Revisiting the effects of $\text{Co}_2\text{O}_3$ on multiscale defect structures and relevant electrical properties in ZnO varistors

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Abstract: Element doping is an effective method to improve the performance of ZnO varistors. Previous studies mainly focused on the variation of microstructures and Schottky barriers. In this study, the effects of Co dopant on electrical properties are investigated from the aspect of multiscale defect structures, including intrinsic point defects, the heterogeneous interface of depletion/intergranular layers, and interface states at grain boundaries. Combining with analysis of phase composition and decomposition of absorbed oxygen and migration of moveable zinc, the reduction of interface charge from both positively charged depletion layers [11, 12]. That is, the overall dynamics of the DSB under external electric field, including both assisted thermal electron emission under low electric field and tunneling under a high electric field. Currently, the DSB is acknowledged consisting of negatively charged interface states and density of donors (\(N_D\)), the remarkable non-linearity is determined by the electron filling of interface states, as well [13]. In addition, the reduction of interface charge from both decomposition of absorbed oxygen and migration of moveable zinc interstitial is generally known as the origin of degradation of ZnO varistor. They are all closely related to the DSB and underlying defect structures.

Doping is one of the most effective methods to modify the DSB by manipulating its basic defect structures, e.g. point defects of zinc interstitial and oxygen vacancy. Cobalt, as an example, is one of the commonly used transition elements to modify the DSBs at grain boundaries. It is presented that the addition of Co could reduce grain boundary resistivity, enhance the non-linearity, prevent $\text{Bi}_2\text{O}_3$ evaporation and improve stability [3]. Cobalt ions in ZnO grains exit as Co$^{2+}$, which replaces Zn at the lattice sites in the manner of tetrahedral coordination [14]. It forms a deep energy level of about 1.9 eV below the conduction band edge in ZnO [15]. It is suggested that Co$^{3+}$ can increase the oxygen partial pressure in the sintering processing and decrease the density of the donor, which decreases the conductivity of the ZnO grains [16]. In addition, Yano et al. suggested that the transition metals, e.g. Mn, Co and Cu, were conducive to forming interface states between the conduction band and the valence band of ZnO, which is attributed to the 3d character of the transition metals and the $\pi$ character of excessively adsorbed oxygen [17]. Cobalt can also form a spinel phase (Co($\text{Co}_4\text{O}_3\text{Sb}_{2/3}$)$\text{O}_4$), which has a limited impact on the average grain size of ZnO [18]. The research of Co-doped ZnO varistors has been mainly focused on the improvement of the performances, the phase composition and the defect structure. However, the effects of Co dopant on the multiscale defect structures have not been systematically presented yet. It is necessary to investigate how Co at different content distributes in ZnO varistors and influences multiscale defect structures. Combining both, the impacts of element dopant on ZnO varistors can be analysed more reasonably, as well as any defect related phenomenon.

In this paper, a series of ZnO varistor blocks with different Co contents were prepared based on a commercial formula. The phase composition and micro-morphology were characterised by X-ray diffraction, scanning electron microscopy and energy dispersive
2 Experimental

A series of ZnO varistor block samples were prepared via the solid-state reaction method with the following raw materials: (94.52–x) mol% ZnO, 1.2 mol% Bi$_2$O$_3$, 1 mol% Sb$_2$O$_3$, 0.5 mol% MnCO$_3$, 1.3 mol% NiO, 1.48 mol% SiO$_2$ and x mol% CoO$_3$ (x = 0, 0.28, 0.55, 0.83, 1.1, 1.38). The raw materials were mixed by ball-milling in polyethylene bottles for 12 h with deionised water and an appropriate amount of polyvinyl alcohol (PVA). The slurry was processed into particles with size at 80–120 μm via spray granulation. The particles were added 3 wt% water to be stable for 24 h. Then, the slurry was pressed into blocks at 100 MPa, and pre-sintered at 600°C to discharge PV A. Then, the blocks were sintered in air at 1150°C for 2 h, and naturally cooled. Finally, ZnO varistor block samples with a diameter of 40 mm and a thickness of about 9 mm were obtained. They were designated as S1, S2, S3, S4, S5 and S6 for short, with the increase of Co content.

The crystalline phases of samples were examined by an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany) at room temperature. Morphologies of polished surfaces were characterised by scanning electron microscope (SEM, VE-8600S, Keyence, Japan) and the relevant element analyses were measured by an energy dispersive spectrometer (EDS, JSM-6390A, JEOL, Japan). Al electrodes were prepared on both sides of the samples for electrical measurements. The current density–electrical field (J–E) characteristics in the small current region were measured by multi-meter (HP 34401A, America) and precision linear high-voltage DC power (WJ10001D, China). In contrast, those in the high current region were measured under 820 μs lightning current pulse by impulse current generator (Keytek EMC Pro, USA) and oscilloscope (Tektronix 7245B, USA). The breakdown field $E_{1mA} = U_{1mA}/d$ and non-linear coefficient $a = 1/\log(U_{1mA}/U_{0.1mA})$ were calculated from the J–E curves, where $U_{1mA}$ and $U_{0.1mA}$ are voltages under a current density of 1 and 0.1 mA/cm$^2$, respectively, and d is the sample thickness. The leakage current density $J_L$ was also acquired at 0.75U$_{1mA}$. Dielectric properties were measured by an impedance analyser (Novocontrol, Germany) in the temperature range of ~110 to 200°C and frequency range of 10$^{-1}$–10$^{7}$ Hz with an AC signal of 1 V in magnitude.

3 Results and discussion

3.1 Phase composition and surface morphology

Fig. 1 shows the XRD patterns of the ZnO varistor block samples. The main wurtzite ZnO phase (JCPDS Card No. 99-0111), Bi-rich phase and spinel phase are identified in all the samples, which is by other reports [18, 19]. Notably, the Bi-rich phase and spinel phase are different in different samples. On the one hand, the α-Bi$_2$O$_3$ phase (JCPDS Card No. 41-1449) is detected in samples S1–S4 while δ-Bi$_2$O$_3$ phase (JCPDS Card No. 27-0052) is detected in samples S5 and S6. δ-Bi$_2$O$_3$ phase trends to appear in those samples with relatively high Co content. That is, a phase transition of Bi$_2$O$_3$ from the α-monoclinic phase to the δ-cubic phase is revealed.

On the other hand, a similar phenomenon is also found for the spinel phase. Two spinel phases Zn(Zn$_{4/3}$Sb$_{2/3}$)$_4$O$_4$ (JCPDS Card No. 15-0687) and Co(Co$_{4/3}$Sb$_{2/3}$)$_4$O$_4$ (JCPDS Card No. 78-0718) are identified in those samples. The latter phase can hardly be detected when Co content is relatively small, i.e. in samples S1, S2 and S3. The intense diffraction peak of it is observed when Co content exceeds 0.55 mol%, i.e. in samples S4, S5 and S6. It is, therefore, reasonable to deduce that Co tends to dissolve into Zn$_2$Sb$_4$O$_9$ grains at low doping rate, while it is likely to segregate at grain boundaries with higher content. Zn(Zn$_{4/3}$Sb$_{2/3}$)$_4$O$_4$ and Co(Co$_{4/3}$Sb$_{2/3}$)$_4$O$_4$ have a similar stoichiometric proportion. It is implied that some Zn atoms in Zn(Zn$_{4/3}$Sb$_{2/3}$)$_4$O$_4$ phase are replaced by Co in those Co-doped samples, because of the similar radius of Co$^{2+}$ (72 pm) and Zn$^{2+}$ (74 pm). This also accounts for the detection of other spinel phases, e.g. Zn$_{4/3}$Co$_{2/3}$Sb$_{2/3}$O$_4$, in Co-doped ZnO varistor ceramics [19].

Fig. 2 is back-scattering electron micrographs of polished surfaces of ZnO varistor blocks. Well grown equiaxed ZnO grains, grey-coloured parts of SEM pictures, are observed in all the samples. ZnO grains are pinned by those sharp spinel phases and intergranular phase, and interfaces at grain boundaries.
distributes in grains so that it can be regarded as an indicator of grain’s boundary line. Also, Bi exists in light-coloured intergranular phases, while Sb mainly exists between ZnO grains and seemingly in the spinel phase. The distribution of Co is relatively homogeneous when its content is small in samples S1–S3. However, clear peaks, accomplished with the agglomeration of Sb, are observed at grain boundaries in samples S4–S6, which arises from the segregation of Co and the formation of the spinel phase \( \text{Co(Co}^{4/3}\text{Sb}^{2/3}\text{)}\text{O}_4 \) detected by XRD in Fig. 2.

### 3.2 Non-linear current–voltage characteristics

Fig. 4 shows the current density-electrical field \( (J–E) \) characteristics of the ZnO block samples. As presented in Fig. 4a, clear electrical non-linearity is observed in all the samples in the small current region, from which breakdown field \( (E_{1\text{mA}}) \), leakage current density \( (J_L) \) and non-linear coefficient \( (\alpha) \) were calculated and summarised in Table 1. In this region, carrier transport in the samples is dominated by the DSBs at grain boundaries. However, DSB is collapsed in the high current region so that the external voltage is almost withstood by the grains, leading to linear \( J–E \) curves in Fig. 4b. Grain resistivity \( (\rho_g) \) is, in consequence, calculated as the slope and listed in Table 1, as well.

As shown in Table 1, decreased \( E_{1\text{mA}} \), \( J_L \), \( \rho_g \) and improved \( \alpha \) were acquired after Co was added into the sample, although these electrical parameters did not change monotonously. By other reports, the addition of Co results in enhanced electrical properties of ZnO varistors [3]. It is worth noting that the morphology shown

![Fig. 3: Line-scanning EDS results covering several grains and grain boundaries of ZnO varistor samples](image)

(a) S1, (b) S2, (c) S3, (d) S4, (e) S5, (f) S6

![Fig. 4: J–E curves of ZnO varistor samples in (a) Small-current region and (b) High-current region](image)

**Table 1** Electrical parameters of ZnO varistor block samples

| Sample | \( E_{1\text{mA}}, \text{V/mm} \) | \( \alpha \) | \( J_L, \mu\text{A/cm}^2 \) | \( \rho_g, 10^{-3} \Omega \cdot \text{m} \) |
|-------|-----------------|--------|-----------------|-----------------|
| S1    | 319.66          | 0.08   | 1.08            | 18.32           |
| S2    | 253.89          | 0.23   | 13.18           | 13.89           |
| S3    | 307.27          | 0.18   | 13.45           | 13.45           |
| S4    | 275.82          | 0.16   | 20.84           | 12.40           |
| S5    | 226.80          | 0.09   | 12.40           | 13.48           |
| S6    | 247.53          | 0.16   | 13.48           |                  |
in Fig. 2 varied little in different samples while largely improved properties are obtained. In this case, the DSBs, along with their defect structures, should take the major responsibility for it [22, 23].

3.3 Frequency-domain dielectric responses

The frequency-domain dielectric spectroscopy (FDS) is a powerful method to explore the inside electron trapping behaviours of defects in ZnO varistor ceramics. FDS of sample S5, as an example, at varying temperatures is shown in Fig. 5. Two explicit permittivities ($\varepsilon'$) steps are shown at low temperatures in Fig. 5a. They are correlated with two dielectric relaxations, which are marked as Relax. A and Relax. B, respectively. Only one clear $\varepsilon'$-step, marked as Relax. C, is detectable in the high-frequency range (>10$^2$ Hz) at high temperatures in Fig. 5b. Moreover, a blurry $\varepsilon'$-plateau also appears in the low-frequency range (<10$^2$ Hz), which is marked as Relax. D. The results shown in Fig. 5 indicate that four relaxation peaks should appear in an imaginary part of permittivity ($\varepsilon''$) spectra. However, the entire peak of Relax. D and the partial peak of Relax. C are commonly covered by the intense dc conductance, which is even mistaken as a relaxation process in commonly used impedance and modulus spectra [24, 25].

Facing the difficulty of clearly exhibiting the relaxation processes and relating electron trapping dynamics in ZnO varistor blocks, an optimised ($\partial \varepsilon'/\partial \ln \omega$)/$\varepsilon'$ spectroscopy is employed [26, 27]:

$$\frac{\partial \varepsilon'/\partial \ln \omega}{\varepsilon'} = \frac{-2(\varepsilon_s - \varepsilon_{\infty})\omega^2}{(\varepsilon_s + \varepsilon_{\infty}\omega^2r^2)(1 + \omega^2\tau^2)}$$

where $\varepsilon'$ is a real part of complex permittivity. $\varepsilon_s$ and $\varepsilon_{\infty}$ are optical and static permittivity, respectively. $\omega$ is the angular frequency and $r$ is relaxation time. Only relaxation processes are exhibited as loss peaks in this spectroscopy. Two loss peaks are observed at low temperatures in Fig. 5c, which is accordant with $\varepsilon'$-steps in Fig. 5a. Remarkably, two-loss peaks are also detectable at high temperatures in Fig. 5d, indicating two relaxation processes. All those peaks move toward a higher frequency range, showing thermally activated processes.

A relaxation peak in ($\partial \varepsilon'/\partial \ln \omega$)/$\varepsilon'$ spectroscopy reaches its maximum only when

$$\omega r = \frac{\varepsilon_s}{\varepsilon_{\infty}^4}.$$  \hspace{1cm} (2)

In this situation, the dependence of peak frequency $f_m$ on temperature, as plotted in Fig. 6, follows the Arrhenius equation.

The corresponding activation energies of all the ZnO block samples are listed in Table 2.

Besides the relaxation processes, temperature-dependent conductivity can also be calculated from FDS, as demonstrated in Fig. 7. According to Jonscher's universal relaxation law [28]:

$$\sigma' = \sigma_{dc} + B\omega^s,$$

where $\sigma'$ is a real part of complex conductivity and $\sigma_{dc}$ is dc conductivity. $B$ and $s$ (0 < $s$ < 1) are constants. $\sigma_{dc}$ is approximate to $\sigma'$ at the lowest frequency and its activation energy ($E_{dc}$) shown in Table 2 is thereby calculated from $\ln\sigma_{dc} = 1/T$ curve plotted in the inset of Fig. 7.
As clearly shown in Table 2, activation energies for Relax. A and Relax. B are about 0.22 and 0.33 eV, respectively. Both of them are independent of Co content, indicating intrinsic processes. Generally speaking, Relax. A and Relax. B are supposed to originate from electron trapping of intrinsic point defects Zn⁺ and VO⁺, respectively, with their relaxation activation energies similar to the trap depths [29–31]. In addition, activation energies of Relax. C (E_c) and Relax. D (E_d) depend on the addition of Co content, indicating extrinsic processes, which are ascribed to the intergranular phase and trapping behaviours of interface states, respectively [25]. E_c and E_d are gradually increasing with Co content. E_{dc} is the activation energy of dc conductance, which is not influenced by Co content and then indicates that the dc conductance mechanism of different samples does not change with Co content.

### 3.3.1 Effects of intrinsic defects:

The Cole–Cole model is employed to fit the measured results [32, 33]:

\[
\varepsilon^* = \varepsilon_h + \frac{\sigma_{dc}}{j\omega\varepsilon_0} + \sum_{i=1}^{2} \frac{\Delta\varepsilon_i}{1 + (j\omega\tau_i)^{1-\alpha_i}},
\]

where \(\varepsilon_h\) is the high-frequency permittivity, \(\Delta\varepsilon_i\), \(\tau_i\), and \(\alpha_i\) are magnitude, relaxation time and depression angle of the \(i\)th relaxation, respectively. At −100°C, dc conductance is negligible in the measured frequency range. Two entire Relax. A and Relax. B and partial Relax. C are involved in this range. S5 was taken as an example to exhibit the fitting results, as shown in Fig. 8. Fitting results of all the ZnO block samples are shown in Table 3.

Table 2: Activation energies of relaxations and dc conductivity of the ZnO varistor blocks

| Energy, eV | S1 | S2 | S3 | S4 | S5 | S6 |
|-----------|----|----|----|----|----|----|
| E_a       | 0.22 | 0.23 | 0.22 | 0.23 | 0.25 | 0.23 |
| E_b       | 0.33 | 0.32 | 0.33 | 0.32 | 0.31 | 0.32 |
| E_c       | 0.52 | 0.52 | 0.54 | 0.57 | 0.65 | 0.63 |
| E_d       | 0.78 | 0.80 | 0.81 | 0.87 | 0.87 | 0.83 |
| E_{dc}    | 0.76 | 0.78 | 0.78 | 0.79 | 0.81 | 0.80 |

As clearly shown in Table 2, activation energies for Relax. A and Relax. B are about 0.22 and 0.33 eV, respectively. Both of them are independent of Co content, indicating intrinsic processes. Generally speaking, Relax. A and Relax. B are supposed to originate from electron trapping of intrinsic point defects Zn⁺ and VO⁺, respectively, with their relaxation activation energies similar to the trap depths [29–31]. In addition, activation energies of Relax. C (E_c) and Relax. D (E_d) depend on the addition of Co content, indicating extrinsic processes, which are ascribed to the intergranular phase and trapping behaviours of interface states, respectively [25]. E_c and E_d are gradually increasing with Co content. E_{dc} is the activation energy of dc conductance, which is not influenced by Co content and then indicates that the dc conductance mechanism of different samples does not change with Co content.

**Fig. 7** Dependence of real part of complex conductivity on the temperature in sample S5 (inset showing the activation energy of dc conductance)

**Fig. 8** Fitting results of dielectric properties of sample S5 at −100°C

In ZnO grains, almost all of Co exists in the form of Co²⁺ [35], which substitutes Zn²⁺ with tetrahedral coordination [14]. It forms a deep level about 1.9 eV below the conduction band [15], which hardly changes the concentration of free electrons. Based on the
valence and coordination structure, it is deduced that the Co dopant is not directly correlated with intrinsic point defect concentration. Therefore, the reduction of grain resistivity ($\rho_g$) shown in Table 1 in Co-doped ZnO varistor blocks might originate from increased carrier mobility, which is accordant with previous reports [16]. The only abnormal increase of $\rho_g$ in sample S4 corresponds to the dramatic decrease of the shallow donor Zn$_i$. However, it has to be pointed out that variations of point defects cannot be well explained by themselves. The effects of Co dopant on the extrinsic defects should also be taken into consideration.

### 3.3.2 Effects of extrinsic defects:
Extrinsic defects related relaxations are always observed at high temperatures due to their long relaxation times. Taking sample S5 as an example, the FDS at 180°C is exhibited in Fig. 10. By previous analyses, only the loss peak from Relax. C can be found, while Relax. D is completely covered by dc conductance. Keeping in mind that there are two relaxations existing in ZnO block samples, the measured FDS is fitted by (4), as well. Fitting curves of sample S5 are plotted in Fig. 10 and detailed parameters of all the samples are summarised in Table 4.

A large number of researches show that Relax. C is closely correlated with the intergranular phases in ZnO varistors [22, 36]. The heterogeneous interface between intergranular and depletion layers of DSB acts as a hurdle for electron transport, resulting in space charge polarisation, which can be expressed by the frequency-dependent capacitance

$$C = C_b/(C_b + C_i) + \Delta C/(1 + a^2\tau_C^2).$$  \hspace{1cm} (5)

$$\Delta C = (R_bC_b - R_iC_i)/(C_b + C_i)(R_b + R_i).$$  \hspace{1cm} (6)

$$\tau_C = R_bR_i(C_b + C_i)/(R_b + R_i).$$  \hspace{1cm} (7)

where $\Delta C$ is the additional capacitance that arose from Relax. C and $\tau_C$ is the relaxation time. $R_b$ and $C_b$ are the overall resistance and capacitance of DSB and $R_i$ and $C_i$ are the resistance and capacitance of the intergranular phase, respectively. Based on

| Sample | $\epsilon_h$ | $\Delta\epsilon_a$ | Relax. A | $r_a, 10^{-4}$ s | $\alpha_a$ | $\Delta\epsilon_b$ | Relax. B | $r_b, 10^{-1}$ s | $\alpha_b$ |
|--------|--------------|------------------|----------|----------------|-----------|----------------|----------|----------------|-----------|
| S1     | 594.5        | 30.5             | 3.66     | 0.19           | 14.5      | 1.00           | 0.21     |
| S2     | 593.4        | 24.2             | 4.30     | 0.17           | 15.2      | 1.02           | 0.19     |
| S3     | 588.9        | 34.1             | 4.41     | 0.17           | 14.4      | 1.10           | 0.19     |
| S4     | 467.7        | 36.1             | 4.92     | 0.19           | 17.4      | 1.15           | 0.20     |
| S5     | 564.5        | 15.1             | 6.32     | 0.17           | 9.5       | 1.39           | 0.23     |
| S6     | 551.1        | 26.4             | 6.29     | 0.17           | 15.5      | 1.30           | 0.22     |

**Fig. 9** Dependence of intrinsic defect concentrations of (a) $Zn_i$, (b) $Zn_{ii}$, (c) $Vo$ on Co content

**Fig. 10** Fitting results of dielectric properties of sample S5 at 180°C

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Table 4  Fitting results of dielectric responses of different samples at 180°C

| Sample | $k_0^b$ | $\varepsilon_{h}$ | $\Delta \varepsilon_c$ | $\tau_c$ | $\alpha_c$ | $\Delta \varepsilon_d$ | $\tau_d$ | $\alpha_d$ |
|--------|---------|-----------------|-----------------|----------|----------|-----------------|----------|----------|
| S1     | 21,043  | 768.9           | 777.9           | 6.8      | 0.29     | 1632.3          | 1.3      | 0.46     |
| S2     | 22,826  | 763.7           | 722.6           | 6.8      | 0.29     | 1699.4          | 1.3      | 0.46     |
| S3     | 23,397  | 767.4           | 729.9           | 6.7      | 0.29     | 1699.9          | 1.3      | 0.46     |
| S4     | 25,470  | 661.3           | 617.6           | 6.1      | 0.30     | 1783.6          | 1.4      | 0.44     |
| S5     | 20,721  | 711.6           | 738.2           | 4.4      | 0.28     | 2087.6          | 1.5      | 0.44     |
| S6     | 24,878  | 718.8           | 714.4           | 4.2      | 0.28     | 1927.6          | 1.5      | 0.44     |

\[ k_0^b = \frac{\sigma_{dc}}{\varepsilon_0} \]
\[ \text{unit of } \tau_c = 10^{-4} \text{ s.} \]
\[ \text{unit of } \tau_d = 10^{-3} \text{ s.} \]

Fig. 11  Dependences of intergranular resistance and its activation energy on Co content

Fig. 12  Dependence of (a) Permittivity, (b) Activation energy of dc conductivity, (c) Activation energy of Relaxation D on Co content

$R_i > R_c$ in (9), the additional capacitance and relaxation time can be simplified as

\[ \Delta C = C_p. \]  \hspace{1cm} (8)

\[ \tau_c = R_c C_b. \]  \hspace{1cm} (9)

According to (8), $\Delta C$ contributed by Relax. C should be equal to the capacitance of DSB. As presented in Table 4, its permittivity ($\Delta C$) is indeed similar to $k_0$, which is the apparent permittivity of DSB consisting of polarisations caused by all the intrinsic point defects. From this point of view, intense of Relax. C is just another indicator of DSBs and point defects in grains. Furthermore, its $R_i$ related relaxation time $\tau_c$ makes it possible to study the effects of Co dopant on intergranular phases in ZnO varistors. $R_i$ is calculated according to (9) and its dependence on Co content is plotted in Fig. 11. On the basis that $\Delta C$ is approximately independent on temperature, the activation energy of $R_i$ is equal to the relaxation activation energy ($E_c$), whose dependence on Co content is also shown in Fig. 11.

As demonstrated in Fig. 11, $R_i$ dramatically decreases from $\sim 0.65$ to $\sim 0.45$ MΩ when the Co content is over 0.83 mol%. Meanwhile, its activation energy rapidly increases from $\sim 0.52$ to 0.65 eV. Both of two results indicate that Co content of about 1 mol% (around samples S4 and S5) would be a critical point, at least, for ZnO varistor blocks in this paper. As derived from XRD patterns in Fig. 1, Co tends to dissolve into ZnO grains when lightly doped, so that both $R_i$ and $E_c$ only slightly changed in samples S1–S3. With increasing Co content, Co gradually segregates at grain boundaries leading to the formation of resistive spinel phase Co(Co$_{4/3}$Sb$_{2/3}$)O$_4$ [37]. Therefore, both $R_i$ and $E_c$ increase in samples S4. When the Co content is further increased, $\delta$-Bi$_2$O$_3$ intergranular phase is formed, which is more conductive than $\alpha$-Bi$_2$O$_3$ phase. Generally, $\delta$-Bi$_2$O$_3$ is stable in the temperature range of 729–824°C [38]. However, the substitution of some oxide additives stabilises $\delta$-Bi$_2$O$_3$, down to room temperature [19]. It is supposed that Co segregation in the intergranular phase may stabilise $\delta$-Bi$_2$O$_3$ in a wider temperature range. Therefore, dramatic variations of $R_i$ and $E_c$ appear in samples S5 and S6.

Besides the variations of intergranular resistivity itself, intrinsic point defects in the grains were also affected by the transformation of intergranular phases. As presented in Fig. 9, intensities of intrinsic point defects are almost changeless in lightly doped samples (S1–S3), where Co mainly distributes in ZnO grains in the valence of +2. Dramatic decrease of intensity of $\delta$-Co, which results in a rapid increase of grain resistivity in Table 1, is just accompanied by segregation of Co at the grain boundary in sample S4:

$$7\text{CoO}_2 + 2\text{Sb}_2\text{O}_3 \xrightarrow{\text{ZnO}} 6\text{Co(Co}_{4/3}\text{Sb}_{2/3})\text{O}_4 + 3\text{O}_2.$$  \hspace{1cm} (10)

Extra oxygen is produced during the formation of spinel phase Co(Co$_{4/3}$Sb$_{2/3}$)O$_4$ detected by XRD in Fig. 1. The generation of donors is inhibited by the oxygen-enriched environment, leading to an abnormal increase of grain resistivity. With further increasing Co content in samples S5 and S6, the $\delta$-Bi$_2$O$_3$ phase was detected even at room temperature, which, as a fast oxygen transport channel [38], allowed the produced extra oxygen to escape into ambient during the entire sintering process [39]. In this case, intensities of intrinsic point defects in samples S5 and S6 recovered to the level of that in samples S1–S3.

In addition, interface states are influenced by the addition of Co and its reactions at grain boundaries, as well. Fig. 12 shows the dependence of the intensity of Relax. D ($\Delta \varepsilon_d$), activation energies of dc conductivity ($E_{dc}$) and Relax. D ($E_d$) on Co content. $\Delta \varepsilon_d$ increases with Co content, reflecting the increased density of interface states. As analysed above, extra oxygen was released due
to the addition of CoO$_2$. According to Yano et al. [17], Co is conducive to forming interface states because of the 3d character of the transition metals and the π character of excessively adsorbed oxygen. In addition, $E_D$ is equal to the energy level of interface states, by which barrier height is pinned, and $E_{dc}$ is similar to the barrier height. In consistency with the increase of intensity of Relax. $D$, both $E_{dc}$ and $E_D$ increase with the addition of Co. All those results indicate well-developed barriers at grain boundaries are formed in Co-doped ZnO varistor blocks. This is macroscopically exhibited as reduced leakage current density and improved non-linear coefficient.

4 Conclusion
In conclusion, the effects of CoO$_2$ on phase composition, micro-morphology, electrical performance and dielectric properties of ZnO varistor blocks are investigated in this paper. Great discrepancies of electrical properties are observed, although the morphologies of the samples are similar, indicating the differences of Schottky barriers at grain boundaries, which is closely related to the underlying defect structures. Although Co tends to dissolve into ZnO grains and substitutes Zn$^+$, it affects little on densities of point defects because of iso-valence doping. Alternatively, the formation of the spinel phase of Co(CoO$_2$)$\text{Si}_2$O$_4$ and transformation of intergranular phase from α-Bi$_2$O$_3$ to δ-Bi$_2$O$_3$ would indirectly affect the densities of point defects in ZnO grains by modifying the oxygen ambient at grain boundaries. This was characterised as simultaneous changes of intergranular and grain resistivity. In addition, interface states are also enhanced due to the addition of CoO$_2$, resulting in well-developed barriers and improved electrical non-linearity. From the view of multiscale defect structures of intrinsic point defects in grains, the heterogeneous interface of depletion/intergranular layers and interface states at grain boundaries, effects of Co dopant, as an example, on ZnO varistor are systematically understood.

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