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Self-assembled arrays of ZnO nanoparticles and their application as varistor materials

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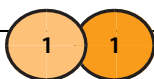Suresh Pillai, Declan McCormack, John Kelly, and Raghavendra Ramesh

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Suresh C. Pillai, John M. Kelly, Declan E. McCormack and Raghavendra Ramesh

Self-assembled linear arrays of ZnO have been prepared through a sol–gel condensation reaction, which allows the fabrication of varistors with a superior breakdown voltage compared to commercial samples.

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Self-assembled arrays of ZnO nanoparticles and their application as varistor materials†

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Linear arrays of ZnO nanoparticles have been successfully prepared by a simple sol–gel condensation reaction involving chemical modifiers, followed by drying (80 °C) and calcination (500 °C). The calcined material (nano-array ZnO) is composed of approximately spherical nanoparticles of average diameter 21 $\pm$ 3 nm, self-assembled to form arrays extending in length 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. The mechanism for formation of these linear arrays has been investigated by examining the intermediates formed at 80 °C and 250 °C using XRD and TEM and by following the decomposition reactions using TGA and DSC. Varistors prepared from the nano-array ZnO by sintering (1050 °C) with appropriate mixtures of metal oxides showed a breakdown voltage of 786 $\pm$ 30 V mm^{-1}, which is substantially higher than that of samples prepared under similar conditions from either micron-sized commercial ZnO (507 $\pm$ 30 V mm^{-1}) or from nano-ZnO (683 $\pm$ 30 V mm^{-1}).

Introduction

ZnO is one of the most widely used semiconducting oxides for electrical,[1] magnetic[2] and optical[3] applications. Nanocrystalline ZnO has received considerable attention recently because of its wide range of possible technological applications such as solar cells,[4] photovoltaic devices,[5] varistors[6] and sensors,[7] the increased importance of nano-materials being a result of the unique properties that can be obtained as a result of nano-structuring.[6,8,9] A number of preparative techniques, many based on the reaction of zinc salt with alkali metal hydroxides or on alkoxide based sol–gel methodologies, have been shown to yield spherical well-defined particles in the range of 2 to 7 nm.[10]

Many different morphological structures of ZnO micro-particles have been reported including stars,[11] rods,[11,12] snow flakes[12] and spheres.[13] However only recently have ZnO nanowires and similar morphologies been reported. These have been achieved using *inter alia* anodic alumina membranes,[14] physical vapour deposition,[15] gold catalysed vapour–liquid–solid growth,[16] and by chemical synthesis.[17] Perpendicularly oriented ZnO rods have also recently been prepared using low temperature solution deposition.[18] Some of these procedures produce ZnO in small quantities restricting their commercial applications. We report here that while sol–gel condensation reaction of zinc acetate and oxalic acid in ethanol solution, followed by drying and calcination, produces agglomerates of ZnO nanoparticles,[19] addition of chemical modifiers (1,2-ethanediol and diethanolamine) yields a product (*nano-array ZnO*) composed of linear arrays of particles of the semiconductor. This method, unlike most of those previously reported, allows the production of self-assembled materials

free of inorganic impurities and in the large quantities necessary for production of varistors and similar electronic components.

One major commercial application for ZnO is the production of varistors. These are devices, used in many areas of electronics and communication technology, whose resistance varies nonlinearly with current, showing a high resistivity (typically $> 10^{10}$ Ω cm) below a certain threshold voltage and a much lower value above this threshold.[1,6,19–22] This ability of the device to become conducting when a critical voltage is exceeded explains the application of these materials as surge suppressors. (Above the threshold voltage the current I depends nonlinearly on the voltage V following the relationship $I = (CV)^{\alpha}$, where α is the coefficient of nonlinearity and C is a constant for the particular material.) The ZnO varistor, originally discovered by Matsuoka[21] is prepared by sintering zinc oxide with mixtures of other oxides.[20,21] Each of the additive metal oxides control one or more of the properties such as electrical characteristics, grain growth and sintering temperature.[20,22,23] During sintering different phases are formed and the microstructure of a ZnO varistor comprises conductive ZnO grains surrounded by electrically insulating grain boundaries.[20] The breakdown voltage of a sintered body is proportional to the number of grain boundaries between the electrodes[19,20,23] and therefore depends inversely on the ZnO grain size. Currently the ZnO used commercially is comprised of irregular-shaped polydisperse micron-sized particles.[20,22] As nanocrystalline material contains large grain boundary volumes, more varistor-active grain boundaries per unit volume should be produced, potentially leading to smaller dimension devices.

It is intriguing to see whether varistor properties can be enhanced by working with nanoparticular ZnO[19,23] and especially those having non-spherical morphology. In this paper we report that *nano-array ZnO* shows a significant enhancement of the breakdown characteristics compared to

that of agglomerates of spherical nano-ZnO or micron-sized commercial materials.

Experimental

Reagents

Zinc acetate dihydrate (Riedel-de Haen, 99.5%), 1,2-ethanediol (Aldrich, 99%), diethanolamine (DEA) (Aldrich, 99%) and oxalic acid dihydrate (Aldrich, 99%) were used as supplied. ZnO (Grillo), Bi_2O_3 (Ferro corporation), Sb_2O_3 (Cookson), CoO (Outokumpu), MnO (Campbell Chemicals), NiO (Campbell Chemicals), Cr_2O_3 (Merck) and Al_2O_3 (Merck) (all reagent grade) and commercial varistor powder were supplied by Littelfuse Ltd., Dundalk, Ireland.

Synthesis of ZnO nanomaterials (*nano-array ZnO* and *nano-ZnO*)

Nano-ZnO was made as previously described.[19] *Nano-array ZnO* was prepared similarly but with the addition of 1,2-ethanediol (EG) and diethanolamine (DEA). Thus zinc acetate dihydrate (10.98 g, 50 mmol) was dissolved in 300 ml ethanol by rotary evaporation at 60 °C under slightly reduced pressure. To this solution EG (5.57 ml, 100 mmol) and DEA (0.5 ml, 5 mmol) were added and the mixture was stirred well for 20 minutes. A solution of oxalic acid dihydrate (12.6 g, 100 mmol) in ethanol (200 ml) was simultaneously prepared by stirring for 10 min at 50 °C. The oxalic acid solution was slowly added with stirring to the warm ethanolic solution containing Zn^{2+}. The thick white semi-gel thus obtained was dried in an oven set at 80 °C for 20 hours, producing a white flaky xerogel (Elemental analysis; C 23.55; H 3.48; N 0.36; Zn 20.44%). This xerogel was heated at a ramp rate of 3 °C min^{-1} to 250, 500 or 1000 °C and held at the desired temperature for a further 2 hours. Samples were collected at each step for microstructure analysis. After calcining at 500 or 1000 °C, X-ray diffraction (XRD) measurement confirmed the presence of crystalline zincite. The material prepared at 500 °C (nano-array ZnO) was subsequently used for varistor preparation.

Varistor material preparation

In a typical experiment nano-ZnO or nano-array ZnO (2 g, 24.5 mmol) calcined at 500 °C was added to Bi_2O_3 (0.06 g, 0.13 mmol), Sb_2O_3 (0.094 g, 0.32 mmol), MnO (0.022 g, 0.25 mmol), NiO (0.012 g, 0.16 mmol), CoO (0.021 g, 0.28 mmol), Cr_2O_3 (0.0196 g, 0.13 mmol) and Al_2O_3 (0.00048 g, 0.0047 mmol), and mixed in an agate mortar for 5 minutes. This mixture was then plastified with 1 drop each of a 10% aqueous solution of poly(vinyl alcohol) and poly(ethylene glycol) and 0.015 g of gum arabic. This was further dried in an oven (100 °C) for 5 minutes and pelletised into 7 mm (diameter) × 0.7 mm (thickness) discs before sintering at 1050 °C for 2 hours under air in a chamber furnace.

Instrumentation

Powder X-Ray Diffraction (XRD) analysis samples were prepared by making a thin film of the sample with acetone on a glass plate and performing the measurement on a Siemens D 500 X-ray diffractometer, using CuKα radiation ($\lambda = 0.154$ nm). The particle sizes for the nanocrystalline ZnO were calculated by the Scherrer equation.[19,24]

Transmission Electron Microscopy (TEM) was performed with a Hitachi 7000 instrument. 400 mesh copper grids coated with formvar were used to prepare the samples. Scanning Electron Microscopy (SEM) studies were carried out using a FESEM (Hitachi S-4300) instrument, which was operated at 5.0 kV or 20.0 kV. Samples for analysis were mounted on aluminium stubs and coated with graphite.

Thermal analysis of oven-dried samples was obtained using Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA). DSC measurements were performed with a Rheometric Scientific DSC QC. A small amount of sample (less than 3 mg) was heated from room temperature (25 °C) to 500 °C at a constant heating rate of 10 °C min^{-1} under a nitrogen atmosphere. TGA was carried out using a Thorn Scientific TG-750 instrument operated at a constant heat flow of 1 °C min^{-1}.

Infrared spectra of samples, prepared as oven dried samples or as a powder calcined at 250 °C and 500 °C, dispersed in KBr were recorded (range 400–4000 cm^{-1}) on a Genesis II FTIR spectrometer.

Density measurements of the sintered samples were performed in water using an Ohaus densitometer 470007-010.

I–V characteristics (from 0.1 μA to 10 mA) were measured using a Keithley Instrument (Model 2410). The breakdown voltage (V_c) is taken as the voltage at a current of 1 mA. The nonlinear constant α was calculated from the voltages measured at a current of 10 mA and 1 mA.[19]

Results and discussion

Zinc acetate is a readily available zinc salt, which has already been shown to be a useful starting material for the formation of zinc oxide[10,19,25,26] and its solubility in ethanol means that it can be used for non-hydrolytic condensation reactions. We have previously described that mixing ethanolic solutions of zinc acetate (0.1 M) and oxalic acid (0.2 M) produces a thick semi-gel.[19] Subsequent drying of this gel and calcination at 500 °C produced ZnO (nano-ZnO). TEM and XRD measurements revealed that this material consisted of unstructured agglomerates of spherical ZnO particles with a diameter of ~ 30 nm (Fig. 1).

It has also recently been reported that diols and amines can act as chemical modifiers in the production of sol–gel materials.[27–29] We have therefore explored how the morphology of the ZnO formed by the reaction of zinc acetate and oxalic acid is affected when 1,2-ethanediol (EG) is added at concentrations up to 0.2 M accompanied by diethanolamine [$HO(CH_2)_2)_2NH$; DEA] up to 0.04 M. As before, the zinc ion and oxalic acid concentration were maintained at 0.1 and 0.2 M respectively and in each case the gels were again dried at 80 °C and subsequently calcined at 500 °C. The TEMs of each sample demonstrate that the morphology is indeed strongly influenced by the inclusion of modifiers. The most striking effect is the formation of self-assembled fibres when Zn : Ox : EG : DEA ratios of between 1 : 2 : 1 : 0.1 to 1 : 2 : 2 : 0.2 are used. The material formed with a ratio of Zn : Ox : EG : DEA 1 : 2 : 2 : 0.1
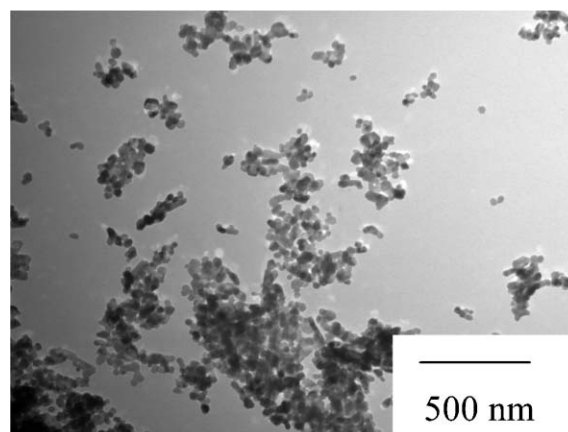

Fig. 1 TEM image of ZnO powder after calcination at 500 °C (nano-ZnO).

has been studied in most detail and its properties compared to those of the ZnO prepared without chemical modifiers. In both cases the XRD pattern is characteristic of the zincite form of ZnO, with the lines showing significant broadening. The size of the nanocrystalline regions estimated using the Scherrer equation (19 $\pm$ 4 nm) is somewhat smaller than that found for the nanoparticular sample (nano-ZnO) prepared in the absence of modifiers (*ca.* 30 nm) (Fig. 1).[19] However the most notable difference, as seen in Fig. 2a and 2b, is revealed by Field Emission Scanning Electron Microscopy (FESEM) which shows that the sample is a fibrous material containing linear arrays of 100 nm width and 2–4 μm in length.

This material (nano-array ZnO) was subsequently suspended in ethanol and ultrasonicated for periods of up to 40 minutes. TEM studies showed that this treatment separates many of the individual wires from the bundle (*e.g.* Fig. 2c). These wires are composed of approximately spherical nanoparticles of average diameter 21 $\pm$ 3 nm, self-assembled to form one-dimensional arrays of length of 2–4 μm.

The xerogel formed at 80 °C was also heated to 1000 °C and the morphology was studied by TEM and FESEM (Fig. 2d). At this higher temperature the individual particles sinter together to form continuous wires of width 0.3–0.4 μm and 10–20 μm in length. By contrast it was noticed that sintering of the xerogel (80 °C) made without using chemical modifiers produced irregular morphologies of grain size ranging from 0.3–0.5 μm (see Supporting information 1, ESI). In both cases these observations can be explained by the thermal fusion of adjacent particles, probably caused initially by ions diffusing along grain boundaries of the surface to the points of contact between particles.[13,26,30] This induces bridging and connection of the grains and results in the fusion of contiguous particles. In the case of the linear arrays this, of course, leads principally to the observed wire-like structure.[31,32] Similar behavior has been observed for linear arrays of gold nanoparticles.[30]

Characterization of the gel, xerogel and calcined powders

In order to investigate the reasons for the formation of these organized arrays, comparative electron microscopy studies were carried out on some of the precursors involved in the synthesis of the ZnO samples, prepared both in the presence and absence of modifiers. Fig. 3 compares the TEMs of the fresh gel as formed at 25 °C (Fig. 3a and 3d) and the xerogels produced by drying at 80 °C (Fig. 3b and 3e) and 250 °C (Fig. 3c and 3f) for the two sets of conditions. It may be observed that reaction in the presence of EG and DEA produces elongated crystals in both the fresh gel and the xerogels (Fig. 3 a, b and c), whereas these features are absent in the ZnO nanoparticle preparation carried out in the absence of modifiers (Fig. 3 d, e and f). It may be concluded therefore that the linear arrays of ZnO particles formed in the presence of modifiers are due to reaction of these rod-like crystals between 250 and 500 °C. (It may also be noted that the linear arrays of ZnO are longer than the precursor crystals implying that aggregation also occurs).

To further study the thermal decomposition of the sample prepared with chemical modifiers we have carried out both TGA and DSC studies of the xerogel — *i.e.* the nano-array precursor previously dried at 80 °C. The TGA curve of the xerogel shown in Fig. 4a exhibits two well-defined stages of weight losses between 130 and 290 °C and between 370 and 460 °C respectively. A total weight loss of 69% is obtained. The weight loss (37%) between 100 and 270 °C may be attributed to the removal of water, 1,2-ethanediol (EG) and acetic acid. This is confirmed by FTIR studies of the product at 250 °C, where a strong peak for the carboxylate group at 1644 cm^{-1} is still present whereas the signal for CH attributable to the acetic acid (2900 cm^{-1}) and that for water (at 3264 cm^{-1}) are greatly weakened. In the next stage 51 $\pm$ 4% of the material formed at 270 °C is lost by 460 °C, at which stage the sole product is ZnO (v_{Zn-O} = 450 cm^{-1}).[19] The precursors at 250 °C both in the presence and absence of modifiers give an XRD (see Supporting information 2, ESI), which agrees with that of anhydrous zinc oxalate (Joint Committee on Powder Diffraction Standard, card no. 37-0718), although the sample derived from reaction in the presence of modifiers does possess significantly weaker and broader peaks, indicating lower crystallinity. The conversion of this to ZnO should result in a weight loss of 47%, in reasonably close agreement with that observed.

More information was obtained from the DSC analysis of the 80 °C xerogel (Fig. 4b). This trace is significantly more complicated than that of the preparation carried out in the
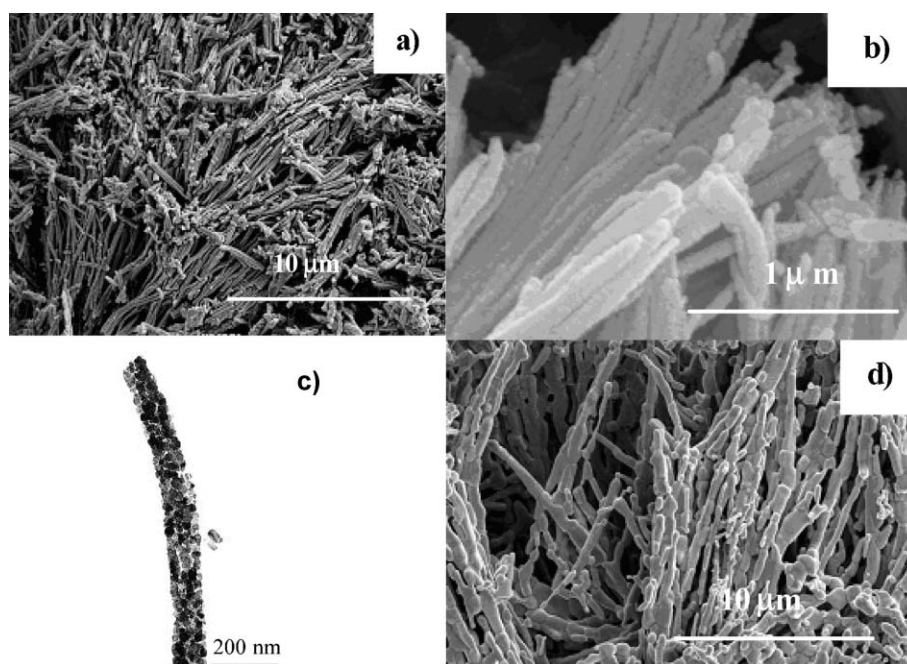

Fig. 2 Electron microscopy images of nano-array ZnO. (a) and (b) FESEM after calcination at 500 °C; (c) TEM of a single array of ZnO nanoparticle separated by ultrasonication in ethanol; (d) FESEM of nano-array ZnO calcined at 1000 °C.
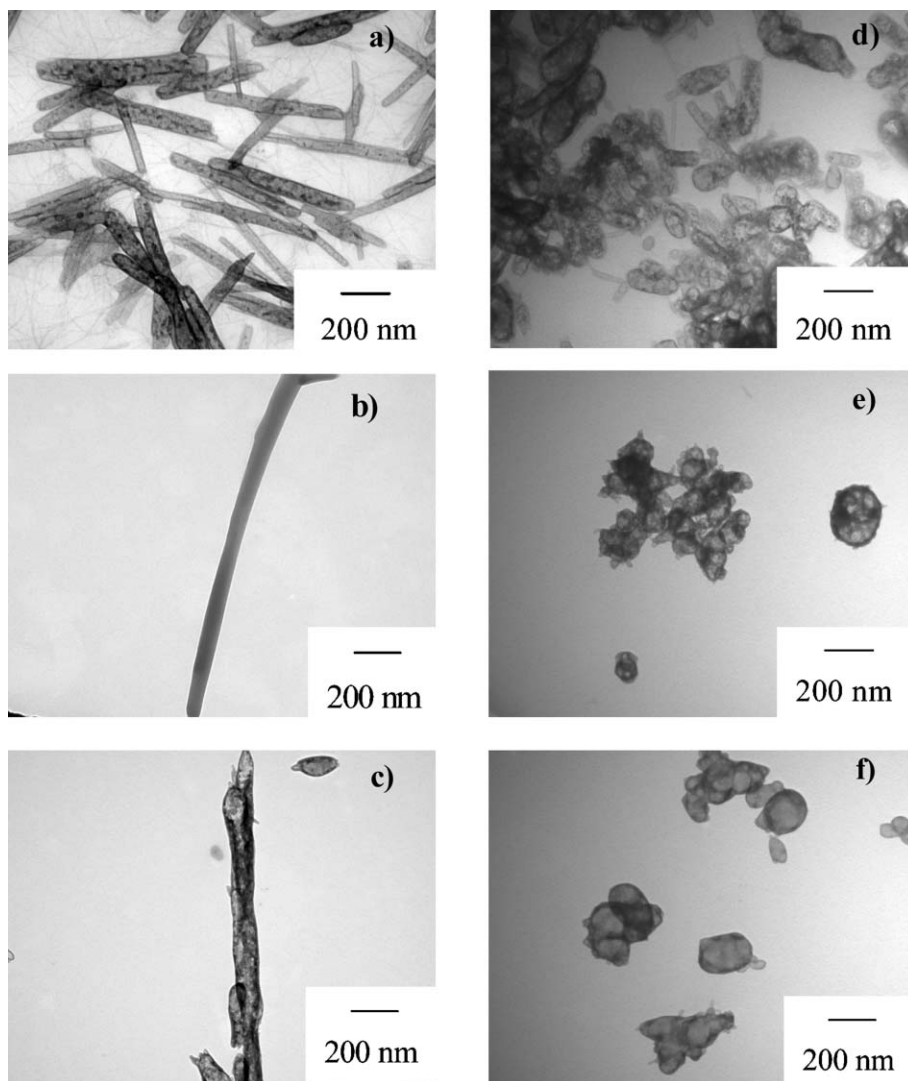
Fig. 3 Effect of modifiers on the morphology of the products formed at various temperatures by the reaction of zinc acetate and oxalic acid. (a) Fresh gel, (b) dried at 80 °C and (c) calcined at 250 °C in the presence of modifiers (Zn : Ox : EG : DEA 1 : 2 : 2 : 0.1). (d) Fresh gel, (e) dried at 80 °C and (f) calcined at 250 °C in the absence of modifiers (Zn : Ox : EG : DEA 1 : 2 : 0 : 0).

absence of modifiers which showed only peaks at 160 °C and 440 °C.[19] The broad endothermic peak at 120 °C is probably due to the removal of water (or possibly some ethanol) most likely bound to the metal ion or associated strongly with the modifiers within the xerogel. Several features appear in the broad endotherm between 150 and 250 °C. The peak at *ca.* 170 °C is probably due to the removal of acetic acid (and corresponds to the peak at 160 °C in the sample without modifiers[19]), while the signals at 210 °C and 240 °C are consistent with the removal of 1,2-ethanediol and diethanolamine respectively.[29,33] The main transition observed at 415 °C may be attributed to the formation of ZnO from anhydrous zinc oxalate[19,26,34] as the XRD shows that at the calcination temperature of 500 °C only ZnO is present.

The xerogel (prepared at 80 °C) showed a characteristic XRD pattern (see Supporting information 2, ESI), which correlates with the data for zinc oxalate dihydrate (JCPDS file number 25-1029) and an additional small amount of unidentified phases. Guo *et al.*[26] recently reported the formation of ZnO nanoparticles from a species assigned to rod-like nano-scale $ZnC_2O_4 \cdot 2H_2O$, prepared by reaction of zinc acetate and oxalic acid using sodium dodecylbenzenesulfonate as a template. It may also be noted that decomposition of $ZnC_2O_4 \cdot 2H_2O$ in the range 330–650 °C has previously been reported to yield agglomerates of 30–60 nm ZnO nanoparticles.[35,36]

Effect of different concentrations of chemical modifiers

It is clear from the above results that the addition of mixtures of 1,2-ethanediol and diethanolamine control the morphology of the ZnO formed. In order to investigate this phenomenon further we have varied the amounts of these two components and examined the morphology of the material formed at room temperature (fresh gel), dried at 80 °C (xerogel) and annealed at 500 °C (calcined material) and compared them to those prepared under the standard conditions Zn : Ox : EG : DEA = 1 : 2 : 2 : 0.1.(Figs. 3a, 3b and 2c).

When no amine is present (Zn : Ox : EG : DEA = 1 : 2 : 2 : 0) the calcined material is composed of short arrays of varying length (Fig. 5c) This result may also be compared to the sample when neither additive is present (Zn : Ox : EG : DEA = 1 : 2 : 0 : 0),[19] where calcination yields unstructured agglomerates of nanoparticles (Fig. 1). It is clear therefore that the 1,2-ethanediol directly aids the formation of the linear arrays. Examination of the xerogels for the sample (Zn : Ox : EG : DEA = 1 : 2 : 2 : 0) (Fig. 5b) shows that EG causes the formation of rod-like crystals, but these are shorter than those when DEA is also present.

Fig. 5d to 5i shows the effect of varying the amount of DEA while holding the ratio of Zn : EG constant at a 1 : 2 ratio. It was found that in the calcined samples the formation of wire-like arrays starts already when DEA is present in small amounts *e.g.* Zn : Ox : EG : DEA = 1 : 2 : 2 : 0.05, (see
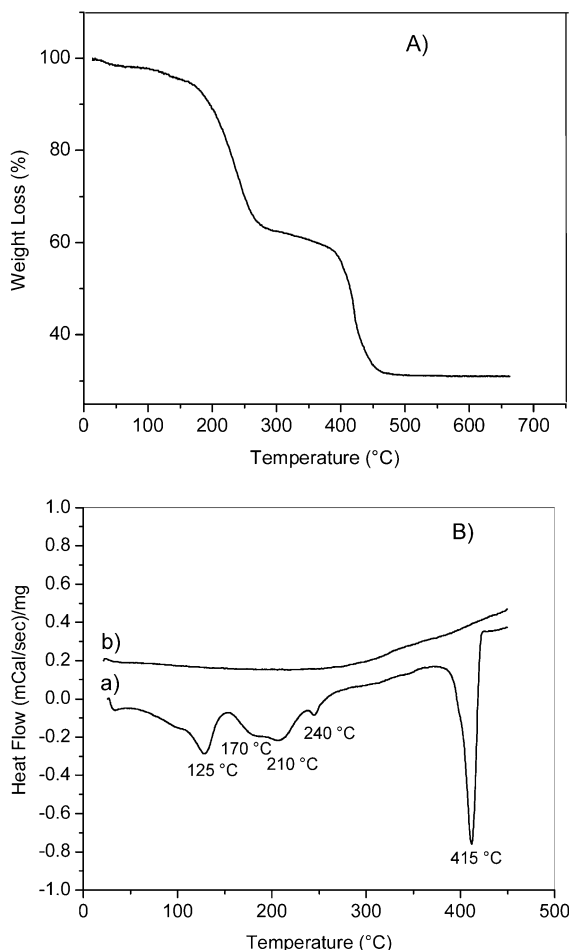
Fig. 4 (A) TGA curve of nano-array xerogel (80 °C). (B) DSC plot of the nano-array xerogel (80 °C). (a) First scan, (b) second scan.

Supporting information 3, ESI) but the 'wires' are much thinner and less well formed. The sample with Zn : Ox : EG : DEA = 1 : 2 : 2 : 0.1 and Zn : Ox : EG : DEA = 1 : 2 : 2 : 0.2 are similar with long arrays of thickness 200 nm, but increasing the DEA concentration further gives rise to less well-defined structures of thicker features (*ca.* 500 nm) (Fig. 5i). Examination of the xerogels (5h) clearly demonstrates that these latter features originate from the larger 'whiskered' crystals already present at 80 °C.

Discussion of the formation of linear arrays

It is evident that the presence of either 1,2-ethanediol or diethanolamine alone is insufficient to confer a highly linear assembly (Fig. 5 and Supporting information 3, ESI). Furthermore it is quite clear that the combined presence of these two chemical modifiers aids the alignment of particles and facilitates condensation as a fibrous semi-gel form. The action of the DEA is superficially similar to that of capping agents such as dodecanethiol,[31] and sodium dodecylbenzenesulfonic acid salt[26] which have been reported to facilitate self-assembly of nanoparticles to give well-defined morphologies. Amines are well known to control the morphology of ZnO[18,27,37–41] and other materials.[42,43] In these cases the role of the amine appears to be to organize the precursor particles in a regular manner. As more DEA is added there is an increase in the length and width of xerogel rods. However the optimum ratio of EG : DEA appears to be 2.0 : 0.1 as at higher DEA concentrations the alignment of particles becomes less precise. Indeed as the amount of DEA increases to 0.4, the regular linear alignment of particles is replaced by a network of crosslinked aggregates (Fig 5i).

Diethanolamine has both a high boiling point (217 °C) and latent heat of vaporisation,[44] which allow the retention of rod-like xerogel morphology close to the formation temperature of ZnO. This formation process can therefore be considered as a co-effect of diethanolamine and 1,2-ethanediol. It is interesting to note that a mixture of acetylacetone and 1,2-ethanediol as modifiers has recently been reported[45] to produce tetrapod-like $CuCl_2$ crystals, whereas the absence of either leads to ill-defined morphologies.

The effect of modifiers was further confirmed from the following reaction. The xerogel (80 °C) of the self-assembled ZnO material was dispersed in ethanol by ultrasonication (10 min) and the microstructure studied by TEM. By such treatment the rod-like morphology is destroyed and the structure (Fig. 6) is similar to the precursor gel without the modifiers (Fig. 3d, e and f). This is probably due to the removal of modifiers during alcohol treatment and ultrasonication.

Varistor studies

To study whether nano-array ZnO can be used to produce varistors with enhanced performance (especially a higher breakdown voltage), mixtures of it with additive oxides (in the proportions used for commercial varistor manufacture) have been sintered at 1050 °C. The properties of these varistors have been compared to those prepared from nano-ZnO and from micron-sized commercial ZnO.

XRD measurements have been carried out on each of the varistors. That obtained from the sample prepared from nano-array ZnO is presented in Fig. 7. Similar patterns were obtained with the other samples and in all cases ZnO, spinel ($Zn_7Sb_2O_{12}$) and Bi_2O_3 may be readily identified. This is consistent with the work of Inada,[46] who studied the formation of different chemical phases during the annealing process. He reported that above 650 °C the ZnO–Bi_2O_3–Sb_2O_3 system forms a pyrochlore phase $Zn_2Bi_3Sb_3O_{14}$, while at higher temperature (similar to that used here for sintering) a spinel ($Zn_7Sb_2O_{12}$) is formed (equation 1).

$$2\ Zn_2Bi_3Sb_3O_{14} + 17\ ZnO \xrightarrow[3]{950-1050\ °C} Zn_7Sb_2O_{12} + 3\ Bi_2O_3 \quad (1)$$
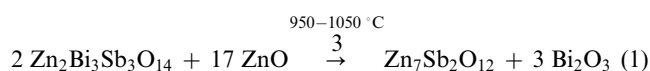
Density and electrical measurements were also carried out with each of the sintered (1050 °C) varistor samples (Table 1).

It may be observed that the varistors prepared from the nano-array ZnO have achieved the same densification as the micron-sized commercial samples. By contrast the densification of the nano-ZnO is much lower. This indicates that the nano-structuring of the ZnO particles into nanowires has a positive effect on the sintering process. Study of the current–voltage dependence of each of the samples revealed that the nano-array material yielded a sample with a breakdown voltage ($V_c = 786 \pm 30\ V\ mm^{-1}$), which was significantly higher than that of the device prepared from nano-ZnO ($V_c = 683 \pm 30\ V\ mm^{-1}$) or the commercial samples ($V_c = 507 \pm 30\ V\ mm^{-1}$) (Fig. 8).

These studies point toward the formation of more varistor-active grain boundaries per unit area[20,47] in both nano samples compared to the commercial samples. As the breakdown voltage of a sintered body in the nano-array sample is highest, this suggests that the nanostructuring of the ZnO has caused an increase in the number of grain boundaries per unit area. It may be noted that both nano-array and nano-ZnO samples exhibit lower α values compared to commercial samples and this may be improved by optimization of additive dopant concentrations such as CoO, MnO, NiO, Cr_2O_3 and Al_2O_3 in the formulation.[20–22,48]

The basic building block of varistors consists of matrix of ZnO grains separated by grain boundaries providing p–n junction semiconductor characteristics. During the sintering process, various metal oxide additives used in the formulation
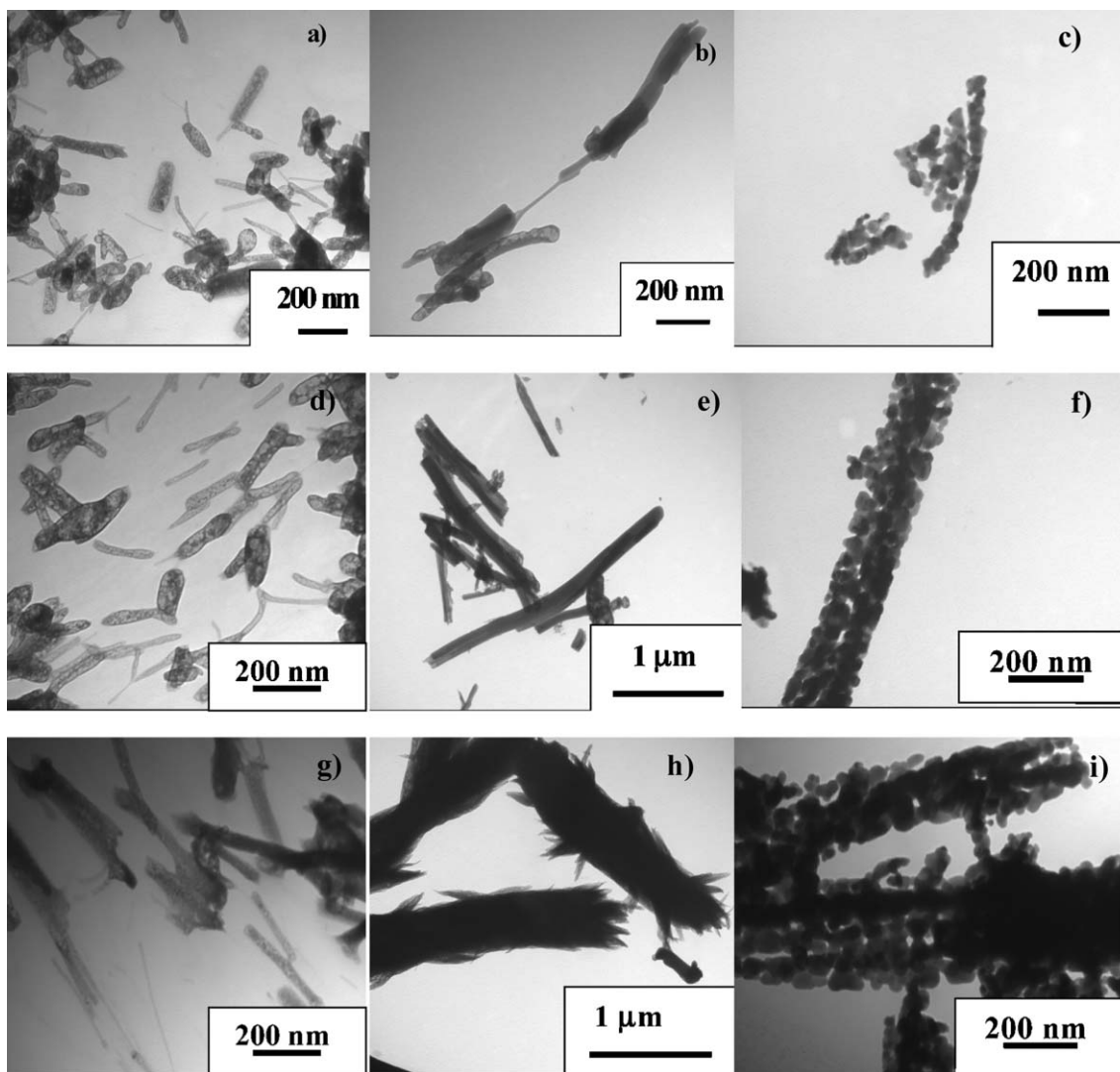
Fig. 5 TEM images showing the effect of different molar ratio of 1,2-ethanediol (EG) and diethanolamine (DEA) on the morphological evolution of nano-arrays. Zn : Ox : EG : DEA 1 : 2 : 2 : 0 (a) Fresh gel, (b) Xerogel (80 °C), (c) Calcined (500 °C); Zn : Ox : EG : DEA 1 : 2 : 2 : 0.2, (d) Fresh gel, (e) Xerogel (80 °C), (f) Calcined (500 °C); Zn : Ox : EG : DEA 1 : 2 : 2 : 0.4, (g) Fresh gel, (h) Xerogel (80 °C), (i) Calcined (500 °C).

get distributed in such a way that the grain interior becomes highly conductive and the grain-boundary region becomes highly resistive.[20,22] These resistive grain boundaries are responsible for blocking conduction at low voltages and are the sources of the non-linear electrical conduction at higher voltages. As the non-linear electrical behaviour occurs at the boundary of each semi-conducting ZnO grain, the varistor can be considered as a multi-junction device composed of many series and parallel connections of grain boundaries. Mean grain size and grain size distribution play a major role in electrical behavior and it is likely that the nano-array material has particularly favourable properties in this regard.
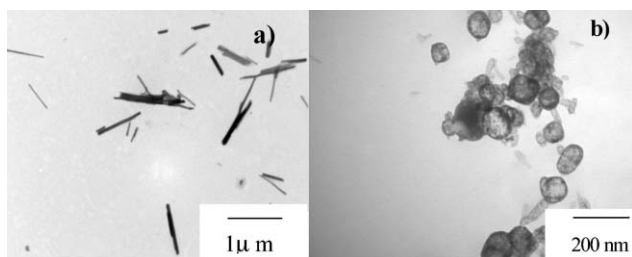
Conclusions

A sol–gel method for creating self-assembled arrays of ZnO nanoparticles has been established, which exploits a synergistic effect of two modifiers, 1,2-ethanediol and diethanolamine. Electron microscopy studies show that this sample contains ZnO arrays composed of nanoparticles of ~20 nm diameter.
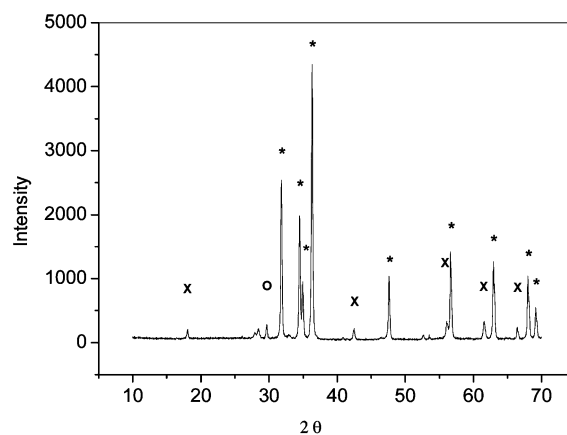

Fig. 6 TEM images of dispersions of the nano-array ZnO precursor xerogel (80 °C): (a) before and (b) after washing with ethanol.

Fig. 7 XRD of the sintered varistor prepared from nano-array ZnO sintered at 1050 °C (* = ZnO; X = $Zn_7Sb_2O_{12}$; O = Bi_2O_3).

Table 1 Densification and electrical properties of samples sintered at 1050 °C for 2 h

Varistor sample	Sintered density/g cm^{-3}	Densification (%)	V_c (± 30)/V	α (± 3)
Nano-array ZnO (A)	5.38	96.00	786	34
Metal oxides (B)[19]	5.17	92.28	683	30
Commercial (C)[19]	5.40	96.44	507	48
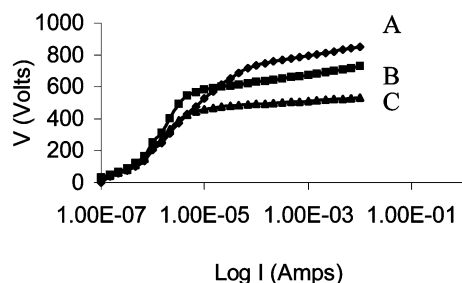
Fig. 8 *I–V* curve of varistor samples prepared by sintering at 1050 °C. A = Prepared from nano-array ZnO samples; B = Prepared from nano-ZnO; C = Prepared from commercial ZnO powder.

The modifiers appear to act by causing the formation of needle-like crystals of zinc oxalate dihydrate.

Varistors made after doping these self-assembled arrays showed a breakdown voltage superior to that prepared from commercial ZnO materials and from agglomerated spherical ZnO nanoparticles (nano-ZnO). Further improvement of these materials may lead to the fabrication of smaller devices. Because of the simplicity of the preparation procedure, scale-up is readily achieved and these materials have already been successfully produced in 500 g batch in an industrial scale pilot plant operation.

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References

1 A. Gulino and I. Fragala, *Chem. Mater.*, 2002, **14**, 116.
2 D. P. Norton, S. J. Pearton, A. F. Hebard, N. Theodoropoulou, L. A. Boatner and R. G. Wilson, *Appl. Phys. Lett.*, 2003, **82**, 239.
3 S. Fujihara, H. Naito and T. Kimura, *Thin Solid Films*, 2001, **389**, 227.
4 B. O'Regan, D. T. Schwartz, S. M. Zakeeruddin and M. Gratzel, *Adv. Mater.*, 2000, **12**, 1263.
5 Y. Chen, D. Bagnall and T. Yao, *Mater. Sci. Eng. B.*, 2000, **75**, 190.
6 P. Duran, F. Capel, J. Tartaj and C. Moure, *J. Am. Ceram. Soc.*, 2001, **84**, 1661.
7 H-M. Lin, S- J. Tzeng, P-J. Hsiau and W-L. Tsai, *Nanostruct. Mater.*, 1998, **10**, 465.
8 G. B. Biddlecombe, Y. K. Gun'ko, J. M. Kelly, S. C. Pillai, J. M. D. Coey, M. Venkatesan and A. P. Douvalis, *J. Mater. Chem.*, 2001, **11**, 2937.
9 M. Venkatesan, S. Nawka, S. C. Pillai and J. M. D. Coey, *J. Appl. Phys.*, 2003, **93**, 8023.
10 (*a*) L. Spanhel and M. A. Anderson, *J. Am. Chem. Soc.*, 1991, **113**, 2826; (*b*) E. A. Meulenkamp, *J. Phys. Chem. B.*, 1998, **102**, 5566; (*c*) V. Noack and A. Eychmuller, *Chem. Mater.*, 2002, **14**, 1411.
11 R. A. McBride, J. M. Kelly and D. E. McCormack, *J. Mater. Chem.*, 2003, **13**, 1196.
12 J. Zhang, L. Sun, J. Yin, H. Su, C. Liao and C. Yan, *Chem. Mater.*, 2002, **14**, 4172.
13 M. C. Neves, T. Trindade, A. M. B. Timmons and J. D. P. de Jesus, *Mater. Res. Bull.*, 2001, **36**, 1099.
14 (*a*) Y. Li, G. W. Meng, L. D. Zhang and F. Phillipp, *Appl. Phys. Lett.*, 2000, **76**, 2011; (*b*) Y. Li, G. S. Cheng and L. D. Zhang, *J. Mater. Res.*, 2000, **15**, 2305.
15 Y. C. Kong, D. P. Yu, B. Zhang, W. Fang and S. Q. Feng, *Appl. Phys. Lett.*, 2001, **78**, 407.
16 (*a*) M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber and P. Yang, *Adv. Mater.*, 2001, **13**, 113; (*b*) M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo and P. Yang, *Science*, 2001, **292**, 1897.
17 J. Zhang, L. Sun, H. Pan, C. Liao and C. Yan, *New J. Chem.*, 2002, **26**, 33.
18 D. S. Boyle, K. Govender and P. O'Brien, *Chem. Commun.*, 2002, 80.
19 S. C. Pillai, J. M. Kelly, D. E. McCormack, P. O'Brien and R. Ramesh, *J. Mater. Chem.*, 2003, **13**, 2586.
20 T. K. Gupta, *J. Am. Ceram. Soc.*, 1990, **73**, 1817.
21 M. Matsuoka, *Jpn. J. Appl. Phys.*, 1971, **10**, 736.
22 L. M. Levinson and H. R. Philip, *Ceram. Bull.*, 1986, **65**, 639.
23 R. N. Viswanath, S. Ramasamy, R. Ramamoorthy, P. Jayavel and T. Nagarajan, *Nanostruct. Mater.*, 1995, **6**, 993.
24 A. R. West, *Solid State Chemistry and Its Applications*, John Wiley & Sons, London, 1984, p. 174.
25 P. V. Radovanovic, N. S. Norberg, K. E. McNally and D. R. Gamelin, *J. Am. Chem. Soc.*, 2002, **124**, 15192.
26 L. Guo, Y. Ji, H. Xu, Z. Wu and P. Simon, *J. Mater. Chem.*, 2003, **13**, 754.
27 T. Sugimoto, X. P. Zhou and A. Muramatsu, *J. Colloid Interface Sci.*, 2003, **259**, 53.
28 S. Fujihara, Y. Kadota and T. Kimura, *J. Sol–Gel Sci. Technol.*, 2002, **24**, 147.
29 J. T. Dawley, P. G. Clem, M. P. Siegal, D. R. Tallant and D. L. Overmyer, *J. Mater. Res.*, 2002, **17**, 1900.
30 S. Fullam, D. Cottel, H. Rensmo and D. Fitzmaurice, *Adv. Mater.*, 2000, **12**, 1430.
31 B. A. Korgel and D. Fitzmaurice, *Adv. Mater.*, 1998, **10**, 661.
32 J. Richter, R. Seidel, R. Kirsch, M. Mertig, W. Pompe, J. Plaschke and H. K. Schackert, *Adv. Mater.*, 2000, **12**, 507.
33 X. Zhao, B. Zheng, C. Li and H. Gu, *Powder Technol.*, 1998, **100**, 20.
34 A. K. Nikumbh, S. K. Pardeshi and M. N. Raste, *Thermochim. Acta*, 2001, **374**, 115.
35 V. Bolis, B. Fubini, E. Giamello and A. J. Reller, *J. Chem. Soc., Faraday Trans. I*, 1989, **85**, 855.
36 J-P. Auffredic, A. Boultif, J. I Langford and D. Louer, *J. Am. Ceram. Soc*, 1995, **78**, 323.
37 T. Trindade, J. D. P. de Jesus and P. O'Brien, *J. Mater. Chem.*, 1994, **4**, 1611.
38 P. O'Brien, T. Saeed and J. Knowles, *J. Mater. Chem.*, 1996, **6**, 1135.
39 B. Liu and H. C. Zeng, *J. Am. Chem. Soc.*, 2003, **125**, 4430.
40 L. Vayssieres, K. Keis, S. E. Lindquist and A. Hagfeldt, *J. Phys. Chem. B*, 2001, **105**, 3350.
41 L. Vayssieres, K. Keis, A. Hagfeldt and S. E. Lindquist, *Chem. Mater.*, 2001, **13**, 4395.
42 Z. H. Han, Y. P. Li, J. Lu, S. H. Yu, H. Q. Zhao and Y. T. Qian, *Mater. Res. Bull.*, 2000, **35**, 1825.
43 Y. Li, M. Sui, Y. Ding, G. Zhang, J. Zhuang and C. Wang, *Adv. Mater.*, 2000, **12**, 818.
44 S. H. Kim, C. E. Kim and Y. J. OH, *J. Mater. Sci.*, 1995, **30**, 5630.
45 Q. Li, M. Shao, G. Yu, J. Wu, F. Li and Y. Qian, *J. Mater. Chem.*, 2003, **13**, 424.
46 M. Inada, *Jpn. J. Appl. Phys.*, 1980, **19**, 409.
47 Y. Lin, Z. Zhang, Z. Tang, F. Yuan and J. Li, *Adv. Mater. Opt. Electron.*, 1999, **9**, 205.
48 J. Fan and R. Freer, *Br. Ceram. Trans.*, 1993, **96**, 221.

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