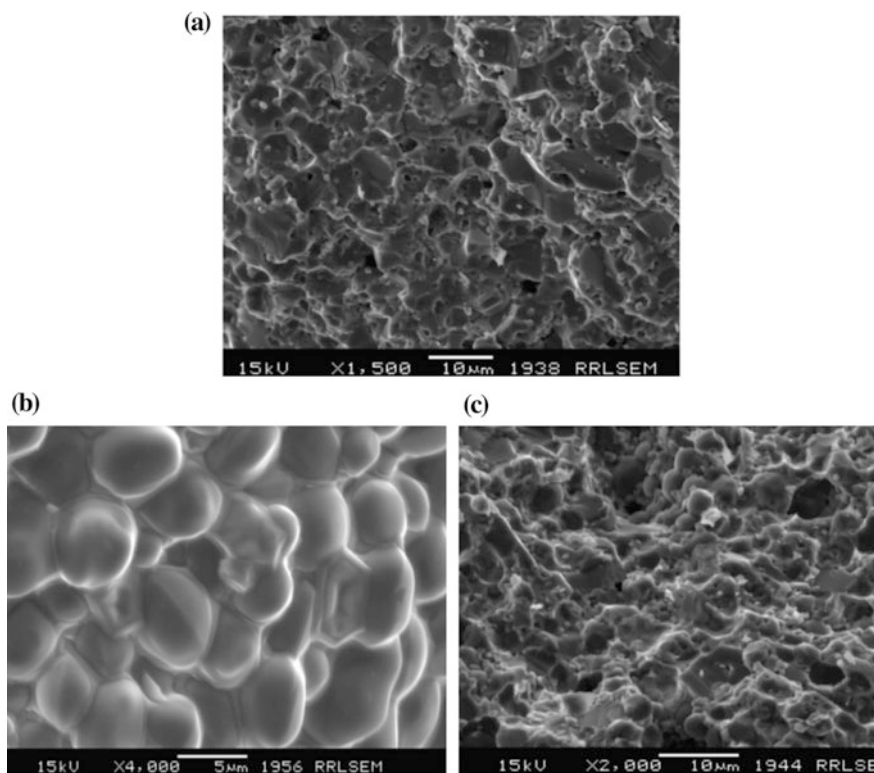


Fig. 2.20 Microstructures of step-sintered varistors at 1050–850 °C **a** commercial varistor disc **b** nanopowder varistor disc **c** composite varistor disc (powder **a** + 5 wt% powder **b**) (reproduced with permission from [16])

down to a low temperature drastically), homogeneous distribution of additives at the grain boundaries were achieved. Uniformly coated secondary additives on the varistor grain boundaries can be seen from these images. As a result of the liquid-phase sintering, the commercial micron-sized varistor discs were resulted with an average grain size of 8 μm , nanopowder varistor discs with 4 μm and nanofilled varistor powder sample with an average grain size of 2 μm .

2.6.3 Use of Economic and High-Quality Raw Materials

For any varistor device applications, one must not compromise with the quality of the components. It should be very high [4, 59, 72]. At the same time, the raw materials should be available abundantly, at low cost. Zn dust is a readily available and a low-cost source material which can be effectively utilized for developing high-performance varistors. For example, very recently, Maria et al.

(2016) introduced a new thermal oxidation method for the much economic production of high-performance varistors from Zn dust. The ceramic–metal composite (Cermet) varistor mixture was processed by mechanical blending of micron-sized metallic Zn dust with rare earth oxides (La_2O_3 , CeO_2) and other varistor-forming minor additives (CoO , Cr_2O_3 , Al_2O_3 , MnO_2 and SiO_2). The cermet varistor mixture was uniaxially pressed into cylindrical pellets and sintered at various temperatures to obtain ZnO varistors. In this method, the zinc dust was converted to different zinc oxide nanostructures like nanorods, mutipods and nanowires at elevated temperatures through sequential thermal oxidation. The cermet-derived varistors yields dense, nano-micro-mixed, fine-grained varistor microstructures with good current–voltage properties. At 1250 °C, the Zn dust derived cermet composition showed 99% theoretical density, average sintered grain size $<2\text{ }\mu\text{m}$, breakdown voltage $V_b = 480\text{ V mm}^{-1}$ and nonlinear coefficient $\alpha = 46$.

2.7 Sol-Gel Ceramic–Polymer Composite Varistors

2.7.1 Varistor–Epoxy Composites

Polymer composites containing varistor fillers exhibit nonlinear electrical–thermal switching properties [52–54, 56, 93]. Varistor–polymer composite can exhibit two nonlinearities in electrical conductivity. In the conducting state above the varistor filler breakdown, the polymer matrix reduces the conductivity, if a critical temperature is reached. Here, the overvoltage is limited by the fillers (i.e. varistor effect) and the overcurrent is limited by the polymer matrix. Above the breakdown field, the nonlinear effect dominates and then melting takes place. These materials act as positive thermal resistance coefficient (PTCR) due to microcontact separation in the insulating polymer matrix and they acts as varistors mainly due to the nonlinear properties of the grain boundaries.

Figure 2.21 shows the electrical–thermal dependence of a varistor–polymer composite [56, 79]. The high-current paths are visualized by the increase in temperature caused by Joule heating. In the nonlinear regime (B), the current increases exponentially and is then limited to a certain value in the upturn regime (C). The nonlinear phenomenon can be explained by the semiconducting behaviour of the varistor filler. Starting at around 100 °C, the epoxy matrix expands strongly due to the melting of crystalline areas. This leads to a separation of the varistor fillers and causes an increased resistivity. This is known as the electrical–thermal switching effect. Thus the nonlinear electricity determined by the quality of effective grain boundaries of the varistor fillers dominate the overall behaviour only as long as the microcontact resistances are smaller than the filler resistance. The resistance effects are always accompanied by losses in the form of heat. The PTCR effects can be used to limit the dissipated energy because the melting polymer does not allow a further increase in the electrical field. When the applied field is larger than the

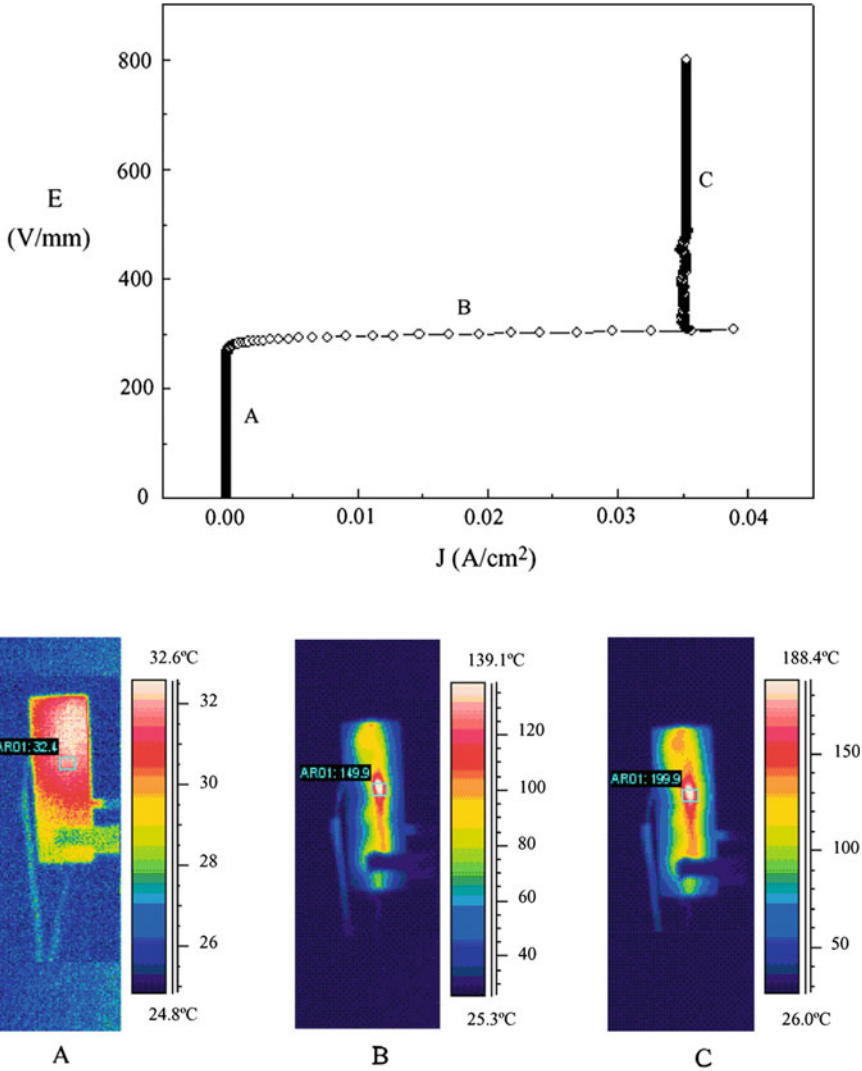


Fig. 2.21 Composite nonlinear electrical–thermal dependence of the epoxy polymer composite varistors. Here, the fillers (45 vol%) were sintered at 1100 °C for 5 h and the composite was cured at 120 °C for 10 min. ‘a’ is pre-breakdown region with very low current; ‘b’ is nonlinear region with high-current paths which can be visualized by the increase in temperature caused by Joule heating; ‘c’ is upturn region with limited current which is controlled by the melting point of epoxy (reproduced with permission from [56])

breakdown field and melting does not occur, there is a relatively wide distribution of current paths, i.e. the nonlinear effect. On the other hand, when the applied field is further increased and local melting occurs, the melting eliminates a portion of the connections and creates new tunnelling paths at the same time.

2.7.2 ZnO–PANI Composites

ZnO/Polyaniline nanostructure heterojunction devices show characteristic room temperature I–V properties. The heterojunction devices can be developed using a PANI thin film (200 nm, on top of a conducting Au film) [94]. On top of the PANI film, a ZnO film should be deposited (high-purity ZnO powder, 70–400 nm) along with a polarizing Al contact (200 nm, deposited using thermal evaporation). At the microscopic level, the structure of PANI should consist of highly conducting islands embedded in a non-conductive sea of the polymer [95, 96]. The electrical properties of these devices can be varied from a standard diode (rectifying in forward polarization) to those of a varistor (rectifying in both forward and reverse polarizations) by tuning the thickness of the ZnO thin film or the polymer doping state. The nonlinear I–V characteristics for the ZnO/PANI heterostructures are likely due to intrinsic surface and interface effects, which are a common feature between grain boundaries of PANI and ZnO.

2.7.3 ZnO–PANI–PVA Composites

Low-voltage varistors with good nonlinearity can be achieved using ZnO–polyaniline–polyvinyl alcohol composites. The polymer composite thin films can be easily prepared by solution-casting technique. Mixing PANI with ZnO inorganic oxide and pressing the mixture resulted in brittle discs which were not suitable for use in electrical devices. So, to prepare uniform and mechanically stable films, solution-casting method can be used. To increase the elasticity of final films, and to prevent them from tearing, polyvinyl alcohol (PVA) can be effectively employed in the varistor matrix.

As shown in Table 2.5, an increase in the polymer content leads to a decrease in the breakdown voltage [52–54, 79]. On the other hand, by increasing the amount of ZnO powder or, alternatively, decreasing the amount of polymer matrix, the number of back-to-back Zener diodes in a unique thickness increases and this leads to a higher breakdown voltage. Since the devices with high nonlinearity coefficients (α) and low breakdown voltages are useful in protecting sensitive electrical circuits, samples with higher amount of polymer content are suggested for modern sophisticated devices.

2.7.4 GaAs–PANI–PE Composites

Low-voltage varistors can be made out of a low-band gap semiconductor, gallium arsenide—as filler and polymers—e.g. polyaniline and polyethylene—as matrix

Table 2.5 Parameters of composite varistors [52–54]

Film No.	ZnO content (%)	Polymer matrix (%)	Breakdown voltage (V)	α	Band gap (eV)
1	20	80	120	4.084	3.23
2	40	60	200	3.632	3.21
3	60	40	280	2.920	3.17
4	80	20	350	2.700	3.16

[52–54, 93, 97]. The efficacy of this composite as low-field varistor depends completely on the material properties of each of the individual constituents. Gallium arsenide, the key III–V semiconductor used for these varistor formulations, normally possess higher saturated electron velocity, direct band gap transition and higher electron mobility. Due to these benefits, they are commonly used in devices for high-frequency and low-power applications. PANI is a rigid polymer with weak mechanical stability. It functions as a semiconducting polymer, due to the probability of electron movement along the polymer chain [52–54, 94]. Conductivity of emeraldine salt form of PANI is about 1 S cm^{-1} which is comparable to the conductivity of any semiconductors. The composite samples without PANI do not show nonlinearity and its I–V characteristic is, unlike varistors, i.e. linear. Addition of PANI reduces resistance of the second phase and causes samples to exhibit nonlinearity [96]. In spite of its unique properties, low mechanical stability of PANI is a major disadvantage. To overcome its fragility, one method followed is to combine it with a thermoplastic polymer, e.g. polyethylene, which consists of long hydrocarbon chains. Polyethylene normally exhibits excellent thermal and electrical insulating properties. Within the framework, they show high resistance to chemicals and possess good mechanical and optical properties.

The composite varistor with GaAs–polyaniline–polyethylene compositions can be easily prepared as thin discs using hot pressing method [52–54]. GaAs–PANI–PE composite varistors with higher content of PANI possesses lower breakdown voltages, nonlinearity coefficients and optical impurity band gaps. They protect circuits against over voltages ranging from ~ 55 to 70 V . The composite varistor has hysteresis which increases through increase in its polyaniline content. However, samples with higher percentages of GaAs ($>50\%$) display the varistor properties. They can be used to protect circuits from $\sim 60 \text{ V}$ up to over 90 V voltages. The higher the content of GaAs in the varistor, the lower the breakdown voltage would be. Their nonlinearity coefficients, hysteresis, optical impurity bandgaps and electrical bandgaps would also be higher. The composite varistor sample exhibits hysteresis which decreases through the increase in sintering temperature. This causes the varistors to have longer lifetime due to their low degradation. Changing the sintering temperature affects properties of GaAs–PANI–PE composite varistors in such a way that its increment increases their breakdown voltages, nonlinearity coefficients and impurity bandgaps as well as their lifetime; whereas leakage current and barrier heights of these varistor normally decrease.

2.7.5 Si-Polymer Composite Varistors

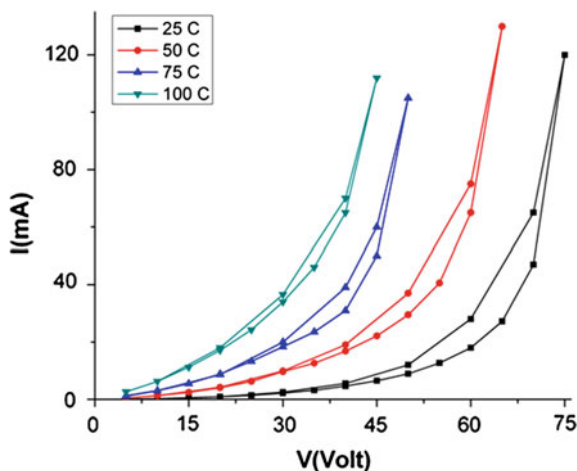
Silicon has some unique properties that make it important in varistor industry. It is a hard, relatively inert metalloid which possesses a low-band gap value of 1.1 eV. It is a good thermal conductor, which enables very dense packing of transistors that need to get rid of their heat of operation. As a varistor, the breakdown voltages of Si-polymer composite varistors are low in comparison with similar ZnO-polymer composite varistors [98, 99]. By Si content exceeding 65% of the whole Si-polymer mixture, samples exhibit varistor behaviour with nonlinear coefficient of about 10. Studies on (I–V) characteristics of samples show that by increasing Si content in the Si-polymer mixture, nonlinear coefficient and hysteresis loop increase whereas breakdown voltage and potential barrier height decreases.

There are two reasons to observe hysteresis loop on I–V diagrams, which have effect on lifetime of a varistor: (a) Joule heating and (b) existence of dipole moments. The former is very important because of lower band gap of Si that causes higher leakage current compared with ZnO varistors. For these varistors, leakage current is in mA range, which increases operating temperature and results in lifetime reduction. One of the most important effects of Joule heating is that it can directly affect polymer structure. Heating could change electrical parameters such as intergranular resistivity. Polymer may be decomposed during long inactive operating time resulting in more degradation. The latter is less important with respect to the first one. On the other hand, in the absence of an external electric field, dipole moments of superficial conditions of two contacting surfaces are randomly oriented; they can even be antiparallel. By increasing the applied voltage, majority of dipole moments orient along the applied electric field. Apparently, by decreasing the applied field, a limited number of dipole moments remain along the field direction; however, most of them do not align with the field. Therefore, a hysteresis on (I–V) curves will be observed. As shown in Fig. 2.22 [98, 99], the hysteresis loops shrink by increasing temperature because of the mechanisms' equalization.

For Si-polymer varistors, the leakage current is in mA range; as a result, it is one of the most probable reasons for instability of grain boundaries, especially for samples with higher amount of Si content. The temperature dependence of current–voltage characteristic shows that the increase in ambient temperature lowers breakdown voltage as well as nonlinearity coefficient. It should be noted that Si-PANI-PE composite varistors cannot be used at higher temperatures because of the following two reasons:

1. PE starts to melt at 130 °C, so the discs would become spoiled.
2. Nonlinear behaviour of the sample is not good enough for varistor application even at 100 °C. At temperatures between 100 °C and 130 °C, the nonlinear conductivity of varistor gradually turns to Ohmic conductivity.

Fig. 2.22 Hysteresis loops for the Si-polymer sample at different temperatures (reproduced with permission from [98, 99])



Si-PANI-PE composite varistor, with lower breakdown voltage, can be a suitable substitute for ZnO-based varistors for the purpose of protection from low overvoltage.

2.8 Conclusions

The chapter presented an overview on ‘sol-gel derived varistors’. The full potential of sol-gel method is explored in the current chapter by not only presenting simple sol-gel processing routes for preparing multicomponent nanoparticles system, but also by analyzing their derived products for high-performance miniaturized varistor applications. The unique characteristics of sol-gel syntheses which make them useful for varistor applications are their capability to do atomic level mixing of reactants, homogeneous distribution of low-level dopants and additives, stable oxide network formation through controlled hydrolysis and polycondensation reactions at room/low temperatures, control in nanoparticles preparation and the capability to produce high surface area particles with greater homogeneity. The advantage of sol-gel method is that it can be easily integrated with any varistor processing methods. Scalable, multicomponent particles can be prepared through sol-gel methods with a strict control in the stoichiometry by mere mixing sols of different compounds. Miniaturized varistors can be processed through these promising methods which yields higher breakdown voltage, low leakage current and good nonlinear characteristics. By integrating these simple processing routes and sophisticated sintering methods, high-performance or next-generation varistor devices can be achieved.

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