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Nano-MgO and Nanostructured ZnO/MgO Films – Topology, Morphology and Dielectric Properties

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Abstract— **High leakage current and low dielectric constant, *k* has been reported as drawback of commercialize dielectric material which leads to the exploration of new dielectric materials. In this study, nano-MgO films and nanostructured ZnO/MgO bilayer dielectric films were synthesized using sol-gel spin coating method and deposited at various MgO solution concentration. The uniform nano-ZnO film was utilized as the oxide dielectric template to produce nanostructured ZnO/MgO bilayer films. The effect of MgO solution concentration towards topology, morphology and dielectric properties of nano-MgO films and nanostructured ZnO/MgO bilayer films were investigated. The variation of solution concentrations revealed that nano-MgO film and nanostructured ZnO/MgO bilayer film with 0.4 M MgO concentration produced improvement in the dielectric properties (dielectric constant, *k*) which is 4.9 and 5.71 respectively. This is caused by the uniform particle distributions and well-defined structure produced in these films. Besides, the bilayer film structure (nanostructured ZnO/MgO bilayer films) was found to produce slightly higher *k* value in comparison to single layer structure (nano-MgO films).**

Index Terms—**Dielectric constant, Nano-MgO, nanostructured ZnO/MgO, solution concentration.**

I. INTRODUCTION

Dielectric layer is an important layer in the capacitor configuration as it influences the capacitor performance. For dielectric thin film deposition, thin film with high relative dielectric constant value is preferable as it will contribute to high capacitance value. Material with high dielectric constant is suitable for storing charges which is due to its high polarizability in an electric field. The utilization of silicon dioxide as dielectric layer was quite common, and the relative dielectric constant reported was around 3.9. However due to limitation in electrical leakage, the researchers decided to look for alternative oxide materials to replace the silicon dioxide.

Among other oxide materials, Magnesium oxide (MgO) and Zinc Oxide are the potential alternative materials to replace SiO_2. The bulk properties of MgO such as high band gap (7.8 eV), high dielectric constant (9.8) and high dielectric strength (12 MV/cm) make this material suitable to be used as dielectric material [1][2]. Besides, due to its chemical inertness, electrical insulation, optical transparency, high temperature stability, high thermal conductivity and secondary-electron emission with a lattice constant of 4.21 Å, MgO is comparable with commonly used dielectric layer which is SiO_2 [3]. Meanwhile, Zinc Oxide (ZnO) has been reported as a promising dielectric material with the dielectric constant value around 4 to 13 [4][5]. The formation of nanoparticle ZnO film with small surface roughness was reported as a good template layer for other materials [6]. In addition, the dielectric constant of dielectric layer can further be enhanced by multilayer film configuration [7]. Therefore, this research focuses on the deposition of nano-MgO and nanostructured ZnO/MgO dielectric films via spin coating method at different MgO solution concentrations (0.2 M to 1.0 M). The influence of MgO concentration towards topology and morphology of the deposited films was then observed. The effect of the topology and morphology of films to the dielectric properties of nano-MgO films and nanostructured ZnO/MgO bilayer films were then investigated. The dielectric properties of the prepared films as affected by film configurations are studied through impedance analysis.

II. METHODOLOGY

A. Materials

The MgO solutions were prepared by using Magnesium Acetate Tetrahydrate (precursor), Ethanol (solvent) and Nitric Acid (stabilizer) while for ZnO solution the Zincacetate Dehydrate (precursor), 2-Methoxyethanol (solvent), Mono-Ethanolamine (stabilizer).

B. Deposition of Nano-MgO and Nanostructured ZnO/MgO Bilayer Films

Prior to the deposition of MgO films, the glass was clean and coated with platinum as a bottom electrode. The MgO solutions were prepared via sol-gel method at different solution concentrations (0.2 M, 0.4 M, 0.8 M and 1.0 M). The prepared solutions were then undergoing stirring, aging and sonication process, then the solution was spin coated on Pt coated glass at

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3200 rpm for 30 secs. The prepared films were then dried and annealed at 200 °C and 500 °C respectively. Meanwhile, for ZnO/MgO films, the prepared MgO solutions (0.2 M, 0.4 M, 0.8 M and 1.0 M) were spin coated on the ZnO/Pt films where the thickness of ZnO film was approximately 80 nm. Then the drying and annealing process with the same parameter as MgO films were performed.

C. Characterization of Nano-MgO and Nanostructured ZnO/MgO Bilayer Films

The topology of deposited MgO and ZnO/MgO bilayer films was determined via atomic force microscope (AFM-XE 100) while the field emission scanning electron microscopy (FESEM-JEOL JSM 7600F) was used to investigate the surface morphology and particle size of the films. The impedance spectroscopy analyzer (Solartron S1 1260A) was used to determine the dielectric constant while surface profiler (KLA-Tenco P-6) was used to measure the thickness of the deposited films.

III. Result and Discussion

A. Nano-MgO Films

The morphology of nano-MgO films at different MgO solution concentrations are shown in Fig. 1. It can be seen, the 0.2 M grain structure was not well-defined and as the solution concentration increased to 0.4 M, well-defined spherical-like grains were observed. The film was apparently compact with less grain boundaries. This suggests that the increase in solution concentration results in primary nucleate and the grains become isolated. As the solution concentrations increased up to 0.8 M, agglomerated particles were observed and further increased the solution concentration to 1.0 M caused secondary changes and this resulted in particle suspension and formation of more aggregates. This result is consistent with the result found by Chul et al where the grain growth is influenced by solution concentration which caused formation of aggregates particles [8]..

The particle size of the deposited film was observed via FESEM and the results revealed that as the solution concentrations was increased, the particle size retains their nanometer range where the average particle size was 37.5 nm, 42.8 nm, 58.1 nm, 73.1 nm, and 52.5 nm for the concentrations of 0.2 M, 0.4 M, 0.6 M, 0.8 M and 1.0 M respectively**.** This might be due to the sonication process applied during solution preparation where sonication is one of the promising methods for particle reduction [9][10]. As the solution concentration increased from 0.2 M to 1.0 M, the particle size was found to be increased. The result is consistent with Shinde et al [11] and it is probably due to the number of nuclei increased with the increased of solution concentration.

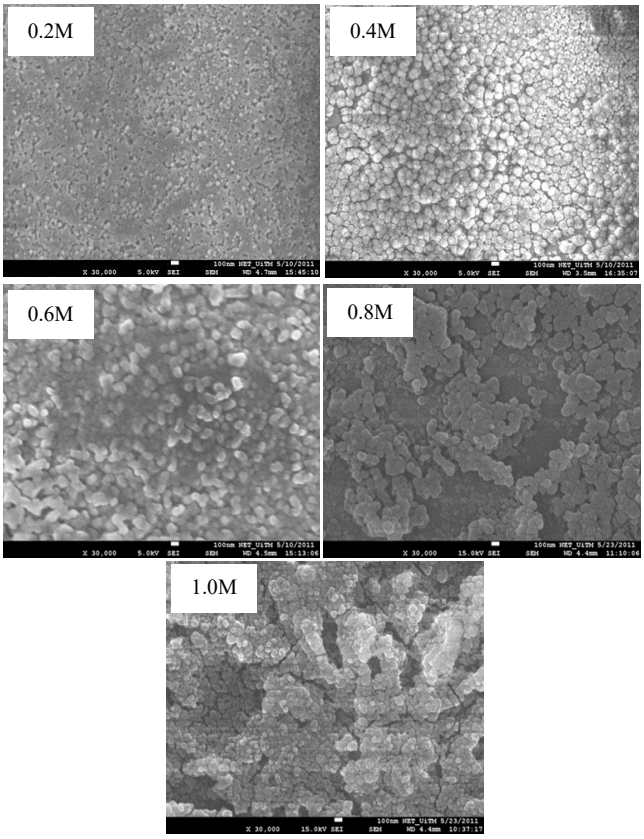

Fig. 1. Morphology of Nano-MgO Films at Various Solution Concentrations.

The topology study was conducted by measuring the root mean square, RMS surface roughness of deposited nano-MgO film and the result obtained together with their thickness are tabulated in Table I. It is observed that the surface roughness increased with an increase of solution concentration from 0.2 M to 0.8 M. This result is consistent with the morphological images in which the grain size increased at solution concentration ranging from 0.2 M to 0.8 M. A significant increment was found in RMS value for solution concentrations of 0.6 M and 0.8 M. This is in good agreement with the morphological images obtained for the same concentrations, in which agglomerated particles were significant. The slight drop in the RMS value was observed for 1.0 M film concentration, which may be due to the reduction in MgO particle size in the film.

TABLE I. Topology Properties of Nano-MgO Films at Various Solution Concentrations

Solution Concentrations [M]	Root Mean Square Surface Roughness [nm]	Thickness [nm]
0.2	9.5 ± 0.3	258 ± 4
0.4	33.0 ± 2	300 ± 5
0.6	83.3 ± 5	364 ± 4
0.8	111.8 ± 2	597 ± 4
1.0	91.8 ± 5	1080 ± 11

Fig. 2 shows the *k* values of nano-MgO films at applied frequency range of 1Hz to 100 kHz. The result shows significant decrease in *k* value at the low frequency region (A) which is due to interfacial and space charge polarization. This is because at low frequency region, the hopping electrons are trapped by defect at the film interface, and it was dominant by space charge polarization [12]. At high frequency region (B), the *k* value observed remained constant, where most of the dipoles have difficulty in keeping pace with the rapid changes of the electric field, which led to the constant value of *k* at high frequencies. In this research, the *k* value was taken at 1 kHz frequency due to low dielectric loss at this frequency. The result at 1 kHz shows decreasing trend of *k* value as the MgO solution concentrations were increased from 0.2 M to 1 M (from 5.16 to 4.18). This trend was closely related to the Mg content of the prepared MgO solution, which at low concentration (0.2 M), the Mg^{2+} ion tends to occupy the interstitial position of the film and creates an easy pathway for migration of charges. Thus, it builds up the space charge polarization, which resulted in high value of *k* [13]. Space charge refers to the trapped charge between electrodes and polarization charge caused by non-uniform polarization. As the number of charges trapped increases, better dielectric properties produced [14][15]. Nevertheless, as the solution concentration is increased up to 1.0M, the Mg^{2+} ions tend to occupy preferentially substitutional position, and this reduces the polarization in the dielectric film.

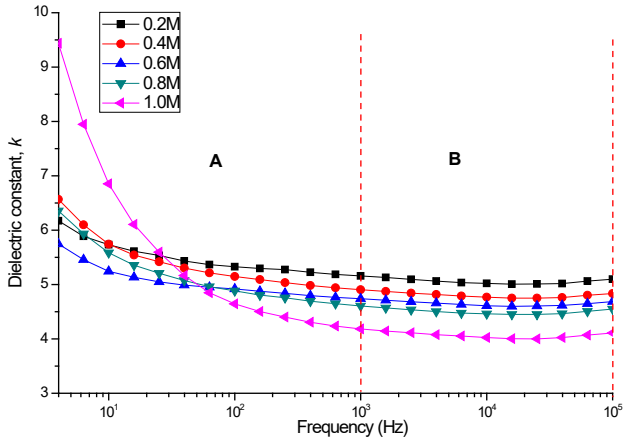

Fig. 2. Plots of Variation on *k* values of Nano-MgO Films at Various Solution Concentrations as a Function of Frequency.

B. Nanostructured ZnO/MgO Films

Fig. 3 shows the morphology of ZnO/MgO bilayer films at various MgO concentration at the magnification of 30k. As revealed in previous section (nano-MgO), the nano-MgO film layer were in the form of spherical-like shape grains. However, an interesting finding was observed when ZnO layer was pre-deposited prior to the MgO layer in which there was a modification in the film morphology. The ZnO/MgO bilayer film formed by 0.2 M MgO solution concentration was observed to be flower-like grain structures, whilst the ZnO/MgO bilayer film formed by 0.4 M MgO concentration showed rod-like grain structures. A further increase to the MgO solution concentration from 0.6 M to 0.8 M, caused formation of rose-like grains with aggregations. However, at the highest MgO solution concentration of 1.0 M, mass agglomerated structures like the structures as in Fig. 1 were observed. This signifies that ZnO layer not only behaved as a template for MgO, but the ZnO has the capability to modify the MgO structures formed through the variation of the molarity of MgO solution concentrations [16][17]. In terms of particle size, it was found that the average particle size in these bilayer films where increased from 35 nm to 58 nm as the MgO concentration increased from 0.2 M to 0.8 M. However slight reduction in particle size (48 nm) was obtained for bilayer film with 1.0 M MgO concentration. This is probably due to high solution concentration which caused densification effect, whereby small crystallites aggregate to form agglomerated grain.

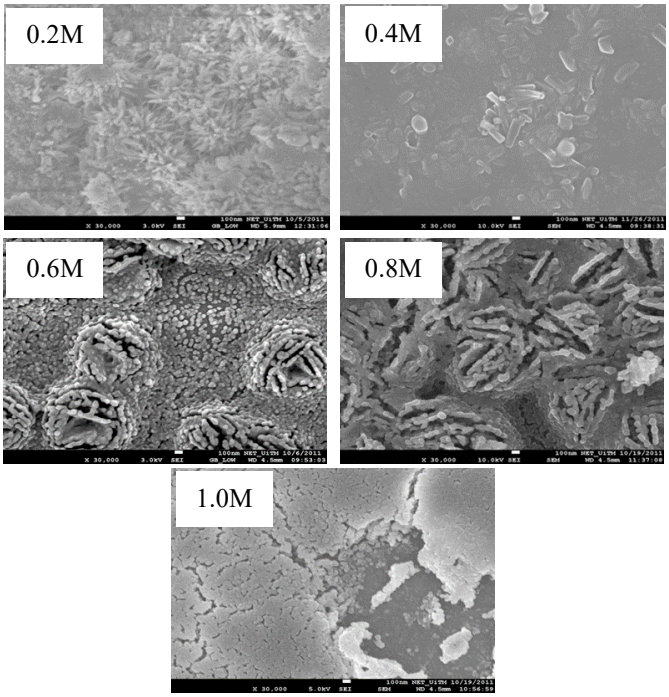

Fig. 3. FESEM Images of Nanostructured ZnO/MgO Bilayer Films at Various MgO Solution Concentrations at 30k Magnifications.

The topology in terms of surface roughness and the thickness for ZnO/MgO bilayer films are tabulated in Table II. It is observed that as the MgO concentration were increased from 0.2 M to 0.4 M, the RMS surface roughness of these bilayer films were decreased slightly from 24.0 nm to 17.8 nm. This is evident from the morphology of 0.4 M bilayer films in which the bilayer film produced uniform particle distribution in comparison to 0.2 M bilayer film. Nevertheless, a large increment in surface roughness was observed for ZnO/MgO bilayer films with MgO concentration from 0.6 M to 1.0 M which was due to strong aggregations with some grain boundaries observed in these bilayer films.

TABLE II. TOPOLOGY PROPERTIES OF NANOSTRUCTURED ZnO/MgO BILAYER FILMS AT VARIOUS MgO SOLUTION CONCENTRATIONS

Solution Concentrations [M]	Root Mean Square Surface Roughness [nm]	Thickness [nm]
0.2	24.0 ± 1	213 ± 1
0.4	17.8 ± 1	272 ± 5
0.6	71.8 ± 4	684 ± 3
0.8	92.7 ± 5	790 ± 2
1.0	309.0 ± 5	1441 ± 1

Fig. 4 shows the *k* values of ZnO/MgO bilayer films deposited at various MgO concentrations. The variation in *k* values was closely related to the morphology of bilayer films previously attained. At the frequency of 1 kHz, the 0.2 M and 0.4 M bilayer films were found to have a slightly higher *k* value (5.75 and 5.71) in comparison to bilayer films deposited with 0.6 M to 1.0 M (5.66, 5.56 and 5.65). This may be due to the rod like structures observed in these bilayer films (0.2M and 0.4M) shown in Fig.2. Ideally, the rod structure exhibited high surface polarization due to its structural in-homogeneities [18][19], caused by defect and the surface defects caused a change of positive and negative space charge distributions at the interfaces. When an electric field is applied, these space charges moved under the field and were trapped by defects at the interfaces, thus forming large numbers of dipole moments. Therefore, the high dipole moment enhanced the polarization in the film, which led to high *k* value [20]. Besides, it is found that the 0.8M film produced lowest *k* value however the reduction was found to be insignicant. The slight reduction in *k* value for 0.6M to 1.0M films was due to the morphological changes of the films from rod-like grain structure to rose-like grains with the aggregations. The aggregation formed in the films caused deterioration of the k value of film [21][22].

In addition, the slight enhancement in *k* value is observed for ZnO/MgO bilayer films compared to single layer MgO films. This might be due to formation of nanoparticles in which the particle per unit volume is large thus resulted in high dipole moment per unit volume [23].

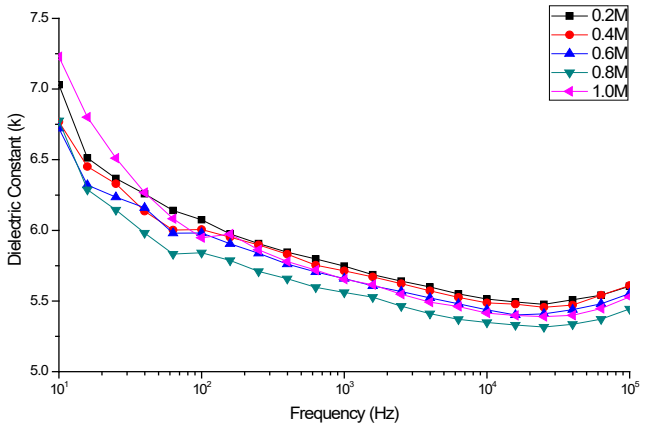

Fig. 4. Plots of Variation on k values of Nanostructured ZnO/MgO Bilayer Films at Various Solution Concentrations as a Function of Frequency.

IV. CONCLUSION

This research work explores the influence of MgO solution concentrations towards topology, morphology, and dielectric properties of nano-MgO and nanostructured ZnO/MgO bilayer films. From the result obtained, it can be concluded that the solution concentration significantly changes the grain growth of the prepared dielectric films. For nano-MgO, the morphology of the film changed from well-defined grain to the agglomerated particles. Meanwhile, for nanostructured ZnO/MgO films, addition of ZnO seed layer underneath of MgO layer caused surface modification where the flower-like grain and rod-like grain structure were observed. In addition, the variation in MGo concentration resulted in the changing of the surface morphology for both nano-MgO and nanostructured ZnO/MgO films and markedly increases the *k* value of the dielectric films.

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