THE CHARACTERIZATION OF TiO_2 AND ZnO THIN FILMS BY SPIN COATING TECHNIQUE VIA SOL-GEL METHOD

Nay Myo Tun[1], Hnin Nandar Shwe[2], Thin Thin Naing[3],
Thet Naing[4] and Khin Mya Mya Soe[5]

Abstract

Nowadays, the nano-materials have gained great interest all over the world due to high their surface area to mass or volume ratios. In the present study, Titanium Dioxide (TiO_2) and Zinc Oxide (ZnO) thin films were investigated. Zinc acetate dehydrate , potassium hydroxide, methanol (CH_3OH), Titanium isopropoxide and 2- methoxy ethanol were used as the starting materials for Titanium Dioxide (TiO_2) and Zinc Oxide (ZnO) sol-gel to enhance the thin films. Non-electrolytic glass was also used as the substrate for both thin films. Spin coating technique was mainly applied for fabrication of the TiO_2 and ZnO thin films. X-ray Diffraction (XRD) analysis was used to compare the characterization of the crystal nature and crystallite sizes of those obtained thin films. Scanning Electron Microscopy (SEM) analysis was also mentioned to monitor the morphology of both thin films. LCR meter was finally used to characterize the electrical properties of TiO_2 and ZnO thin films.

Keywords: Sol-gel, Spin coating, X-Ray Diffraction, Scanning Electron Microscopy (SEM), LCR meter

Introduction

Nanotechnology is the branch of engineering which deals with design and manufacture of extremely small electronic circuits and mechanic devices built at the molecular levels of matters. It enables the ability to build a molecular system with atom by atom reproducing multiple variety nanomachines. Recently, nanocrystalline powder with uniform size and shape have been shown interesting properties of them. They are already having a significant commercial impact, which will assuredly increase in the future. Furthermore, ZnO and TiO_2 with its good electrical and optical properties which can be used in many applications such as photoconductors, integrated sensors and transparent conducting oxides electrodes. Here one looks at the photo-degradation of hydrocarbons either in water or in air using suspended small particles or thin films of TiO_2 and ZnO.

In this research, the comparison of the electrical characterization of TiO_2 and ZnO thin films were presented by Sol-gel method. The advantages of using Sol-gel processing methods are low synthesis temperature, high purity, novel materials and low capital costs [Xia and et al]. X-ray diffraction (XRD) was used for the structural nature of TiO_2 and ZnO thin films and scanning electron microscopy (SEM) was also used for the morphology of thin films. LCR meter measurement was performed for their electrical characteristics such as dielectric constant with various frequencies.

Theory Background of TiO2 and ZnO particles and thin films

TiO_2 thin films for photo catalytic application has several naturally occurring modifications, the most common ones being Rutile, Anatase and Brookite. Most research with respect to photocatalysis is performed using Anatase, while in all other aspects Rutile has been much more thoroughly characterized. This is mostly due to the preparation methods: while it is easier to obtain Anatase than Rutile at low temperatures below 600 °C, it is impossible to obtain

anything but Rutile at temperatures above 800 °C, the transition temperature to the thermodynamically most stable phase rutile. While TiO_2 powders or films obtained at low temperatures are finely grained (nanocrystalline) because little grain growth can occur, grain growth at temperatures above 800°C can be substantial. Therefore, depending on the preparation method, the nature of the TiO_2 particle or film surface, as well as the active surface area are usually very different for Anatase and Rutile powders and thin films.

Zinc Oxide is an also important, inexpensive, versatile n-type semiconducting material with wide direct energy band gap of 3.37 eV and large exciton binding energy of about 60 MeV at room temperature. ZnO has unique structural, optical and electrical properties. Due to its high trans parent conducting properties, it has many potential applications like light emission display devices, piezoelectric transducers, surface acoustic devices and optoelectronic devices. Various deposition techniques were employed for the preparation of ZnO thin films such as magnetron sputtering, spray pyrolysis, pulsed laser deposition, electron beam evaporation and sol-gel method.

In this work, TiO_2 and ZnO films were prepared by an inexpensive sol-gel spin coating technique and were also studied the effect of electrical characterization as dielectric properties on their structural nature.

Experimental Details for TiO_2 and ZnO thin films

Titanium–isopropoxide (TTIP) and 2-methoxy ethanol with the weight percent of 1:2 were used as the starting chemical materials for TiO_2 sol-gel to perform the TiO_2 thin film. These two materials were mixed together in a closed-beaker by using the magnetic stirrer with vigorous speed at 45 °C to get the homogeneous solution. During the stirring process, some drops of acetic acid were used again to make the transparent solution. In order to control the viscosity of the solution, De-ionized water was used. The obtained sol-gel of TTIP and 2-methoxyethanol was carried on as desired chemical materials to develop the TiO_2 thin film by using spin-coating method. Non-electrolytic-glass was taken as a substrate of the thin film. Before making the spin coating technique, the substrate must be etched with acetone and DI water for releasing the contaminations.

To investigate the ZnO thin films, 15 g of KOH and 45 ml of methanol (1:3) were mixed into the covered-beaker with under constant stirring at the desired temperature of 60 ℃ about 10 min to get the homogeneous solution (1) with transparent colour. Simultaneously 15 g of ZnAc and 45 ml of methanol (1:3) were mixed again into the covered-beaker with under constant stirring at the desired temperature of 60 ℃ about 10 min to get the homogeneous solution (2) with transparent colour. The solution (1) and the solution (2) were mixed together into the next covered-beaker with under stirring at the temperature of 60 ℃. After one day, these ZnO sol-gel composites were obtained. Those obtained ZnO sol-gel were used with the spin coating method to performed ZnO thin films and then both TiO_2 and ZnO thin films were calcined by annealing with the temperature of 300 ℃, 400 ℃ and 700 ℃ about 1 hour to perform TiO_2 and ZnO crystallization on both films. The obtained TiO_2 and ZnO thin films were synthesized by XRD and SEM techniques to examine their structures, morphologies and crystallite sizes. The LCR meter also used as the determination of their electrical characterizations as dielectric properties.

Results and Discussion

The ultra fine TiO_2 and ZnO powders were investigated to know the crystalline state of thin films by calcining the TiP/ 2 Methoxyethanol sol-gel at 400 ºC and 700 ºC and ZnO sol-gel at 300 ºC and 400 ºC. The crystallite diameters '*D'* were obtained from XRD peaks according to the Debye- Scherrer equation:

$$D = \frac{0.89\,\lambda}{\Delta W \cos\theta}$$

where 'λ' is the wavelength of the incident X-ray beam (1.5405 Å for Cu / K-α1), 'θ' is the Bragg's reflection angle, 'ΔW' is the width of X- ray pattern line at peak half peak height in radians. According to the XRD results that all particles possessed polycrystalline nature of tetragonal structures from planes: (101), (004), (200), (211), (213) for TiO_2 and hexagonal wurtzite structures from planes: (100), (101), (102), (110), (103) for ZnO. The average particles sizes were 8.42 nm at 400 ^oC and 36.20 nm at 700^oC for TiO_2 thin films and 27 nm at 300 ºC and 25 nm at 400 ºC for ZnO thin films. The size distribution was not in homogenous and the crystal quality was not in optimum condition because of uncontrolled of the ambient conditions for both films. The average thickness of the TiO_2 thin films for both temperatures was about 595 nm and 714 nm for ZnO thin films as shown in figures (9-12).

In order to realize the electrical characterization such as dielectric properties should be performed on TiO_2 and ZnO thin films. Using Digital impedence Analyzer (insteak: 8110G LCR Meter), the dielectric properties of TiO_2 and ZnO thin films were measured over the frequency range between 100 Hz to 100 kHz. The dielectric constant and dissipation factor were calculated by the following equations as; $\varepsilon_r = \frac{C\,d}{\varepsilon_0\,A}$; $tan\delta = \frac{D}{\varepsilon_r}$ where 'ε_r' is dielectric constant, 'C' is capacitance measured, 'd' is the thickness of the film, 'A' is the area of the top electrode, 'D' is dielectric loss and '$tan\delta$' is dissipation factor. The change in capacitance and dissipation factor with various frequencies at temperatures of 400 ^oC and 700 ^oC for TiO_2 and 300 ^oC and 400 ^oC for ZnO thin films were presented in Tables (1, 2, 3, and 4).

As the results, when the low frequency (<100 Hz) was applied to the TiO_2 thin films, the change in capacitance and dielectric loss were not detected in TiO_2 thin films by the Digital impedence Analyzer (insteak: 8110G LCR Meter). This is due to the properties of the highly response of photons in TiO_2 which can't detect in low energy or frequencies. However, when the high frequency (>1 kHz) was applied to the TiO_2 thin films, the change in dielectric constant and capacitance were found to be decreased as shown in Figures (13-16). Moreover, the dissipation factor was also decreased with various frequencies at different temperatures. In contrary, the change in capacitance and dielectric loss were detected in ZnO thin films under 100 Hz frequency range. But, the change in dielectric constant and capacitance were found to be decreased as the same as TiO_2 thin films shown in Figures (17– 20). Especially, the higher dielectric constants were found to be in ZnO thin film compared than in TiO_2 thin films. In addition, when the frequencies ranges >10 kHz were applied to TiO_2 thin films, they would well response and maintain the electrical charges as shown in Tables 1 and 2. However, when the frequencies ranges >10 kHz was applied to ZnO films, they were not response and maintain the electrical charges as TiO_2 thin films. This is because of the optical properties of ZnO particles, most of the molecules cannot retain the charges in high frequencies ranges. Therefore the optimum frequencies ranges for electrical properties for TiO_2 films were about >10 kHz and

<100Hz for ZnO thin films. They can be used as high speed digital, high power gain and low noise performances for the micro and nanoelectronics devices.

Table 1 The values of capacitance, dielectric loss, dielectric constant and dissipation factor with various frequencies for TiO_2 thin film at 400 ºC

Frequency (kHz)	Capacitance 'C_P' (pF)	Dielectric Loss (D)	Dielectric Constant (ε_r)	Dissipation factor (tan δ)
1	125.54	0.09	15.06	6.38×10^{-3}
10	111.85	0.05	13.42	3.84×10^{-3}
20	109.32	0.04	13.11	3.25×10^{-3}
50	107.71	0.03	12.92	2.49×10^{-3}
100	106.27	0.04	12.75	2.75×10^{-3}

Table 2 The values of capacitance, dielectric loss, dielectric constant and dissipation factor with various frequencies for TiO_2 thin film 700 ºC

Frequency (kHz)	Capacitance 'C_P' (pF)	Dielectric Loss (D)	Dielectric Constant (ε_r)	Dissipation factor (tan δ)
1	257.52	0.28	30.89	9.13×10^{-3}
10	158.90	0.21	19.06	11.14×10^{-3}
20	157.88	0.18	18.94	9.47×10^{-3}
50	136.35	0.14	16.36	8.47×10^{-3}
100	134.40	0.12	16.13	7.43×10^{-3}

Table 3 The values of capacitance, dielectric loss, dielectric constant and dissipation factor with various frequencies for ZnO thin film 300ºC

Frequency (Hz)	Capacitance 'C_P' (pF)	Dielectric Loss (D)	Dielectric Constant (ε_r)	Dissipation factor (tan δ)
1	994	10.90	78.25	0.14
100	372	7.03	9.93	0.71
1000	107	4.31	2.84	1.52
10000	0.98	0.49	0.03	18.84
100000	0.69	0.18	0.02	9.44

Table 4 The values of capacitance, dielectric loss, dielectric constant and dissipation factor with various frequencies for ZnO thin film 400 ºC

Frequency (Hz)	Capacitance 'C_P' (pF)	Dielectric Loss (D)	Dielectric Constant (ε_r)	Dissipation factor (tan δ)
1	790	15.12	21.05	0.71
100	535	12.75	14.26	0.89
1000	477	5.23	12.69	0.41
10000	1.78	1.14	0.05	23.97
100000	0.65	0.29	0.02	16.72

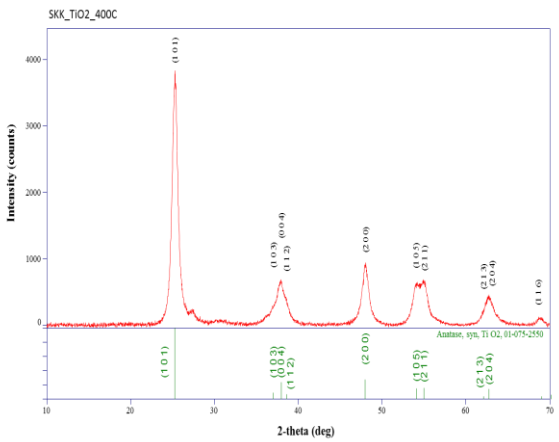

Fig (1)

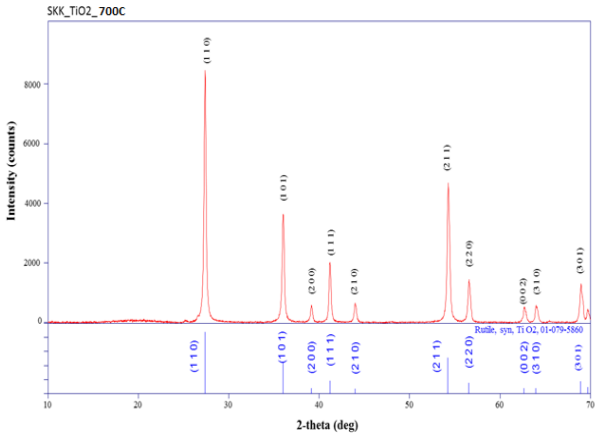

Fig (2)

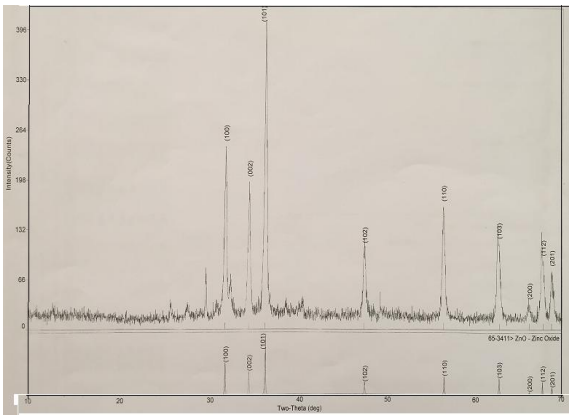

Fig (3)

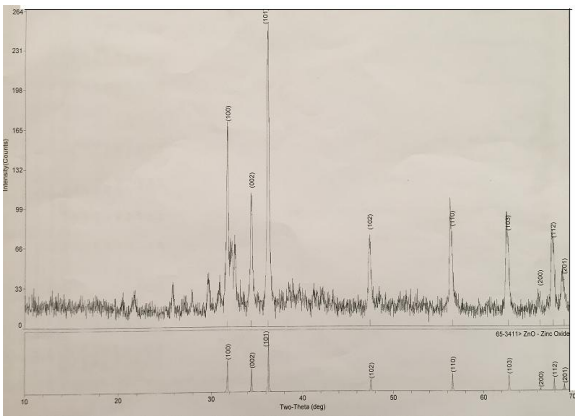

Fig (4)

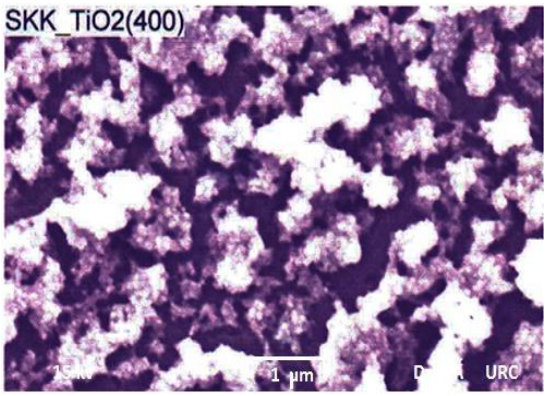

Fig (5)

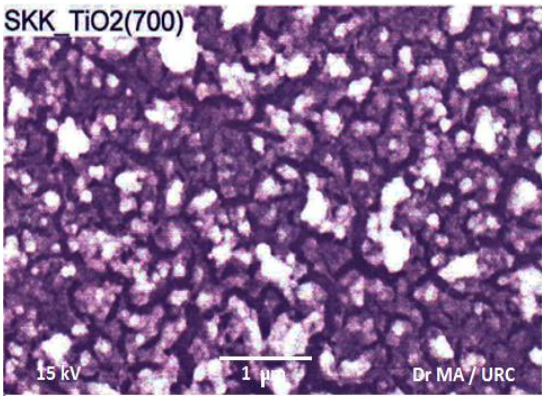

Fig (6)

Figure 1 XRD spectrum of TiO_2 particles at 400 ° C, Figure 2. XRD spectrum of TiO_2 particles at 700 ° C, Figure 3. XRD spectrum of ZnO particles at 300 °C, Figure 4. XRD spectrum of ZnO at 400 °C, Figure 5. The Photograph of SEM for TiO_2 particles on the TiO_2 thin flim at 400 °C, and Figure 6. The Photograph of SEM for TiO_2 particles on the TiO_2 thin flim at 700 °C

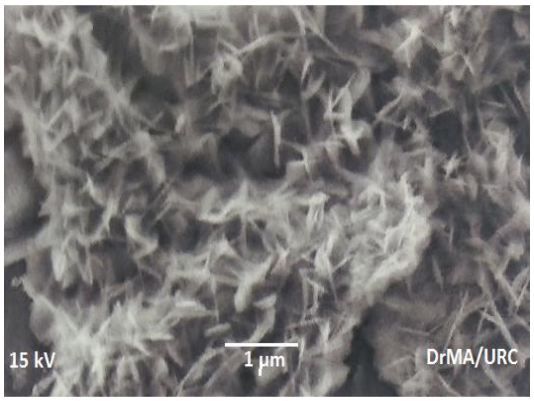

Fig (7)

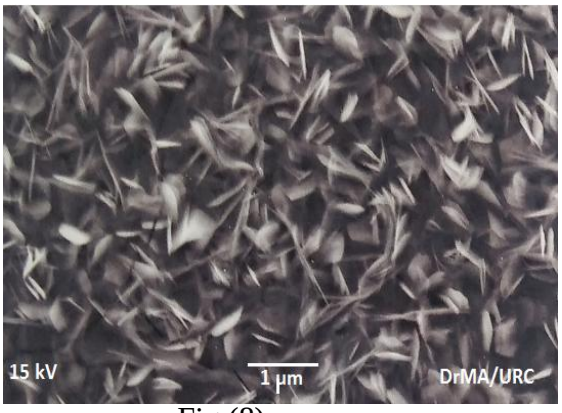

Fig (8)

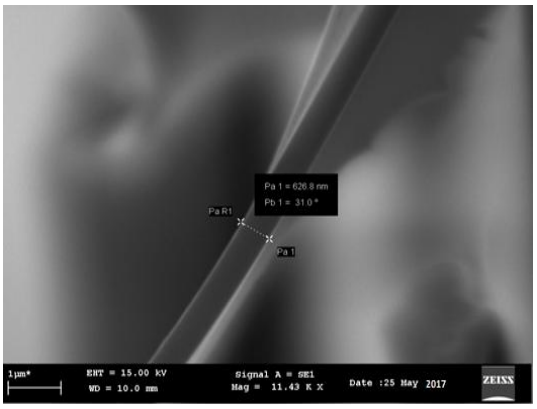

Fig (9)

Fig (10)

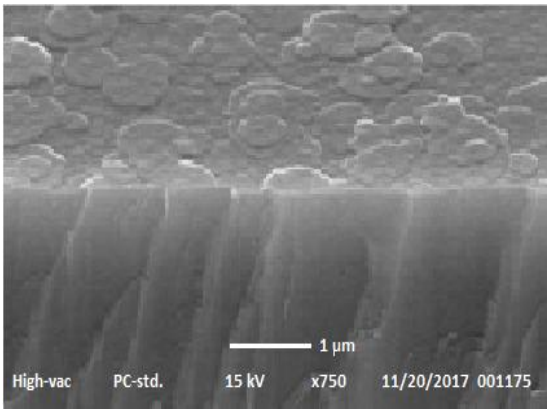

Fig (11)

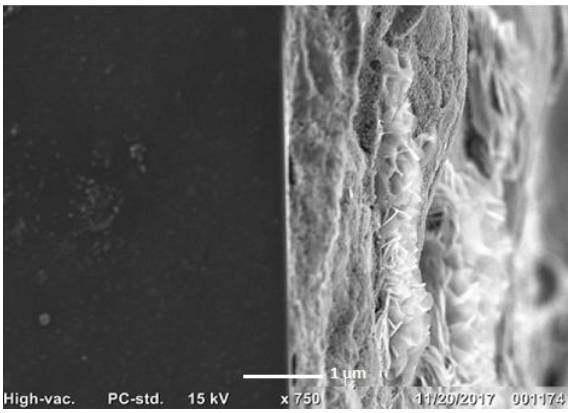

Fig (12)

Figure 7 SEM image of ZnO particles on the ZnO thin flim at 300 ºC, Figure 8. SEM image of ZnO particles on the ZnO thin flim at 400 ºC, Figure 9. SEM image of thickness measurement for TiO_2 thin film at 400 °C, Figure 10. SEM image of thickness measurement for TiO_2 thin film at 700 °C, Figure 11. SEM image of thickness measurement for ZnO thin film at 300 ℃, and Figure 12. SEM image of thickness measurement for ZnO thin film at 400 ℃

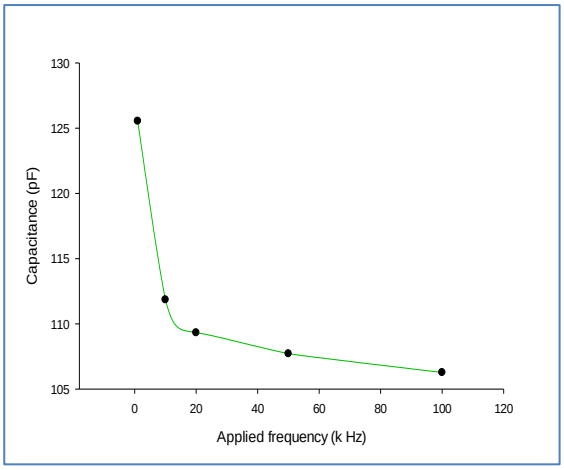

Fig (13)

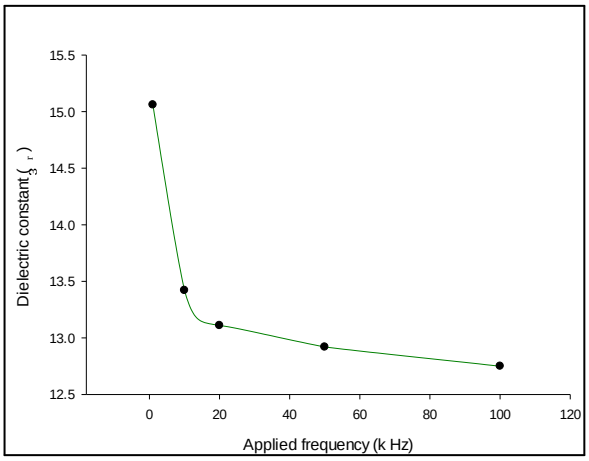

Fig (14)

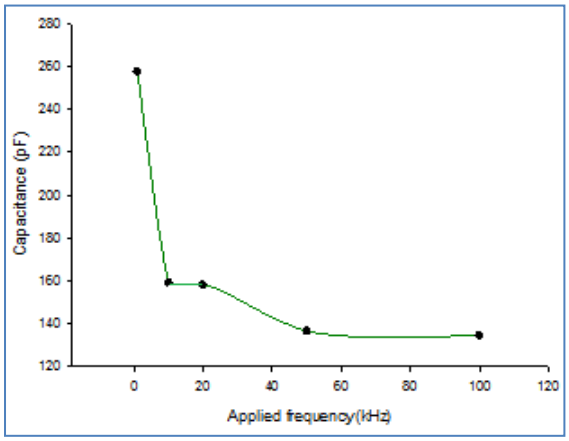

Fig (15)

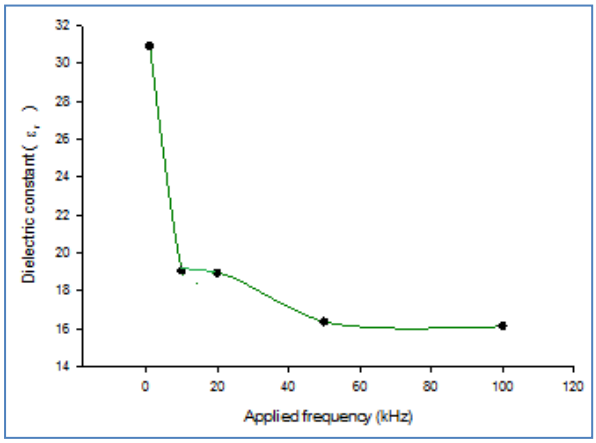

Fig (16)

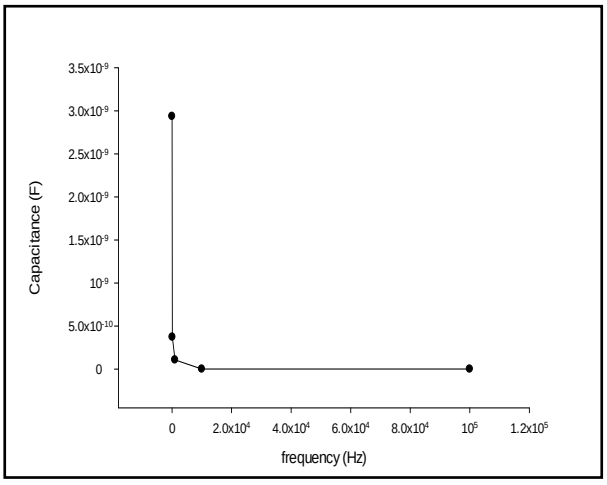

Figure (17)

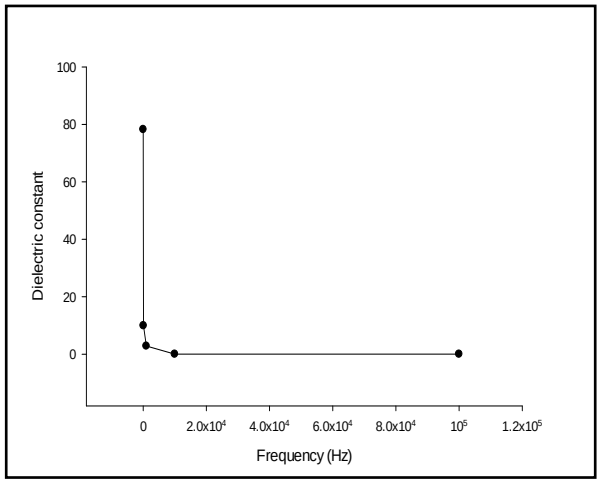

Figure (18)

Figure 13 The variation of Capacitance with applied frequencies at 400 ºC for TiO_2 thin film, Figure 14. The variation of Dielectric constant with applied frequencies at 400 ºC for TiO_2 thin film, Figure 15. The variation of Capacitance with applied frequencies at 700˚C for TiO_2 thin film, Figure 16. The variation of Dielectric constant with applied frequencies at 700 ºC for TiO_2 thin film and Figure 17. The variation of Capacitance with applied frequencies at 300˚C for TiO_2 thin film, Figure 18. The variation of dielectric constant with applied frequencies at 300 ºC for ZnO thin film

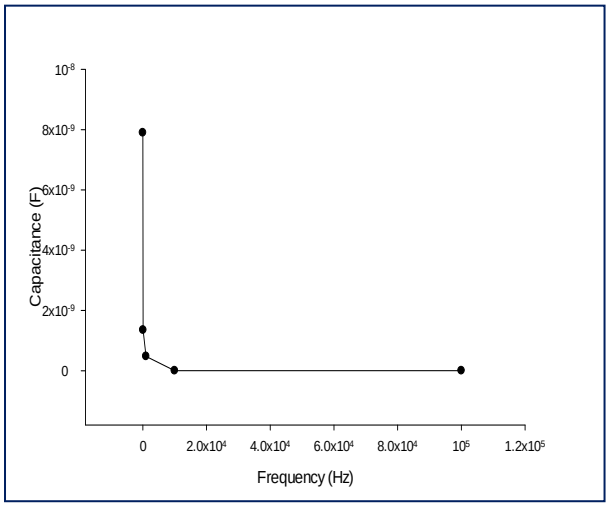

Figure 19 The variation of capacitance with applied frequencies at 400 ºC for ZnO thin film

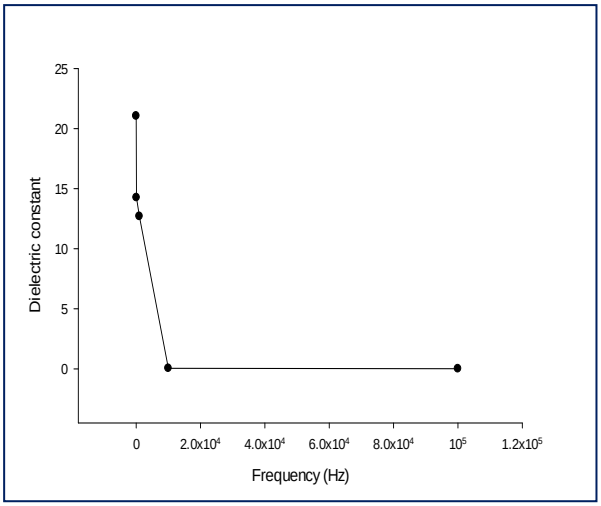

Figure 20 The variation of dielectric constant with applied frequencies at 400 ºC for ZnO thin film

Conclusion

Zinc acetate dehydrate , potassium hydroxide, methanol (CH_3OH), Titanium isopropoxide and 2- methoxy ethanol were used as the starting materials for Titanium Dioxide (TiO_2) and Zinc Oxide (ZnO) sol-gel to enhance the thin films via spin coating method. Non-electrolytic glass was also used as the substrate for both thin films. The average particles sizes were calculated by Debye's Scherrer equation as 8.42 nm at 400 ^oC and 36.20 nm at 700 ^oC for TiO_2 thin films and 27 nm at 300 ºC and 25 nm at 400 ºC for ZnO thin films. The size distribution was not in homogenous and the crystal quality was not in optimum condition because of un-controlling the ambient conditions for both films. As the SEM results, the average thickness of the TiO_2 thin films for both temperatures was about 595 nm and 714 nm for ZnO thin films.

In order to realize the electrical characterization, the dielectric properties should be performed on TiO_2 and ZnO thin films by using Digital impedence Analyzer (insteak: 8110G LCR Meter). As the results, when the low frequency (<100 Hz) was applied to the TiO_2 thin films, the change in capacitance and dielectric loss were not detected in TiO_2 thin films by the Digital impedence Analyzer. When the high frequency (>1 kHz) was applied to the TiO_2 thin films, the change in dielectric constant and capacitance were found to be decreased. In contrary, the change in capacitance and dielectric loss were detected in ZnO thin films under 100 Hz frequency range. But, the change in dielectric constant and capacitance were found to be decreased as the same as TiO_2 thin films. Especially, the higher dielectric constants were found to be in ZnO thin film compared than in TiO_2 thin films. However, when the frequencies ranges >10 kHz was applied to ZnO films; they were not response and maintain the electrical charges as TiO_2 thin films. Therefore the optimum frequencies ranges for electrical properties for TiO_2 films were about >10 kHz and <100Hz for ZnO thin films. They can be used as high speed digital, high power gain and low noise performances for the micro and nano electronics devices.

Acknowledgements

I would like to thank to Professor Dr Kyaw Lwin Oo, Principle, Technological University (Sittwe) for his kindly permission to carry out this research. I also would like to thank to Professor Dr Khin Mya Mya Soe, Head of Department of Physics, East Yangon University, for her valuable advice to do this research. I also would like to thank to Professor Dr Thet Naing, Department of Physics, East Yangon University, for his warmly discussion to complete this research. Finally, I would like to thank to all of the stuffs in Technological University (Sittwe), Physics Department, East Yangon University and all my family for supporting to complete this research.

References

Kato H, Sano, Michichiro, Miyamato, Kazuhiro, Yao and Takafumi, (2002), "Growth and Characterization of Ga-doped ZnO layers", Journal of Crystal Growth, 237-239

Noboru I, Ozaki Y, Kasu S and James M, (1992), "Chemical Manufacturing processes, Super fine particle technology" Springer Ver Lag, New York

Ohgaki, Takeshi, Ohashi, Naoki, Sugimura, Shigeaki, Royken, Haruki,

Qin Y, Wang X D, and Wang Z L, (2008), "Microfiber – Nanowire Hybrid Structure for Energy Scavenging Nature", 451, 809-813

Sima M, EnculescuI,SimaM,Enache M, Vaslile E, and Ansermet J P, (2007),Phys Status Solid B, 244, 1522

Sun JH, Dong SY, Wang YK, and Sun SP, (2009), J Hazardous Mat, 172 1520