THE EFFECT OF NANO ZnO MORPHOLOGY ON STRUCTURE, DIELECTRIC CONSTANT, AND DISSIPATION FACTOR OF CA-NANO ZnO/ITO FILMS

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ABSTRACT

It has been studied ZnO morphological difference on the microstructure and the dielectricity of CA-ZnO /ITO composite films. The morphology of nanoparticles and nanorods of ZnO were analyzed in more detail concerning its microstructure and dielectric properties. It revealed that the change of ZnO morphology from nanoparticles to nanorod increase the capacitance and dielectric constant significantly from the order of the nano to the micro and decrease the dielectric loss. The dielectric constant of CA-ZnONP/ITO and CA-ZnONR/ITO are 2569 and 97159 at 100 Hz, respectively. The capacitance and dielectric loss of CA-ZnONP/ITO and CA-ZnONR/ITO are successively 69.809 nF; 678 and 2.15765 µF; 13,23

Keywords: Cellulose Acetate; ZnO; Nanoparticles; Nanorod; Dielectric Constant; Dissipation Factor.

Introduction

The dielectric material is an electrostatic energy storage.[1,2] This energy store is applied to electronic and electric power system.[3] In general, electronic materials could be obtained from inorganic materials such as mica,[4] silicon oxides, graphene oxides[5,6] and ceramic.[7] Many polymers have been used widely as dielectric due to some reason as follows. It shows the ease of processing, its flexibility, and also show an excellent resistance from chemical reaction.[8] The origin of dielectric of polymer material may be determined by its molecular orientation, charge distribution, and thermal static from polar group.[8]

In the case of polar polymers, the dielectric constant decreases at a particular frequency. Molecular dipoles cannot break themselves in low temperatures. On the other hand, at high temperatures, there is a thermal expansion resulting in dipole orientation occur. Dipole orientation in the polymer may improve its dielectricity. The dispersion of dielectricity arising at high temperatures shows the movement of molecules from a quasi-stable position to a skeletal bond that includes the confirmation of the primary chain bond arrangement, called the primary dispersion or α-relaxation region. At low temperatures, a dispersion of dielectricity is associated with the dielectric response of the side group and more commonly known as the secondary dispersion or β-relaxation region.

The polymer is basically noncrystalline. In some polymer and at a specific condition it could show a several amorphous as well as crystalline.[10,11] In the amorphous part, the arrangement of molecules is irregular and entangled so that the polymer molecules will be more readily affected by the external field.

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On the other hand, in the crystalline section, the regular molecular arrangement causes the density to be more significant so that the polymer molecules are more difficult to displace, reorientation, or other possible creating the polar dielectric system. The obstruction is assumed as potential energy. When the polymer is heated, the displacement of polymer molecules will be more comfortable. The surface density will also affect the dielectricity. The load carrier gets trapped at the crystalline and amorphous interface which increases the dielectricity at low frequencies.[11] In this work, we focus on the natural polymer of cellulose acetate (CA). From the previous report, the CA/glass film shows a dielectric constant as 35.154 with capacitance as 0.1456 nF.[12]

Another crucial semiconducting material is zinc oxide (ZnO). ZnO is one of actives materials which show excellent potential as a supercapacitor. It has a high energy density 650 Ah/g.[13] ZnO has a uniqueness compare to other materials. It also indicates an optoelectronic properties.[13] ZnO is showing a good range of electronic-optical band gap of 3.2–3.4 eV,[14,16] which is in the optical range.[17] Its excitonic stability reaches up to 60 MeV.[18] Based on its dielectric response as a function of temperature, ZnO film exhibits a polarization mechanism.[18,19] ZnO is showing other exciting feature as inexpensive, simple processing, environmentally friendly, and also excellent of electrochemical properties. Due to its electrochemical and its dielectric properties make it a perfect candidate for supercapacitor elecrodes.[20] The combination of CA-ZnO composite has been reported to have a relatively high dielectric and make it an excellent material as supercapacitor system.[12]

A distortion or other general change of structures and lattice strain could change its dielectric constant. The transformation from one to different dimensional, size as well as its form or physical appearance may change it physical or electronic properties. In this work, we report a two different kind of ZnO, i.e. as nanoparticle and as nanorod on its structures, and electronic properties of CA-ZnO.

Methods

A sample of CA-ZnO nanoparticles (CAZONP) nanocomposite was prepared using precursors of powder cellulose and zinc oxide nanoparticles via simple blending. The zinc oxide nanoparticles (ZONP) have been synthesized using zinc acetate dehydrate precursor. On the other hand, samples of CA-ZnO nanorod (CAZONR) were prepared under a hidrothermal using zinc nitrate: HMT (1:1) precursors. The fabrication of CAZONP and CAZONR composites films we have been treated using a spin coating deposition technique.

Synthesis of cellulose acetate (CA)

The cellulose acetate was obtained from the process as follows. A 10 grams cellulose from water hyacinth extraction and glacial acetic acids were mixed for 1 hour at 40˚C. It continues with pouring sulfuric acid and glacial acetate while stirring for about 40 minutes. This mixture was kept at 18˚C and then add acetate anhydrate acid, sulfuric acid, and glacial acetic acid at 40˚C. The mixture was then hydrolyzed for 15 hours at room temperature. This process was followed by adding a dropwise of DI water until precipitation occurs and successively followed by washing to neutral pH. The precipitate was heated to a temperature of 70 ˚C for 5 hours to obtain a white powder of CA. The obtained CA were put on H_2SO_4 64 wt% at 45 ˚C for 20 minutes and diluted 10 times using aquadest. It was dilluted on H_2SO_4 for fast decreasing the Ph of CA . The mixture was set in centrifuge machine at 4000 rpm followed by heating at 70˚C.

Synthesis of CA-ZnO nanopartcles (CAZONP/ITO) film

The liquid of CAZONP for spin coating method was prepared using CA and zinc acetate dehydrated for 0.5 grams and 0.3 grams, respectively. Both precursors were firstly dissolved using organic solvents of dimethylformamide (DMF): ethanol at a ratio

of 1:2. This process was performed for 2 hours at a temperature of 90 ℃ until transformed into a transparent solution. The next steps were taking about 0.15 mL of the solution then deposited onto ITO/glass substrate using a spin coater. The obtained CAZONP/ITO films were then dried under a temperature of 100℃.

Synthesis CA-ZnO nanorod (CAZONR/ITO) films

The previous CAZONP/ITO films were used as a seeds film for the growth of ZnO nanorods. The nanorods crystals of ZnO were growth using hidrothermal methode. It is because water and temperature is used to growth the ZnO on CAZONR although the low temperature. It was to be effective method. The CAZONP/ITO was immersed in a solvent growth. The solvent growth was previously prepared from a mixture of 30 mM zinc nitrate: HMT with a ratio of 1:1 in 50 mL DI-water. A steady immersion was performed for 6 hours at 90℃. The immersed films were washed to remove residual ingredients and followed by heating at 100 ℃ for 1 hour.

Microstructure Characterization

The microstructure characterization of CAZONP and CAZONR were performed using x-ray diffraction method (X-RD) with Cu-Kα wavelength and scanning electron microscopy (SEM). The observed of diffraction patterns can be analyzed by means of CAZONP and CAZONR dimension, orientation and possible phase change of the compounds. The small shift of lattice parameters or small local distortion due to interface interaction between CA and ZnO can also be evaluated using Cellreff. The phases were identified by Cellreff methods using Zincite model (0005203) from AMCSD and the CA model (4114994.cif) from COD. The morphology and surface were characterized using SEM. Further analyses of SEM image of deep contour profile inform detail porosity due to the morphological change of ZnO by the equation 1.[21]

$$porosity = \frac{V_{total} - V_{solid}}{V_{total}} \qquad (1)$$

Where the V_{total} is volume total of porous and solid of material. and the V_{solid} is the volume of material that is known by integrated surface and depth of materials in pixels using origin. The porosity is the vacancy of material as fractional volume that is analysed by mikrograph of SEM.

Dielectric constant measurement using LCR-meter

The dielectric measurement has been performed using an AC-LCR. The samples were prepared as a film deposited on ITO/glass with using silver paste as an electronic contact. The design of the sample structure under measurement is glass/ITO/CA-ZnO/silver paste as depicted in Figure 1. By using the instrument, capacitance measurement has been done by reading directly on LCR meter. The measurement capacitance was carried out by 30 data per variation of ZnO composition with frequencies at 100 Hz.

Figure 1. Schematic illustration of constant dielectric measurement of CAZO/ITO using LCR meter

The obtained data are capacitance (C), dissipation factor (tan δ) with various frequency. The data is then processed using equation 2 to achieve the real dielectric constant (ε_r or ε'). Equation 3 was used to find the imaginary and real dielectric constants.[22]

$$\varepsilon_r = \frac{C.d}{\varepsilon_o.A} \qquad (2)$$

$$\tan \delta = \frac{\varepsilon'}{\varepsilon''} \qquad (3)$$

Where ε_r or ε' is a real dielectric constant, C is capacitance (F), d is sample thickness (m), A

is sample area (m^2), ε_o is permittivity in vacum (8.854 x 10^{-12} C^2/N m^2).

Results and Discussion

Microstructure of CAZO film

Microstructural materials include crystallographic and morphological structures can be obtained through the characterization of XRD and SEM. CA as the matrix has a higher concentration than ZnO which is 0.5 gram compared to 0.3 gram respectively. The CA-ZnO thin film composite looks transparently close to white and seems shiny in the presence of a depleted ZnO nanoparticle. The physical appearance of a material can not be used as a measure that composite material has been formed. More accurate measurements for the identification of CA-ZnO composite materials can be demonstrated with crystallographic and morphological parameters of a specific magnification.

We can obtain the crystallographic parameters of CAZONP and CAZONR composite films by implementing diffraction pattern analysis[21]. The main crystal parameters which could be obtained are lattice parameters a, b, c, α, β, γ and unit cell volume. The CAZONP diffraction pattern is identified as two phases. This means that the CAZO material is a composite material. The lattice parameters of CA are expressed in a, b, c of 7.784, 8.201, 10.30 Å with respectively α, β, γ and volume respectively 90º, 90º, 96.55º and 658.30 Å^3. ZONP phase is shown by only one peak appears with a

preferred orientation direction of (010). The lattice parameters of ZONP are denoted by a = b, c of 3.2494, 5.2038 Å and α = β, γ and the subsequent volume is 90º, 120º, and 47.58 Å^3. The crystal parameter was obtained from phase and structure analysis using Cellref. The principle of this analysis is the matching model of each phases that are Zincite model (0005203) from AMCSD and the CA model (4114994.cif) from COD. with CAZO composite data. The crystal system of CA and ZnO are monoclinic (P 2 c) and hexagonal (P 6$_3$ m c), respectively.

The growth of ZONR in CAZO composites affects the diffraction pattern in which ZnO peaks appear in higher numbers. It also seems that the crystallinity of ZnO increases with the growth of ZnO nanorod. The orientation of ZnO changed to (011) after ZnO was grown to ZnO nanorod. This crystal orientation supports the growing direction of ZnO nanorod in the morphology of the SEM results. The CA-ZnONR composite also has two phases: CA and ZnO. The change of lattice parameters in CAZONP and CAZONR of both phases is shown in Table 1. Table 1 shows the decrease in unit cell volume of CAZONR.

The morphology observed by the SEM image shows that the porosity of CA in this composite is highly dominated in CAZONP composite films as shown in Figure 3. The color scale indicate the highest or the thickness of the sample on film substrate. The light blue color scale indicates the lowest depth. The blue scale shows 8,200.
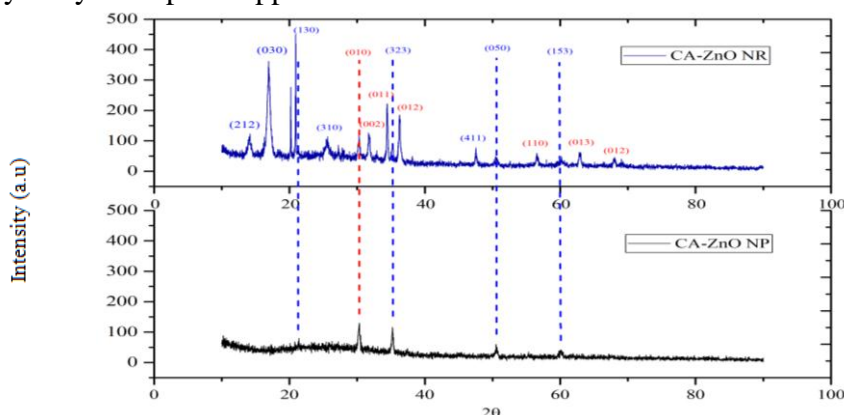

Figure 2. XRD Pattern of CAZONP and CAZONR films. The CA and ZnO phases appear in the diffraction pattern. Blue and red colored curves represent each phase.

Table 1. Lattice parameters of ZnO in CAZONP and CAZONR

parameters	CAZONP		CAZONR	
	CA	ZnONP	CA	ZnONR
a (Å)	7.7840	3.2494	7.7904	3.2467
b (Å)	8.2010	3.2494	8.2015	3.2467
c (Å)	10.3000	50.238	10.3675	5.2105
$\alpha = \beta$ (°)	90	90	90	90
γ (°)	96.55	120	96.47	120
system	monoclinic	hexagonal	monoclinic	hexagonal
Space grup	P 2 C	P 6_3 M C	P 2 C	P 6_3 M C

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The lowest color scales indicate the lowest level of the surface to the substrate. On the other hand, the highest color scales show the most top surface of the sample from the substrate. The highest color is greenlight 65,600. The data of highest and lowest color as z, and the axis and basis on the color scale picture as long and width. The three parameter can be obtained to calculate the volume total. the volume total is 3,280,000. The volume solid is known by 2D integrate using Origin. The volume solid is 1,839,878.3145632. The fraction of it using equation 1, the porosity of CAZO is 0.680.

The color scale from low to high indicates the difference in sample height from the surface of the substrate. The existence of the height difference shows the appearance of porosity macroscopically on CA-ZnONP material. The CA-ZnONR composite has a larger surface area which is indicated by the presence of a nanorod grown within the CA and surfaces to the CA surface. The porosity of CA is reduced, but CAZONR composite surface is increasingly widespread in the presence of Nanorod. It is indicated by the lowest color scale (dark blue) showing an altitude of zero. The scale was then calibrated to actual height. The highest color is 32,800 based on Fig.3b. The total volume is 3,280,000. As function as the preview discuss, the volume solid is 1,124,733.7178608. Based on that, the porosity of CA-ZONR is 0.657. The CA-ZONR morphology is shown in Figure 4.
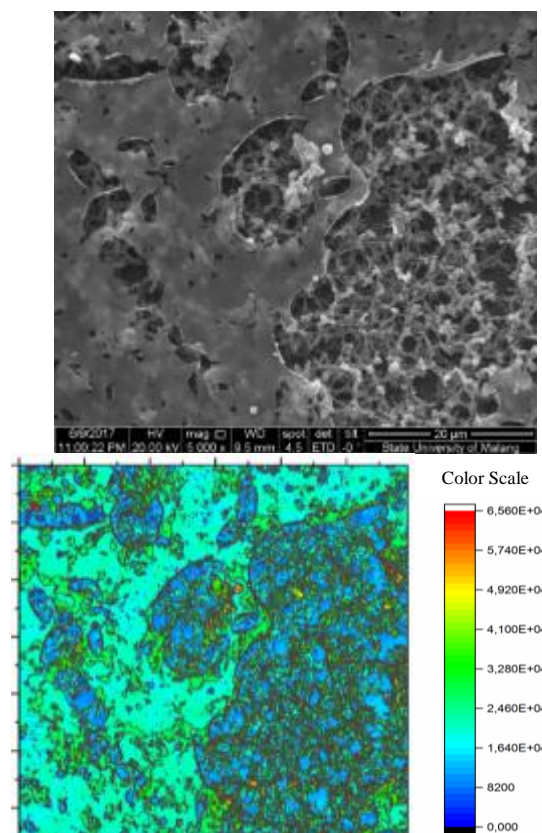

Figure 3. The morphology of CA-ZnONP with the distribution of porosity shown by the color scale.
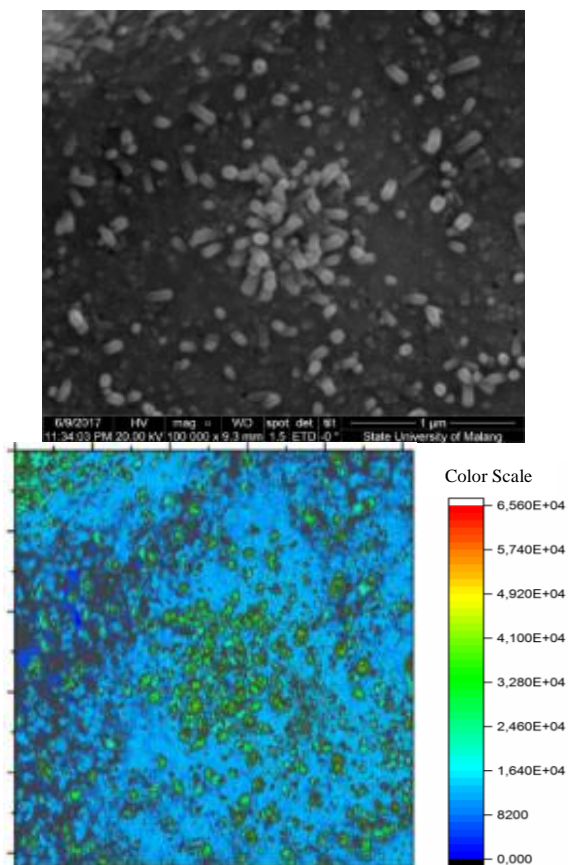
Figure 4. CAZONR morphology with ZnO nanorod distribution indicated by a color scale. The green color shows the height of the nanorod from the surface of the substrate.

The morphology of SEM results shows that the porosity of CA in this composite is predominantly in CA-ZnONP composite films as shown in Fig. 3. a Similar to ZONR, the light blue color scale indicates the lowest depth. The blue level shows a height of 26.5 μm. The color scale from low to high notes the difference in sample height from the surface of the substrate. The existence of the height difference shows the appearance of porosity macroscopically on CAZONP material. From this analysis, it is found that the CA-ZnONR composite has a larger surface area indicated by the presence of a nanorod grown within the CA and surfaces to the CA. The composite porosity reduce but CA-ZnONR surface is increasingly high in the presence of nanorod. This is indicated by the lowest color scale with dark blue which is equivalent to 8200 depth. The scale then converts to real height, so that the lowest depth of ZONR is 13.025 μm. The surface

morphology image of CAZONR is shown in Figure 4. The more significant CAZONP porosity is shown by the number of color differences in the contour shown in Fig. 3 compared with CAZONR.

It is known that porosity affects physical properties such as dielectric loss and dielectric constant. The solid material has tan δ close to zero.[23] Therefore, if the material is porous, then tan δ will have a significant value. This relationship is shown by Equation 3.

$$\tan \delta = \tan \delta_0 + AP^n \qquad (3)$$

Where tan δ is the dielectric loss, A and n are constants with values of 1.298×10^{-2} and 1.73 respectively. Tan δ_0 represents a tangent of dielectric loss in solid material. While P express the porosity.

The dielectric constant of CAZnO composite film

The dielectric constant was generated from capacitance LCR-meter measurements. From the LCR meter measurement will obtained information of capacitance and dissipation factor. The other physical parameters of the dielectric properties can be obtained from calculations using Equations 1, 2 and 3. The frequency relation curves to the CAZONP and CAZONR capacitances show the most appropriate frequency to produce high capacitance in this composite material. A material has a characteristic frequency that indicates the polarization contribution and the optimum capacitance possessed by the material.

Figure 5 shows that the 120 Hz frequency produces the highest capacitance of about 69809.23 pF (about 69.80923 nF). On the other hand, the dissipation factor (tan δ) indicates its relation to the capacitance. A material having high capacitance then low dissipation factor, vice versa. In FIG. 6 it is also seen that the highest capacitance exists on measurement with a frequency of 120 Hz 2157.65 nF (about 2.15765 μF). Nano shaped change of ZnO very pronounces the difference in capacitance in this material. The

capacitance relates to the surface area CAZONR is higher than CAZONP. Fig. 5 (b) and 6 (b) it is also seen that the higher the applied frequency, the tendency to lower the material capacitance of either CAZONP or CAZONR. Increased frequency causes transmitted waves every second more and more, but before the polarization is fully formed discharges due to the direction of the electric current is turned so that the dielectric constant decreases. High dielectricity at low frequencies because the load carrier is trapped in the crystal and amorphous parts of the CA-ZnO film.[12]
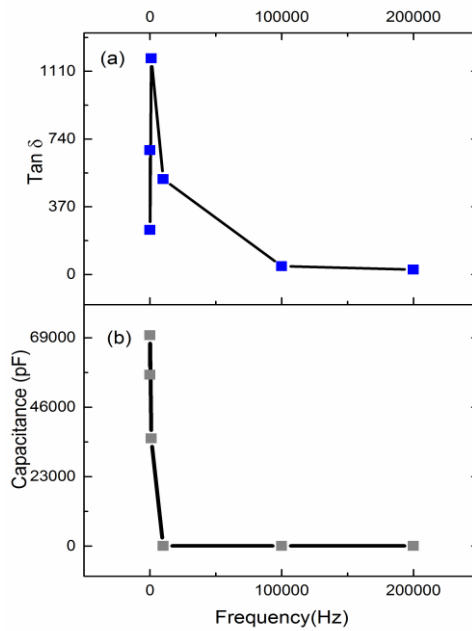

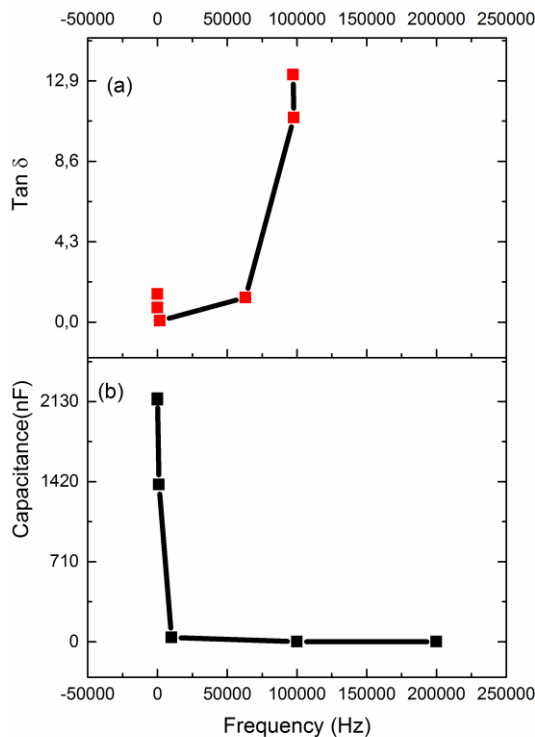**Figure 5.** The effect of frequency on Tan δ (a) and capacitance (b) of CAZONP.

Figure 6. The effect of frequency on Tan δ (a) and capacitance (b) of CAZONR.
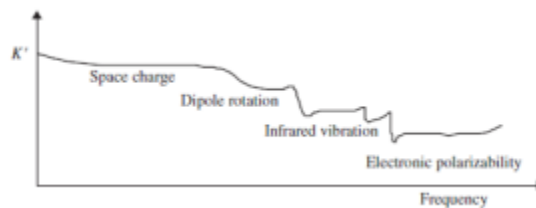
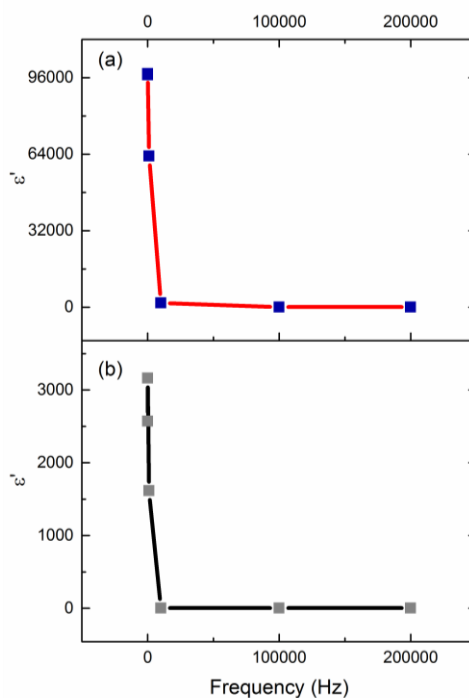**Figure 7.** The relaxation frequency of the 4 polarization types.[24]

Figure 8. The frequency effect on the real dielectric constant at (a) the CAZONR film, (b) CAZONP showing the polarization mechanisms in this material.

Tan δ is a factor of dissipation related to quality factor (Q). The quality factor of the capacitor is related to the energy lost in the energy storage process in the capacitor. The energy lost is generally heat. The reverse dissipation factor or reciprocity with the quality factor. The low-quality factor indicates low energy loss resulting in high dissipation factor.

The frequency range of the dielectric constant as illustrated in Figure 7 can be used to obtain the most prominent polarization mechanism in the sample. The role of the polarization mechanism acting on this material is electronic polarization and space charge. The curve of the frequency relationship and the dielectric constant are shown in Fig. 8 (a), (b). The electronics polarization generally exist in every material,

and the polarization of the space charge is due to the uneven distribution of particles.

Morphological changes in CA-ZnO material increase the dielectric constant and decrease the dielectric loss. This relates to the porosity shown in the SEM results. The dielectric constant at CA-ZnONP is 2569 and CA-ZnONR of 97159 at a frequency of 100 Hz. The dielectric constant increased significantly with the morphological changes in CA-ZnO material. Dielectric loss or Tan δ decreased dramatically from 678 to 13.23 at the same frequency.

Conclusion

The porosity of CAZONP is so high that it can be referred to as a porous material. The CAZONR sample shows a denser material, with a robust reduced porosity. The porosity

also different i. e. 0.680 and 0.657 respectively for CAZONP and CAZONR. These morphological changes increase the capacitance, and the dielectric constant but decrease the dielectric loss. The dielectric constant, capacitance and dielectric loss (tan δ) of CAZONP samples were respectively of 2569; 69.809 nF; and 678. The dielectric constant, capacitance, and dielectric loss or tan δ sample of CAZONR are 97159, respectively; 2.15765 μF; and 13.23.

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