Enhancement in Dielectric Constant and Structural Properties of Sol-Gel Derived MgO Thin Film using ZnO/MgO Multilayered Structure

Habibah Zulkefle, Lyly Nyl Ismail, Raudah Abu Bakar, Mohamad Hafiz Mamat, and Mohamad Rusop

***Abstract*—High dielectric constant, low porosity and nano-dimension particle of single layer magnesium oxide, MgO and multilayer ZnO/MgO were synthesized at different MgO solution molar concentration by the simple chemical solution technique. The MgO molar concentration was found to alter the properties of both single and multilayer films. Observation reveals the surface morphology change form uniform to agglomerate and porous structure with corresponding increase in molar concentration. The increment in particle size and the formation of agglomerated particle were observed by FESEM (JEOL JSM-J600F). The best prepared dielectric film for both single and multilayer is the film that deposited using 0.4 molar concentration MgO solution due to its high dielectric constant, uniform film, and the particle is in nanometer dimension with nonorod like structure.**

***Index Terms*—Dielectric, impedance, Nano-MgO, solution molarity.**

I. Introduction

Magnesium oxide, *MgO* is a best candidate to be used as dielectric layer due to its excellent properties such as has high dielectric constant (~ 9.8), large band gap in the range of 7.3 eV -7.8 eV and has higher breakdown field (12 MV/cm) compared to commonly used dielectric layer which is silicon dioxide (SiO_2) [1]-[3]. Due to its excellent dielectric properties, MgO has been proposed to be used for capacitor applications because MgO can improve the storage capability of a capacitor. Other characteristics of MgO that comparable to SiO_2 are 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 [2]. Due to its excellent properties, MgO has been proposed to replace current dielectric material (SiO_2) [2]-[4].

Zinc oxide, ZnO is a semiconductor material with direct bandgap (3.37 eV) and has high exciton binding energy (60 meV) has a great attention in device fabrication such as light emitting diode, solar cells and various type of sensors [5], [6]. Optical transparency and mechanical flexibility is the main reasons of using ZnO as dielectric layer in device fabrication such as memory or micro-laser [7]. The dielectric behavior and charge carrier transport of ZnO can be enhance by fabricating ZnO in nano-rod structure due to high surface area per unit volume, small particle size and quantum confinement of charges [8].

There are several research have been done on the deposition of oxides and semiconductor to be used in the device fabrication because via this material there are improvement in electrical and optical properties compared to single layer thin films [9]. Multilayer ZnO/MgO has widely used in tunable the bandgap either by varying the ZnO layer or MgO layer. For the composite of Mg_xZnO_{1-x}, the thermodynamic solubility of MgO in ZnO is less than 4 mol% [10]. ZnO crystal structure which is in hexagonal form is different from cubic structure of MgO, however their ionic radius for both material is quite similar and can be replace in matrix.

In the capacitor application, it is hypothesized that using this material will result in used of thin dielectric layer with high dielectric constant which can improve the storage capability of a capacitor.

Both single and multilayer MgO can be deposited using several methods such as pulsed laser deposition, electron beam evaporation, chemical vapor deposition and sol-gel spin coating technique [6], [11]. Compared to others, sol-gel offers several advantages, such as good film homogeneity, easy stoichiometry control, purity, ease of processing and controlling the composition, and the ability to coat at large and complex area substrates [12], [13].

Recently there are intensive studies in deposition of multilayer ZnO/MgO due to its ability to tune the band gap without affecting lattice constant because of its similarity in atomic radaii [14]. However, most of the research works only focus on the altering the ZnO layer and using high cost deposition method. Therefore, this research work is focus on the deposition of single and multilayer films with different molar concentration by using simple chemical deposition technique which is sol-gel spin coating. The dielectric behavior and structural properties of deposited films was then investigated.

II. Experimental Procedure

A. Solution Preparation

The MgO solutions were prepared at different molar concentrations which are 0.2, 0.4, 0.6, 0.8 and 1M respectively. Magnesium acetate tetrahydrate was used as the precursor while ethanol as the solvent. Few drops of nitric

Manuscript received December 18, 2011; revised January 18, 2012.

This work is supported by Research Management Institute (RMI) of UiTM and Ministry of Higher Education (MOHE), Malaysia.

H. Zulkefle, L. Nyl, M. Hafiz and R. A. B. Ismail are with the NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Malaysia (e-mail: habibahzulkefle@yahoo.com, lyly2909@gmail.com, raudah@salam.uitm.edu.my, hafiz_030@yahoo.com).

M. Rusop is with the NANO-ElecTronic Centre (NET) and NANO-Sci Tech Centre (NST), Universiti Teknologi MARA (UiTM), 40450 Shah Alam, (e-mail: rusop@salam.uitm .edu.my).

acid were added in the solution to be act as the stabilizer. The MgO solution was then sonicated at 50ºC for 20 minutes and followed by heating, stirring and ageing process.

B. Thin Films Deposition

MgO thin films have been deposited using simple chemical solution technique which is sol-gel spin coating method. For single layer magnesium oxide, the MgO solution was drop onto cleaned glass substrate while for multilayer films the MgO solution was drop onto ZnO film. Cleaning process was performed to remove all residual by using acetone, ethanol, and deionized water in ultrasonic bath for 10 minutes. Deposition parameter was set to 320 rpm for 30 seconds. The deposited MgO thin films was then dried at 200ºC in furnace for 10 minutes and these process were repeated for 10 times in order to archive the desired films thickness. Finally the films were then annealed in furnace at 500ºC for 1 hour.

C. Thin Films Characterizations

Dielectric and structural characterization was performed in order to investigate the prepared thin films properties to behave as a god dielectric layer. Impedance Spectroscopy Analyzer (Solartron S1 1260A-1296) was used to measure the dielectric characteristic of single and multilayer films. Structural characterization was performed using Atomic Force Microscopy (AFM-XE 100 Park System) and Field Emission Scanning Electron Microscopy (FESEM, JEOL JSM 7600F) to observe the films topology and morphology respectively.

III. Results and Discussion

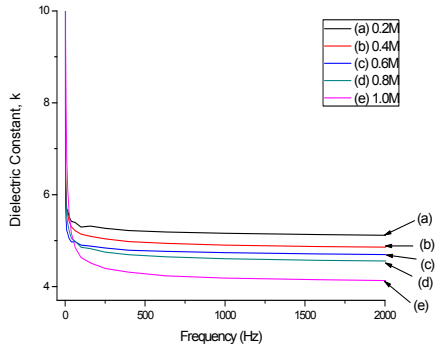
A. Dielectric Behavior

The dielectric behavior of deposited films was measured using impedance analyzer (Solartron S1 1260) with dielectric interface (1296). Dielectric constant, k and dielectric loss, tan δ of single layer MgO in the frequency region 1Hz - 2000Hz is shown in fig. 1(a) and (b) respectively. As can be seen in the figure, the k value is reduced with increase in MgO molar concentration and it start to be constant at frequency 100Hz. The k values of MgO films deposited using 0.2, 0.4, 0.6, 0.8 and 1M are 5.29, 5.14, 4.90, 4.85 and 4.64 respectively.

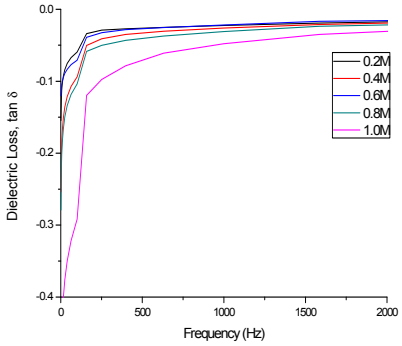
The reduction in the k values is due to the structure of the prepared films. As stated by Varadan et. al the low dielectric constant can be produce by having a porous structure [15]. Besides, Gnade et. al and Shin-Puu Jeng stated that by having a porous structure with porosity between 50% and 80% the capacitance performance will be reduce [16], [17]. The capacitance performance can be calculated using following equation (1);

$$C = \frac{\varepsilon_o \varepsilon_r A}{d} \qquad (1)$$

where C is the capacitance, ε_0 is permittivity of vacuum, ε_r is relative permittivity also known as dielectric constant, A is the area of electrode and d is the thickness of the dielectric layer. From the formula, it shows that the relative permittivity (dielectric constant, k) and also dielectric thickness are the important parameters that will influence capacitor performance.



(a)



(b)

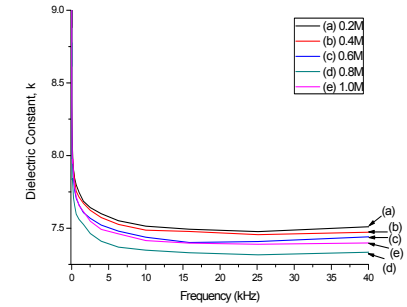
Fig. 1. Dielectric properties in terms of (a) dielectric constant, k and (b) dielectric loss, tan δ of single layer magnesium oxide.

Since the capacitance is porosity dependence and from the formula, capacitance is directly proportional to the dielectric constant of the material, hence the reduction in the dielectric constant value also due to the porosity produced in the film as shown in fig.4. From the previous work, we have report on the growth of single layer MgO in terms of film thickness [18] and by using (1), the value of capacitance for deposited MgO films are calculated. The value of capacitance for films with 0.2, 0.4, 0.6, 0.8 and 1M are 1.63, 1.37, 1.07, 0.65 and 0.34nF respectively.

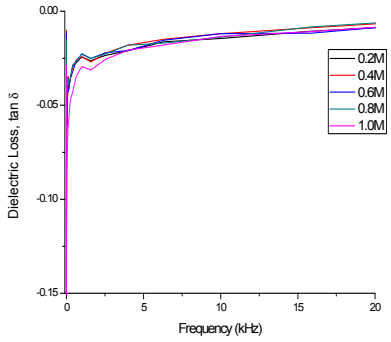
The variation of dielectric constant and loss of multilayer ZnO/MgO films as a function of frequency at different MgO concentration is given in fig. 2 (a) and (b). From the dielectric constant obtained, it can clearly be seen that the k values decreased drastically with increase in frequency at low frequency region (1 Hz – 5 kHz). This is due to the space charge polarization occurred because of inhomogenieties in the structure. Since the structure of ZnO/MgO multilayer obtained is nanorod like structure (fig. 6) so it consist of defects such as dangling bonds, vacancies, and pores at the grain that due to the high surface area per unit volume. Therefore, the surface defects cause dipole moment. From M. Soosen Samuel et.al at the low frequency, the hopping electrons are trapped by the defect at the interface [7], [19] and it was dominant by space charge polarization.

As the frequency increase, the polarization will be decrease. At high frequency, there is no space charge polarization where dipoles fail to follow the change in electric field and there is no dispersion and finally leads to the

constant in the *k* values.



(a)



(b)

Fig. 2. Variation of (a) dielectric constant and (b) dielectric loss at different MgO molar concentration for ZnO/MgO multilayer films.

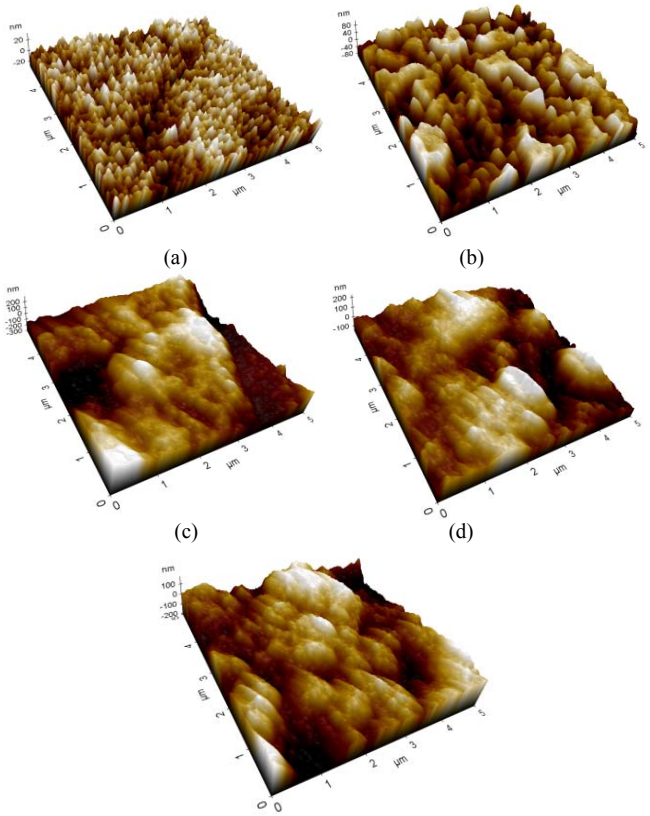
Moreover, the enhancement in the *k* value is observed when MgO films are deposited in multilayer compared to single layer MgO. The *k* values of deposited multilayer ZnO/MgO layer using different MgO solution concentration are 7.51, 7.48, 7.44, 7.35 and 7.41. The reason of this could be the formation of particle in nanometer dimension where the particle per unit volume is large, thus high dipole moment per unit volume is produced [20].

Surface profiler (Veeco) has been used to measure the multilayer films growth in term of thickness and it was observed that the thickness was increased as the molarity of the MgO layer increased from 0.2M to 1M. From the measured thickness, capacitor performance has been calculated using referring (1) and the values are 2.85, 2.22, 0.88, 0.75 and 0.41nF. From the value of capacitance, it can be seen that, when the film is deposited in multilayer the capacitance performance is improved.

B. Topology and Morphology of MgO Films

Fig. 3 shows that topology of MgO thin films at different molarity observed by atomic force microscopy (AFM XE 100 Park System). As can be seen, MgO films become rougher as the molarity increase from 0.2M to 1M where the films roughness are 4.424, 7.280, 20.956, 38.425 and 38.456 nm respectively.

When the molarity is above 0.6M the films has high surface roughness due to the agglomerated particles occurred due to non-dispersion of the particle. These phenomena has been prove by FESEM images in fig. 4 where the high molarity thin films produce agglomerate particle and has porosity. Furthermore, MgO single layer with 0.4M is the optimum molarity to produces the most uniform film compared to others.



(a) (b) (c) (d)

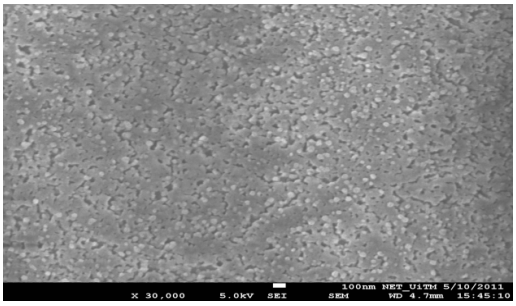
(e)

Fig. 3. AFM images of MgO films using (a) 0.2M, (b) 0.4M, (c) 0.6M , (d) 0.8M and (e) 1M solution concentration.

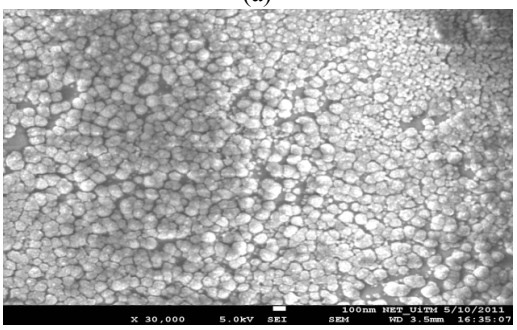
Morphology of prepared single layer MgO films at different molarity are shown in figure 4. FESEM images reveal that MgO films surface become rough, large in particle and porous structure when the molarity increases from 0.2M to 1M. Nevertheless, the particles sizes obtained from this work are in nanometer size. The reduction of particles size is due to the sonication process that was performed before the solution being deposited on the cleaned glass substrate [21]. This is because during sonication, it involved chemical reaction and promote the formation of nano-size structure by instantaneous formation of a plethora of crystallization nuclei. Several researches have stated that chemical reaction throughout sonication process happen due to ultrasonic energy involving the formation, growth, and implosive collapse of bubble in the solution [22]. Although the particle is in nanometer size, however, as can be seen in figure 4, when the molarity reach 0.6M the morphology of the films start to be rough, non-uniform and porous that due to agglomerated particle in the films.

Once the molarity increase, the amount of starting material which is magnesium being introduce to the solution increased and as the results, the particle in the solution start to aggregate when it reach certain molarity. This is because the amount of the surfactant is not enough to break the bonding between molecules. Good in uniformity and non-porous structure, is the best criteria for a good dielectric layer. From the results obtained, 0.4M MgO films is suitable to be used as dielectrics due to it uniform film with small roughness (7.280 nm), particle with nanometer dimension (42.8 nm) and also it has non-porous structure.

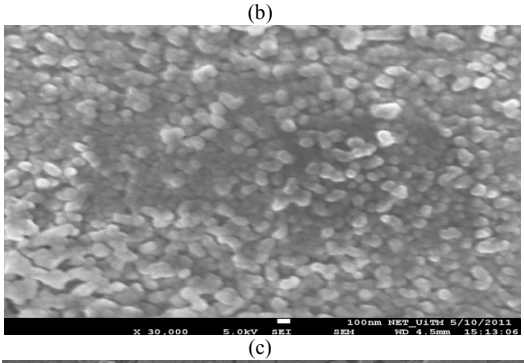
Fig. 5 shows the surface topology of multilayer ZnO/MgO at different MgO molar concentration. Same condition was observed in the surface topology of prepared multilayer films with single layer MgO films where the film surface become rougher as the molarity increase from 0.2M to 1M. This is due to large particle produced in the films with high molar concentration.



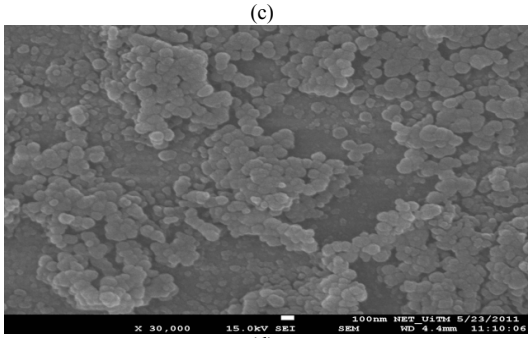
(a)



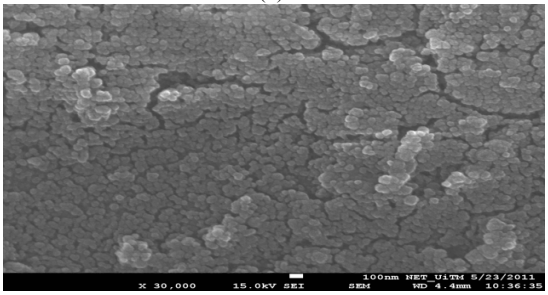
(b)



(c)

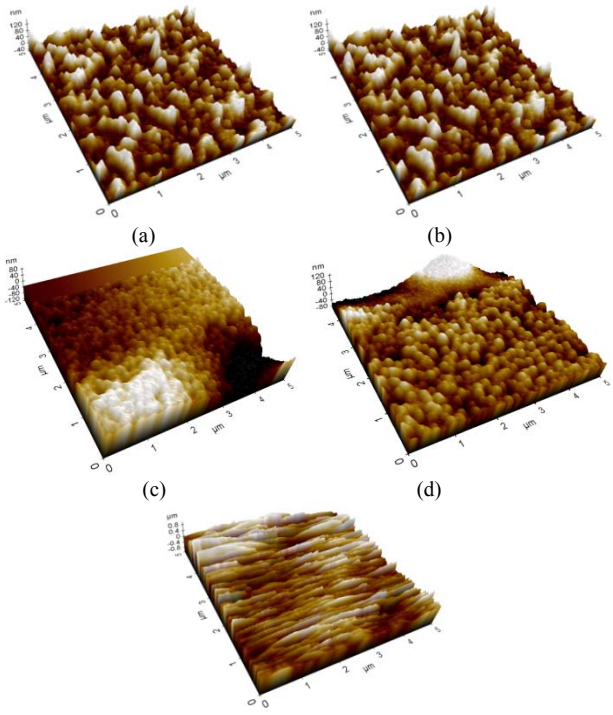


(d)



(e)

Fig. 4. Surface morphology of (a) 0.2M, (b) 0.4M, (c) 0.6M , (d) 0.8M and (e) 1M single layer MgO films.



(a) (b) (c) (d) (e)

Fig. 5. The 5µm x 5µm AFM images of multilayer ZnO/MgO films with different MgO molar concentration.

The MgO molar concentrations also affect the surface morphology and film growth of multilayer ZnO/MgO films. As can be seen in fig.6, initially there is no specific structure in the morphology of prepared ZnO layer.

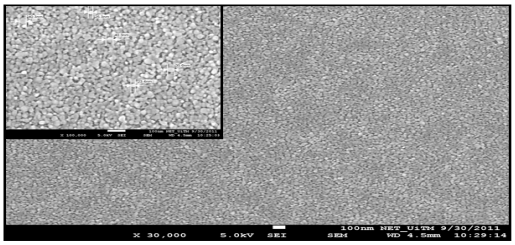
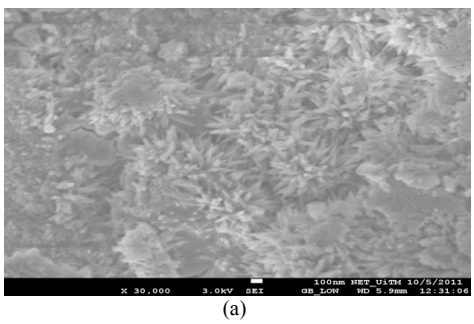


Fig. 6. Surface morphology of zinc oxide single layer observed by FESEM.

However as the MgO layer is deposited on top of that, there is unique panoramic view was observed where there is different structure produced in the multilayer films that depended on the MgO molarity.

The morphology of multilayer films analyzed by FESEM (Fig. 7) shown by using 0.2M and 0.4M molar concentration nano-flower and nano-rod like structure was obtained. The diameter of the nano-rod is 57.4nm. However, when the molarity is above 0.6M, the agglomerated and porous structure is produced.



(a)

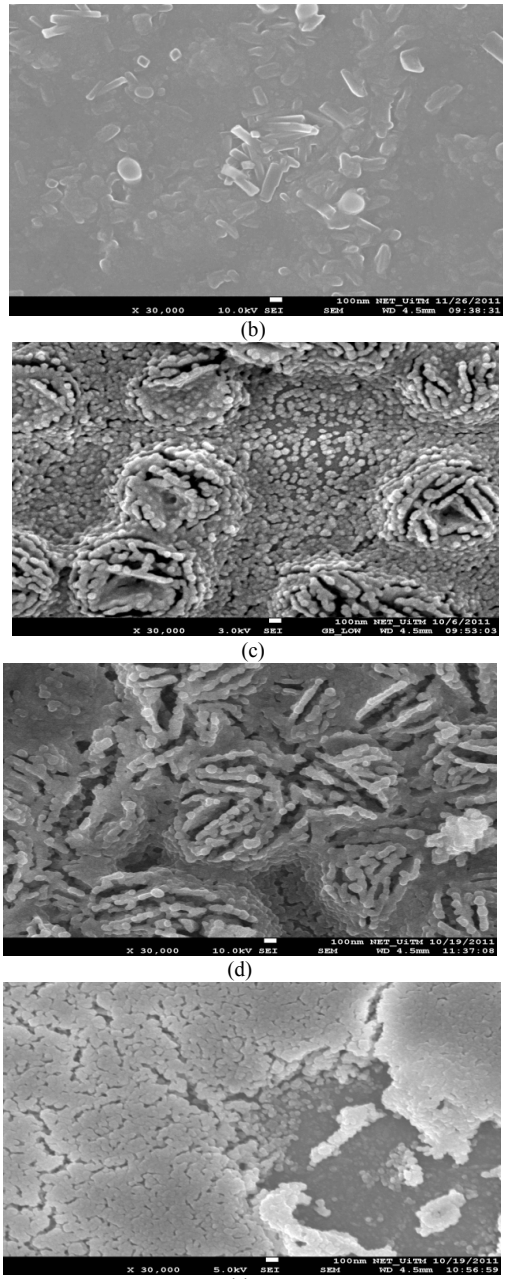


Fig. 7. FESEM images for multilayer ZnO/MgO films using variation of MgO solution concentration.

IV. Conclusion

We have successfully deposited single layer MgO and multilayer ZnO/MgO at different molar concentration (0.2, 0.4, 0.6, 0.8 and 1M) using sol-gel spin coating method. For both single and multilayer films, film with 0.4M is the best candidate to be used as dielectric layer due to its uniformity, non-porous structure and small particle size which is in nanometer dimension. There are enhancement in dielectric constant, capacitance, and surface properties as the MgO is deposited onto ZnO layer which is in multilayer form.

Acknowledgment

The research was carried out at NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering and NANO-Sci Tech Centre (NST), Institute of Science, Universiti Teknologi MARA, Shah Alam, Malaysia.

References

[1] I. -C. Ho, Y. Xu, and J. D. Mackenzie, "Electrical and Optical Properties of MgO Thin Film Prepared by Sol-Gel Technique," Journal of Sol-Gel Science and Technology, vol. 9, pp. 295-301, 1997.

[2] D. -Y. S. and K. -N. Kim, "Electrical and optical properties of MgO films deposited on soda lime glass by a sol-gel process using magnesium acetate," Journal of Ceramic Processing Research vol. 10, pp. 536-540, 2009.

[3] C. Bondoux, P. Prené, P. Belleville, F. Guillet, S. Lambert, B. Minot, and R. Jérisian, "Sol-gel MgO thin films for insulation on SiC," Materials Science in Semiconductor Processing, vol. 7, pp. 249-252, 2004.

[4] E. Miranda, E. O'Connor, G. Hughes, P. Casey, K. Cherkaoui, S. Monaghan, R. Long, D. O'Connell, and P. K. Hurley, "Soft breakdown in MgO dielectric layers," in Reliability Physics Symposium, 2009 IEEE International, pp. 688-691, 2009.

[5] Z. K. Mohamad Hafiz Mamat, Musa Mohamed Zahidi, and Mohamad Rusop, "Performance of an ultrviolet photoconductive sensor using well-aligned aluminium-doped zinc-oxide nanorod arrays in an air and oxygen environment " Japanese Journal of Applied Physic, vol. 50, 2011.

[6] K. B. K. and P. Raji, "Synthesis and characterization of nano zinc oxide by sol-gel spin coating," Recent Research in Science and Technology vol. 3, 2011.

[7] M. Soosen Samuel, J. Koshy, A. Chandran, and K. C. George, "Dielectric behavior and transport properties of ZnO nanorods," Physica B: Condensed Matter, vol. 406, pp. 3023-3029.

[8] N. T. Salim, K. C. Aw, W. Gao, and B. E. Wright, "ZnO as dielectric for optically transparent non-volatile memory," Thin Solid Films, vol. 518, pp. 362-365, 2009.

[9] Z. -Y. Wang, L. -Z. Hu, J. Zhao, H. -Q. Zhang, and Z. -J. Wang, "The fabrication of ZnO/MgO multilayer films on Si (1 1 1) by PLD," Vacuum, vol. 80, pp. 977-980, 2006.

[10] G. N. Panin, A. N. Baranov, Y. J. Oh, T. W. Kang, and T. W. Kim, "Effect of thermal annealing on the structural and the optical properties of ZnO/MgO nanostructures," Journal of Crystal Growth, vol. 279, pp. 494-500, 2005.

[11] A. M. E. Raj, M. Jayachandran, and C. Sanjeeviraja, "Fabrication techniques and material properties of dielectric MgO thin films--A status review," CIRP Journal of Manufacturing Science and Technology, vol. 2, pp. 92-113.

[12] D. CÃ¡ceres, I. Colera, I. Vergara, R. GonzÃ¡lez, and E. RomÃ¡n, "Characterization of MgO thin films grown by rf-sputtering," Vacuum, vol. 67, pp. 577-581, 2002.

[13] S. M. K. and Jun Bin Ko, "Preparation and electric characteristics of MgO films deosited by plasma-enhanced chemical vapor deposition," Ceramic Processing Research, vol. 10, 2009.

[14] B. Sonawane, M. Bhole, and D. Patil, "Structural, optical and electrical properties of post annealed Mg doped ZnO films for optoelectronics applications," Optical and Quantum Electronics, vol. 41, pp. 17-26, 2009.

[15] F. S. Vijay, K. Varadan, and Vasundara V. Varadan "Voltage tunable dielectric ceramics which exibit low dielectric constants and applications thereof to antenna structure." vol. 5,557,286 US: The Penn State Research Foundation, 1996.

[16] P. Shin-Puu Jeng and Tex, "Porous insulator for line-to-line capacitance reduction." vol. 5,548,159 US: Texas Instrument Incoperated, Dalias, Tex, 1996.

[17] B. E. Gnade, Cho, Chih-Chen, Smith, and Douglas M, "Porous composites as a low dielectric constant material for electronics applications." vol. 5,561,318 Us: Texas Instruments Incorporated, 1996.

[18] L. N. I. Habibah Zulkefle, Raudah Abu Bakar, and Mohamad Rusop, "Molarity effect on the structural properties of Nano-MgO thin films," Advance Materials Research, vol. 403-408, 2011.

[19] M. Soosen Samuel, J. Koshy, A. Chandran, and K. C. George, "Electrical charge transport and dielectric response in ZnO nanotubes," Current Applied Physics, vol. 11, pp. 1094-1099.

[20] M. K. Gupta, N. Sinha, B. K. Singh, N. Singh, K. Kumar, and B. Kumar, "Piezoelectric, dielectric, optical and electrical characterization of solution grown flower-like ZnO nanocrystal," Materials Letters, vol. 63, pp. 1910-1913, 2009.

[21] Z. -X. Tang and L. -E. Shi, "Preparation of nano-MgO using ultrasonic method and its characteristics," EclÃ©tica QuÃ-mica, vol. 33, pp. 15-20, 2008.

[22] W. C. Wei Chen, Liang Zhang, Guozhong Wang, and Lide Zhang, "Sonochemical processes and formation of gold nanoparticles within pores of mesoporous silica " Journal of Colloid and Interface Science, vol. 238, 2001.

Habibah Zulkefle was born in Perak, Malaysia in 1987. She received Bachelor Degree (Hons) in Electrical Engineering from Universiti Teknologi MARA, UiTM Shah Alam, Malaysia in 2010. Cureently she in pursuing her study at Ph.D level in Electrical Engineering at NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering, UiTM. Her area of interests includes device fabrication, and nanotechnology.

Lyly Nyl Ismail received her Bachelor Degree in Electrical Engineering at UiTM, Malaysia. She obtained her Master Degree in Microelectronic from Universiti Kebangsaan Malaysia, UKM. She is lecture of Electrical Engineering Department and currently continues her study in Ph.D level at NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering, UiTM, Malaysia.

Raudah Abu Bakar was born in January 1981 at Johor, Malaysia. She received her Master Degree in Electrical Engineering from UiTM and Bachelor Degree in Electronics from University of Surrey, United Kingdom. She is Electrical Engineering lecturer at UiTM Shah Alam, Malaysia. Her areas of interest are MMIC, nanotechnology and device fabrication.

Mohamad Hafiz Mamat received his Master Degree in Electrical Engineering (Nanoelectronics) from Universiti Teknologi MARA (UiTM), Malaysia in 2010. He received his bachelor degree in Electrical & Electronic Engineering and Information Engineering from Nagoya University, Japan in 2005. Currently, he is doing his Ph.D. at NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering, UiTM, Malaysia. His research interests range over metal oxide semiconductors, nanotechnology and nanodevices.

Mohamad Rusop Mahmood obtained his Ph. D in Opto-Electronic Devices and Nanotechnology in year 2003. Currently he is an Associate Professor in the department of Electrical Engineering, UiTM, Shah Alam. He is also a head of NANO-ElecTronic Centre (NET) and NANO-Sci Tech Centre (NST) of Universiti Teknologi MARA, UiTM.