

Nonlinearity coefficient Evaluation of Zinc oxide Doped modulated clay

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Abstract. Doping ZnO with different ratios of modulated clays increases the value of nonlinear parameters. Natural Clays are mixed of oxides with different concentration. Raw clay has been precipitated in the water column, as a result of the difference in the physical properties of the existing phases, the clay will precipitate in layers lighter by lighter from the bottom of the water column. SiO₂ concentrates in lower layers and decreases to the upper layers, whereas Albite, montmorillonite, and dolomite behave in the opposite manner. XRD showed different phases with different percentages along the whole divided layers of the precipitated column. The maximum value of SiO₂ concentrates at layer 3 while the other phases have lower values.

ZnO varistor has been prepared by doping with different layers up to 20 % precipitated clays and sintered at 1200°C for one hour. The obtained samples investigated by different measurements XRD, J-E characteristics, and SEM. The electrical measurements (J-E) declared that the maximum value of α obtained by doping ZnO with layer 7 and layer no. 11. The peak of α obtained at doping levels 10% or 18% for all the precipitated layers, this indicates the proper concentration of Si and Al that stabilize the interface potential barrier and also varistor characteristics.

Keywords: ZnO varistor, Modulated Clays and Varistor

Date of Submission: 29-05-2021

Date of Acceptance: 12-06-2021

I. Introduction

Varistor has a non-ohmic characteristic on the opposite to the completely ohmic behavior of potentiometer or rheostat [1]. ZnO is the base material for making metal oxide varistors and some other additives as a filler between zinc oxide grains. A varistor is known as a voltage-dependent resistor and it is used to protect a circuit from high voltage transients. A small current can pass through the varistor under natural conditions but takes a large current if the voltage rises suddenly, consequently preventing high-voltage pulses from reaching the circuit [2]. ZnO varistor consists of zinc oxide doped with little additives (2-10) % of other metal oxides such as Bi₂O₃, Al₂O₃, Pr₆O₁₁, CoO, MnO₂, SiO₂, and Sb₂O₃. The above additives condense the ceramic and improve the nonlinear properties of the varistor. The doping of SiO₂ and Bi₂O₃ makes the liquid phase during the sintering process and the shrinkage of every sample is about 86%. Doping ZnO with SiO₂ and Bi₂O₃ which enhance other oxides to be propagated evenly in the ZnO grain boundaries. SiO₂ can relevantly upgrade the nonlinear characteristics of ZnO-based varistors [3] also Al₂O₃ additives promote the characteristics of ZnO varistors. It leads to reduce ZnO grain growth rate, and correspondingly increases the microstructural uniformity of ZnO varistor [4]. Clay consists roughly of about 50% SiO₂, 25% Al₂O₃ and some other oxides with low abundance ratio [5-6]. Natural clays have various ratios of phases which is restricted in a certain range, so adding natural clays to ZnO can give nonlinear parameters restricted in a certain range as well. Modification of clay by dissolution and sedimentation improves oxide concentrations to get the best varistor doping composition and obtain the best properties.

II. Experimental

The clay sample was combined from the phosphate mines in the Hamrawein area on the Red Sea Egyptian coast. Clay was crushed manually by hammer and grounded by mechanical mill. The resultant powder burned at 550°C for five hours to eliminate organic matter. After that 500 gm of burned clay is dissolved in 1.5 liters of distilled water and pour into a transparent plastic tube 2.5 m long. After three days all of the clay is precipitated in the removable aluminum part of the precipitation tube. During precipitation, we observe different shapes of precipitated clay, where some layers visually rough and other layers smooth. The water has been pulled out and the removable aluminum part filled with clay has been removed out from the main tube. A

suitable piston has been inserted into the aluminum tube and pushed carefully in steps to give out a layer of nearly 2 cm thickness each step. The obtained layers were dried in an electrical furnace at 120°C for 24 hours. Fourteen layers are structurally modulated from the natural clay were obtained. Layers (1, 3, 5, 7, 9, 11, and 13) have been chosen for doping ZnO (99.5% purity) according to the chemical formula; (1-x) ZnO x (Sn), where Sn the precipitated layer starting from the bottom of the removable part, x is the doping ratio and x takes the values (0.5, 1, 2, 4, 5, 7, 10, 13, 15, 18, and 20) %. These layers ground for 10 hours and are sent for X-ray analysis to check the separation of different phases. An electrical stirrer has been used to mix ZnO with the clay in alcohol for one hour. The mix was dried at 90 °C for 24 hours. The batches were ground by ball milling for 5 hours. The powder was isostatically pressed in cylindrical Pellets (1 ± 0.05 mm thickness and 130 ± 10 mm² area) using a pressure 6 tons /cm², and then sintered at 1200°C for 1 hour, silver paste was used to electrode the samples for electrical measurements. Current-voltage characteristics were investigated up to 5000 V/cm at room temperature by using Keithley electrometers 197 A and 179 TRMS. The microstructure of the highest α samples for all doped samples was studied by SEM and EDAX.

III. Results And Discussion

The ratios of the crystalline phases found in each clay layer (2 cm thickness) obtained from X-ray analysis are shown in table 1.

Tab. 1: Phases detected in the burned clay layers after the precipitation process

Layers Phases (%)	1	3	5	7	9	11	13
1- Quartz	61.8	61.8	66.13	56.81	40.33	45.28	44.33
2- Albite	18.7	15.39	19.35	23.66	30.25	28.3	27.35
3- Montmorillonite	9.7	7.7	6.45	12.42	10.08	5.66	
4- Dolomite	9.7	7.7	8.07	7.1	10.08	11.32	
5- Illite					9.24		5.66
6- Kaolinite 1A						9.44	
7- Microcline							22.64

- 1- SiO₂ 2- NaAlSi₃O₈ 3- Na-Mg-Al-Si₄O₁₁ 4- CaMg(CO₃)₂
 5- K(AlFe)₂AlSi₃O₁₀(OH)₂H₂O 6- (Al₂Si₂O₅(OH)₄ 7- (KAlSi₃O₈)

From the above ratios of the crystalline phases found in all layers, Fig. 1 shows the relation between the abundance of phases (Quartz, Albite, Montmorillonite, and Dolomite) in each clay layer and the precipitated layer number.

As clear from Fig. 1 Quartz phase is the major phase concentrated at layer 3 and decreases slightly to reach plateau at layer 9 and higher layers. Albite phase decreases to layer 3 and increases to make plateau at layer 9 and higher layers. The other phases have the same behavior as Albite. This figure reflects the idea about the possibility of partial separation of the phases present in the natural clay by precipitation in water. At layer 3 quartz phase has its main effect while at layer 9 and higher layers quartz still high, 40 %, but has its lowest effect, so it is expected to participate with albite and other phases in any appeared phenomena.

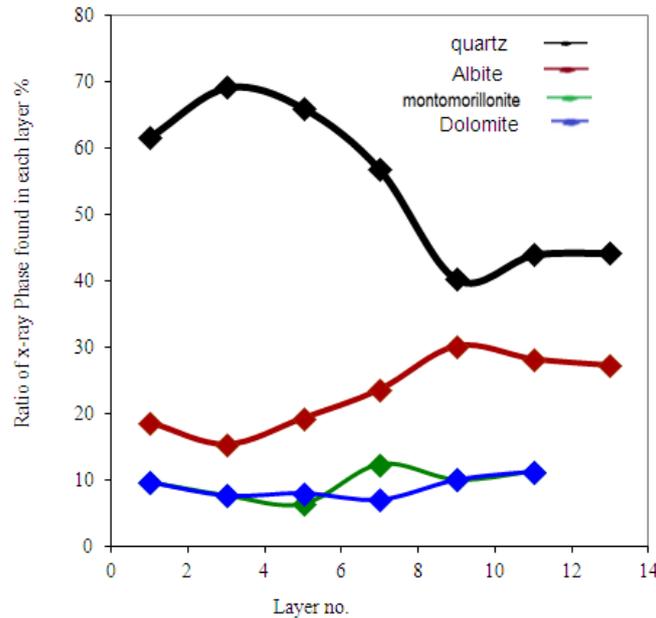


Fig. 1 Ratio of crystalline phases found in each layer (2cm thickness) vs. layer no.

After doping ZnO with different clay layers, electrical measurement (J-E characteristics) was detected for all samples as shown in Fig. 2 and Fig. 3 declared J-E characteristics of ZnO doped with different ratios (up to 20%) from precipitated layer 5 sintered at 1200°C for 1 hour.

All layers (1, 3, 7, 9, 11, and 13) have the same behavior as layer 5, and the values of nonlinearity coefficients α for all layers are given in table no. 2 and calculated as in [7]. We notice that, there is a shift in most of the breakdown electric field E_0 to higher values with increasing the doping ratio, especially at the higher doping.

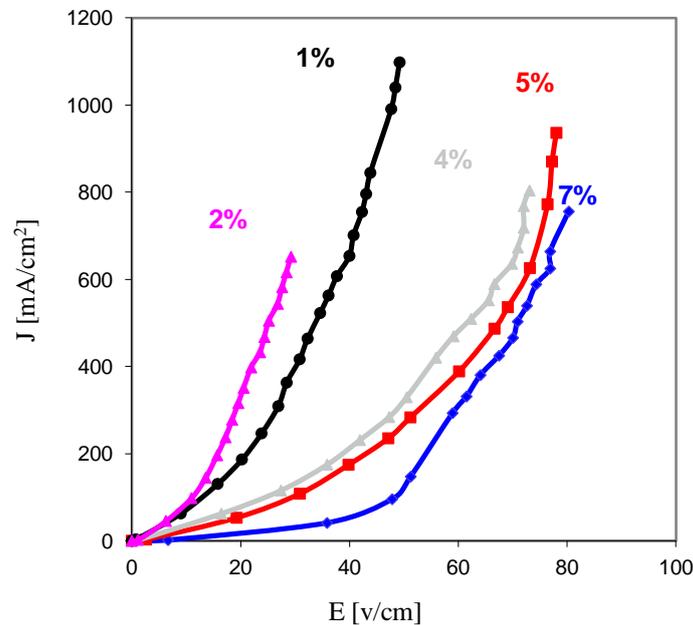


Fig. 2 J-E characteristics results from doping Layer no. 5 with ZnO for low doping.

Tab. 2: Values of nonlinearity coefficient α for ZnO Doped clays from the mentioned layers(up to 20%).

Weight%	1	2	4	5	7	10	13	15	18	20	
Layer no.	1	2	3	2	2	4	3	6	15	20	10
1	2	3	2	2	4	3	6	15	20	10	
3	2	2	2	2	3	4	3	3	6	3	
5	2	2	3	3	4	5	3	5	4	5	
7	3	3	3	3	4	18	3	4	9	18	
9	2	2	4	5	7	13	5	6	10	5	
11	2	4	2	4	4	27	11	19	27	18	
13	2	4	3	3	3	4	6	14		6	

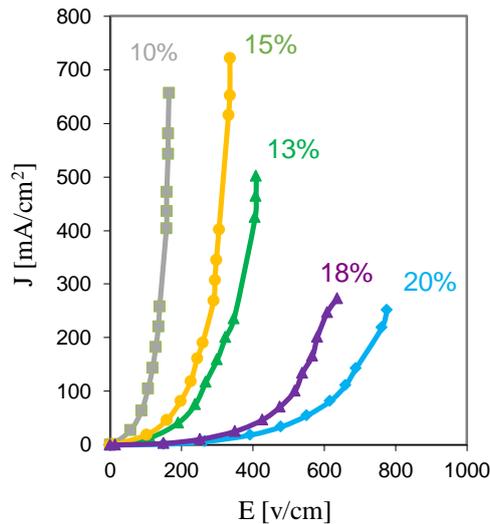


Fig. 3 J-E characteristics results from doping layer no. 5 with ZnO for high doping.

From the above calculation of α , the relation between α and the doping layer is given in Fig. 4 for low doping and Fig. 5 for high doping. As clear, before layer 7 or doping 7%, α values are away from technical application while in Fig. 5 from 10% doping α decrease sharply to layer 3 then raised as a small peak. At layer 5, followed by two peaks at layers 7 and 11. Referring to Fig. 1 the small peak at layer 5 might be due to the Quartz phase. The other two peaks at layer 7 and 11 can be attributed to mixed phases. This may be the reason for the equal height of the two peaks.

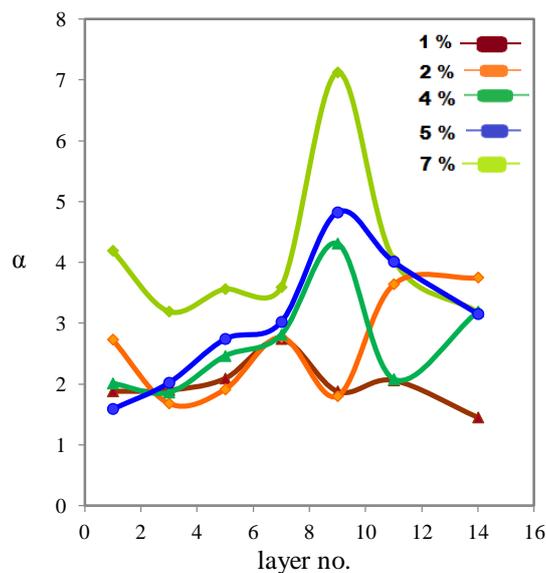


Fig. 4 α vs. layer number at different doping ratio in the range (1% - 7%).

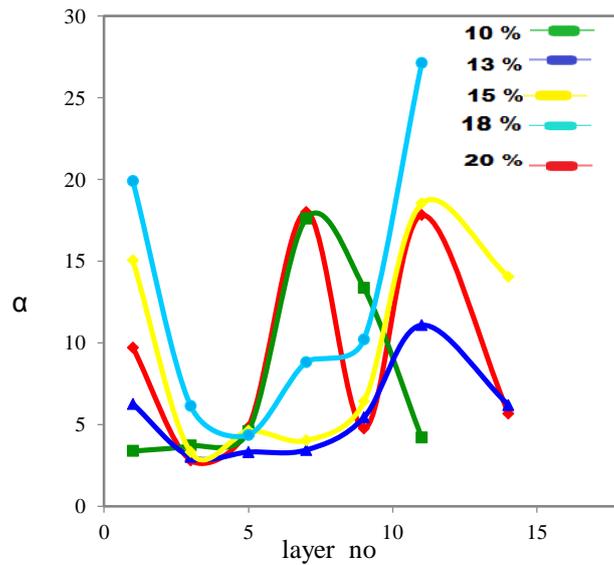


Fig. 5 α vs. layer number at different doping ratio (10% - 20%).

From the above calculation of α (The relation between α and the doping ratio from the different layers) some peaks are observed in Fig. 6 at 2%, 5%, 10%, and 18%. At these points, the proper concentration of Si and Al stabilizes the interface potential barrier and enhances α achieved by doping ratio 10 % and 18 % from the layers (7, 9) and (1, 3, 11 and 13) respectively. Pure Quartz phase has its maximum value at layer 3, but layer 3 is corresponding to the minimum α value, see Fig. 5. These points where pure quartz phase has little effect on the value of α , while mixed ratios of Albite and Quartz are much effective for α enhancement.

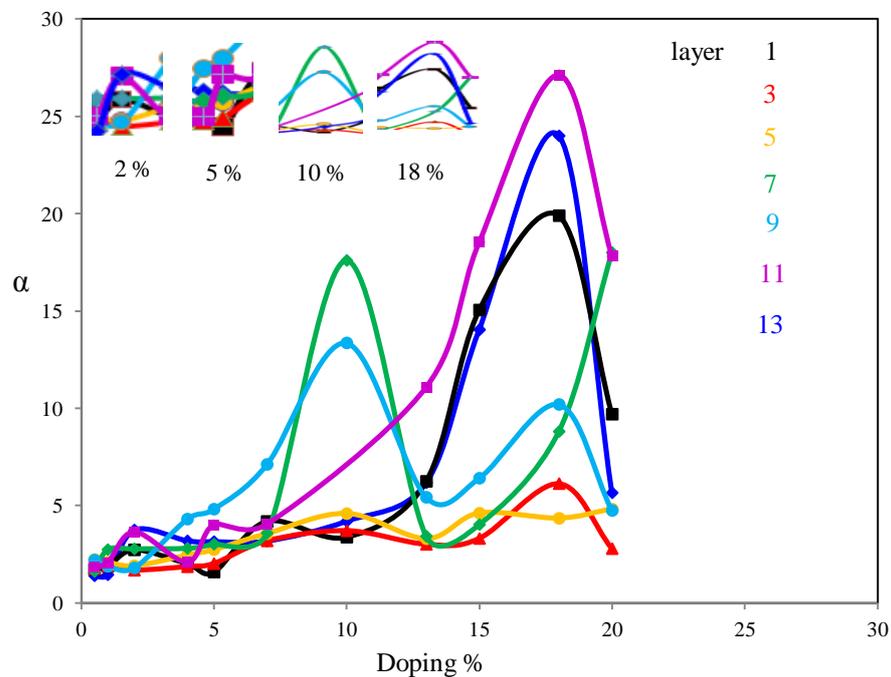


Fig. 6 α vs. doping percent for all the studied Layers. The insertion is the isolation of the appeared peaks in the Fig.

The microstructure of ZnO doped 15 % clay from layer number 5 is given in Fig. 7. The analysis was taken in three different positions.

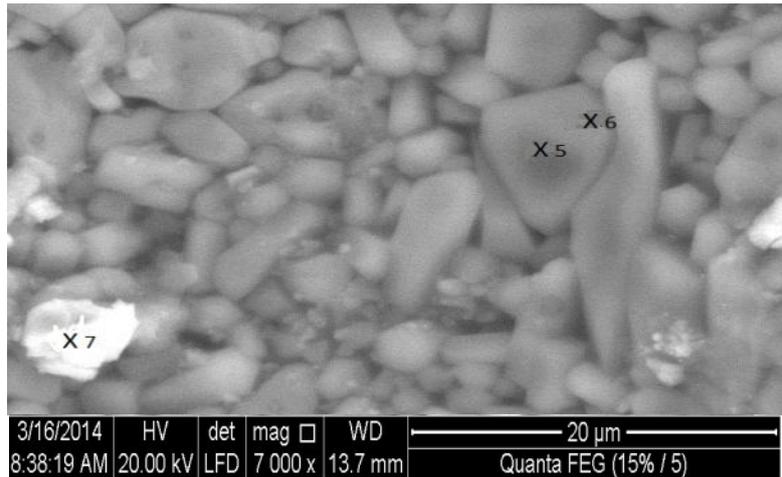


Fig. 7 SEM of ZnO doped 15% clay layer no. 5.

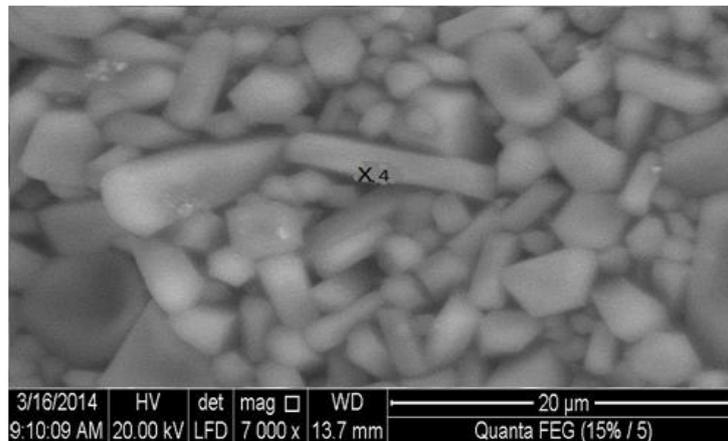


Fig. 8 SEM image of bare like grain.

The elemental analysis was taken in three positions: center of black grain, grain boundary, and white grain as shown in Fig. 7 and tabulated in table 3. A glance to SEM(Fig. 7 and Fig. 8), the presence of two phases black phase and white phase was detected, and also there are two types of grains bare-like grains and rounded edges grains. Elemental analysis declared that bare like grains are zinc silicates contaminated with Al ion as in table 4.

Tab. 3: Elemental analysis for 3 positions of ZnO doped clay layer no. 5.

Positions	O	Al	Si	Fe	Ca	Zn
Center of black grain X5	4.6	1.5	3.6	0.8		85.2
Grain boundary X6	13.5	2.7	9.4	1.4	0.72	66.5
White grain X7	17.7	2	3.8			69.3
Positions	O	Al	Si	Fe	Ca	Zn
Center of black grain X5	4.6	1.5	3.6	0.8		85.2
Grain boundary X6	13.5	2.7	9.4	1.4	0.72	66.5
White grainX7	17.7	2	3.8			69.3

We notice from table 3 that percentages of Si, Al, Fe, and Ca at the grain boundary are higher than other positions, this because silicon oxide has melting point lower than other oxides so it creates a liquid phase during the sintering process at low temperature, which promotes other oxides to be distributed evenly in the ZnO grain boundary [8]. Al, Si, and Fe ions behave as donors that support the grain boundary barrier and increase the nonlinearity coefficient.

Tab. 4: Elemental analysis for bare like grain (rod phase).

Elements	O	Al	Si	Zn
Rod phase X4(Fig. 8)	13.75	1.03	11.06	64.23

IV. Conclusion

Natural clay can be separated into layers enriched with certain phase by dissolving the clay in water. SiO₂ phase concentrates at lower layers, and decreases towards the upper layers, whereas Albite, Dolomite, and montmorillonite behave in opposite. Doping ZnO by separated layers considerably effects on its microstructure and nonlinear properties. It seems that 18 % doping gives the maximum value of α , regardless of the layer number. Layer 11 doping 18 % gives the maximum value of α in the studied samples.

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M. I. Elkhatib. “ Nonlinearity coefficient Evaluation of Zinc oxide Doped modulated clay.” *IOSR Journal of Applied Physics (IOSR-JAP)*, 13(3), 2021, pp. 52-58.