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Electrical and Dielectrical Properties of Zirconium Dioxide

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Abstract: **The ac electrical and dielectrical properties of zirconium dioxide (zirconia) ZrO_2 were studied in details. The measurements of the ac conductivity, dielectric constant and dielectric loss tangent are carried out as a function of frequency from 60 Hz to 3 MHz and temperature of 25 to 300°C. The ac conductivity is found in the range of 4.4×10^{-9} to 4.3×10^{-5} mho, and high dielectric constant from 16 to 33. The dielectric loss tangent shows a normal loss without having any α, β, γ peak, and remain stable with temperatures at 300°C. From this study, it reveals that zirconium dioxide can be use as a potential candidate for complementary metal–oxide semiconductor transistors owing to its large scale electrical properties by tuning frequency and temperature with thermal stability.**

Keywords: **Electrical properties, zirconium dioxide, dielectric constant, temperature effect.**

I. INTRODUCTION

Ceramic materials are extremely strong, showing considerable stiffness under compression and bending. Their electrical and magnetic properties make them valuable in electronic applications, where they are used as insulators, semiconductors, and conductors. Certain ceramics conduct electricity, for example, chromium dioxide, as well as most metals does. Some do not conduct electricity as well, but may still act as semiconductors such as silicon carbide. Other, aluminum oxide, does not conduct electricity at all. Silicon nitride (or oxynitride) is being using as an insulator in metal–oxide–semiconductor field effect transistors [1, 2]. Due to its physical limitations with the thickness, and direct quantum mechanical tunneling results unacceptably high leakage current [3]. In this regard, several dielectric materials are currently being investigated. Among them, zirconium oxide is one of the potential candidate owing to its predicted higher temperature stability on silicon (Si), [4, 5] high dielectric constant, [6] and large conduction band offset with Si [7]. It is, hence, important to study the electrical properties of zirconium dioxide in order to develop better processing techniques to incorporate them into semiconductor devices.

There are three mostly used methods to prepare the zirconium oxide powder; (i) rapid expansion of supercritical fluid solutions, (ii) thermal decomposition of precursors in solutions, and (iii) hydrothermal method from zirconil nitrate aqueous solutions (p^H=1.5). Zirconium dioxide was characterized by XRD, line-broadening analysis, electron diffraction and TEM. Phase composition of products made by all three methods is only monoclinic phase. Another treatment of amorphous zirconium hydroxide, synthesized by adding ammonia (p^H=10) and nitrate solution, under hydrothermal conditions is found a mixture of monoclinic and tetragonal phase [8]. The later is very attractive for its reasonable range of electrical conductivity and dielectric constant. Detailed of the electrical properties of zirconium dioxide is needed for application in semiconductor devices. In this paper, we report the electrical properties of zirconium dioxide, particularly focusing on important fundamental electrical parameters such as ac conductivity, dielectric strength, and loss tangent as a function of wide range of frequency and temperatures.

II. EXPERIMENTAL ANALYSIS

Granular zirconium dioxide was kindly provided by the Department of Physics, Bangladesh University of Engineering and Technology (BUET). Disk shaped of 6 mm radius and 2 mm thick sample was made using hydraulic press with 15000 PSI at 25^{o}C. The surfaces of the pellets were polished and an ohmic contact was made by a fine Cu-wire with the help of silver paste. These Cu wires served as electrode to connect type SE-70 connector of a thermostatic oven.

A type WBG-9 oscillator (AS-76182) was used as a signal source that is able to oscillate at each frequency of 60 Hz, 110 Hz, 330 Hz, 1 KHz, 3 KHz, 10 KHz, 30 KHz, 100 KHz, 300 KHz, 1 MHz and 3 MHz. The apparatus is in conjunctions with a type BDA null detector, on the basis of synchronous selection. For regulation of capacitance and conductance components type TR-10C dielectric loss measurement unit was used. 'Transformer ratio arms bridges' are mounted inside it for matching the frequency ranges. This unit is capable to measure the capacitance from 1 to 200 pF with an interval of 0.01 pF. Conductance measurement range changes with frequency from mho to Siemens. The measurement accuracy is $\pm(5\%+0.3f\times10^{-12}$ S), where f is the measuring frequency in kHz, and 0.3 for any frequency below 330 Hz. A type TO-19 thermostatic oven was used for temperature variation from 25 to 300^{o}C. The dielectric loss tangent measurement accuracy is $\pm(10\%+2\times10^{-5})$ at frequency range from 330Hz to 100 kHz.

The conductance G_x was calculated by multiplying conductance ratio G_r and the difference between initial (without sample), G_o and final conductance (with sample) $G^{/}$. The capacitance C_x was calculated by the same way from the capacitance scale. Finally the dielectric constant, dielectric loss tangent and ac conductivity were calculated using the following formulae:

Dielectric constant, $\varepsilon' = (d/A)\, C_x / \ \varepsilon_o$

Dielectric loss tangent, $\varepsilon'' = G_x/2\pi f\, C_x$

ac conductivity, $\sigma_{ac} = (d/A) G_x$

Where d is the thickness, A is the area of sample and ε_o is permittivity of free space.

III. RESULTS AND DISCUSSION

For all samples ac conductivity, dielectric constant and dielectric loss tangent were measured over a frequency range from 60 Hz to 3 MHz and at the temperature range from 25 to 300^{o}C. The ac conductivity was studied to find the changes with frequencies, temperatures and the conduction mechanism for the zirconium dioxide. The logarithmic plot of frequency, *log f* versus ac conductivity, log σ_{ac} is depicted in Fig. 1. The ac conductivity increases linearly with frequencies for all aging temperatures with a range from 4.4×10^{-9} to 4.3×10^{-5} mho. The values of the electrical conductivity of ZrO_2 obtained in this study are slightly higher than those reported in the literature [3]. This is because the bulk density and size of the sample, are much thicker than those reported in the literature. This is quite interesting that the conductivity changes largely with frequencies.

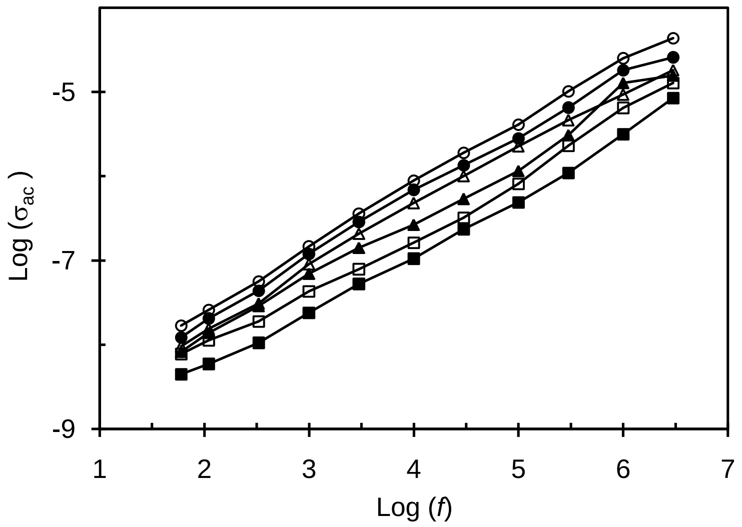

Fig. 1: Frequency versus ac conductivity curves aging at; (■) 25, (□) 100, (▲) 150, (Δ) 200, (•) 250 and (○) 300°C for zirconium dioxide.

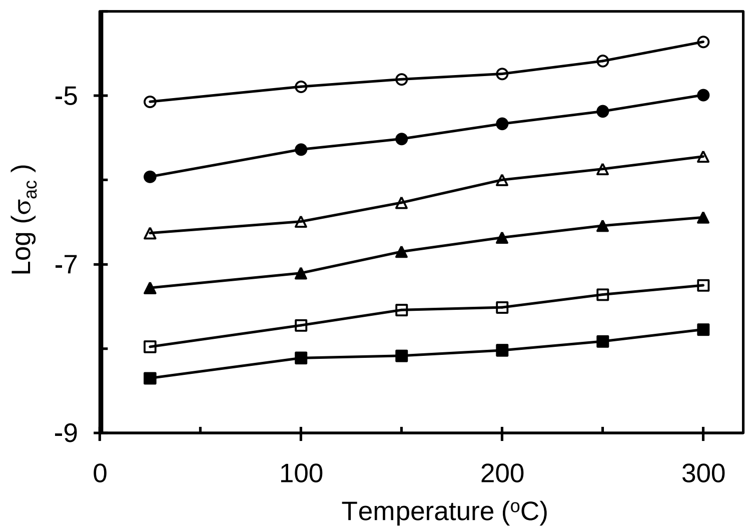

Fig. 2: Temperature dependence ac conductivity as a function of frequencies of ; (■) 60 Hz, (□) 330 Hz, (▲) 3 KHz, (Δ) 30 KHz, (•) 0.3 MHz and (○) 3 MHz for zirconium dioxide.

The temperature dependent conductivity as a function of frequency is shown in Fig. 2. The conductivity increases slightly with temperatures at all frequencies, indicating non metallic behavior. The present studies of ac conductivity points out that electrical conduction in these materials are probably due to electrons. The charge motion might take place by the process of hopping [9]. The frequency and temperature dependent ac conductivity may be attributed to the increase of relaxation times dominated by interfacial type of mechanism. As its electrical property, zirconium oxide is oxygen deficient when nonstoichiometric, therefore the predominant defects have been proposed to be oxygen ion vacancies [10].

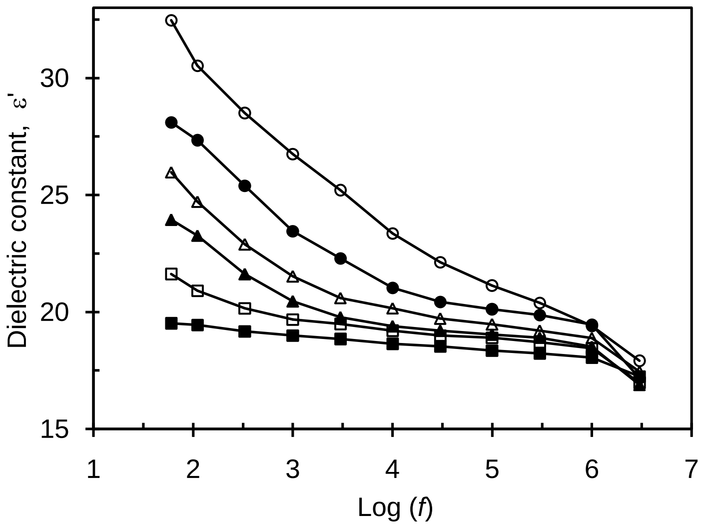

Fig. 3: Frequency dependence dielectric constant as a function of temperature for zirconium dioxide. Symbols are used as in Fig. 1.

The frequency dependence dielectric constants as a function of temperatures are shown in Fig. 3. The dielectric constant initially shows high values at low frequencies and attain more or less constant at lower frequencies and then decreases with further higher frequencies. For example, at 25°C, the dielectric constant slightly goes down from 20 to 16 with frequencies at low aging temperatures; while, it rapidly falls from 33 to 16 at high aging temperatures (300°C). The decrease of the dielectric constant might be related with the grain size of the material due to aging at higher temperatures, where the temperatures enhance the dependencies on frequencies.

From temperature dependent dielectric constant curves shown in Fig. 4, the dielectric constant remains same at all temperatures in higher frequency ranges, where significantly increases with temperature at lower frequencies.

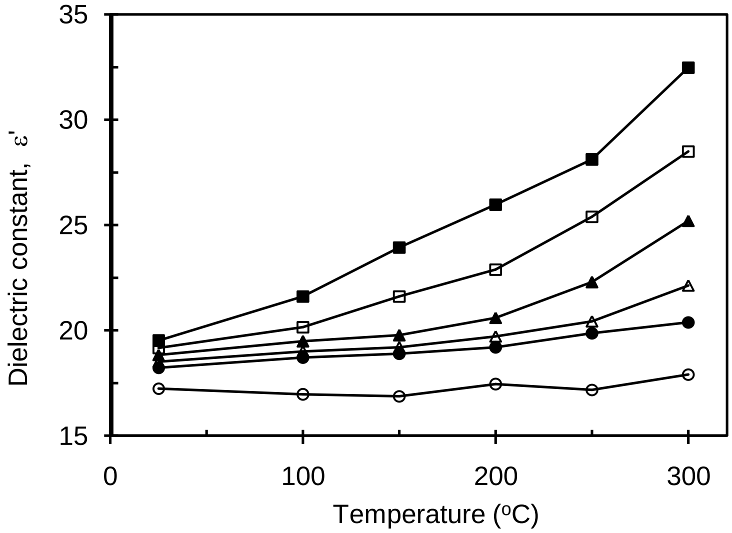

Fig. 4: Temperature dependence dielectric constant as a function of frequencies for zirconium dioxide. Symbols are used as in Fig. 2.

At room temperature the dielectric constant is almost independent of frequencies. These variations are in good agreement with the behavior reported earlier [11]. This behavior may be due to thermal agitation, which does not allow polarization. The dielectric constant is also independent of temperature at very high frequency, which may be due to the pining of dielectric [12]. The dielectric constant increases with temperatures, which may be due to domination of interfacial polarization over dipole polarization. Therefore, it can be concluded that, the interfacial polarization is responsible for the dielectric relaxation in the specimen.

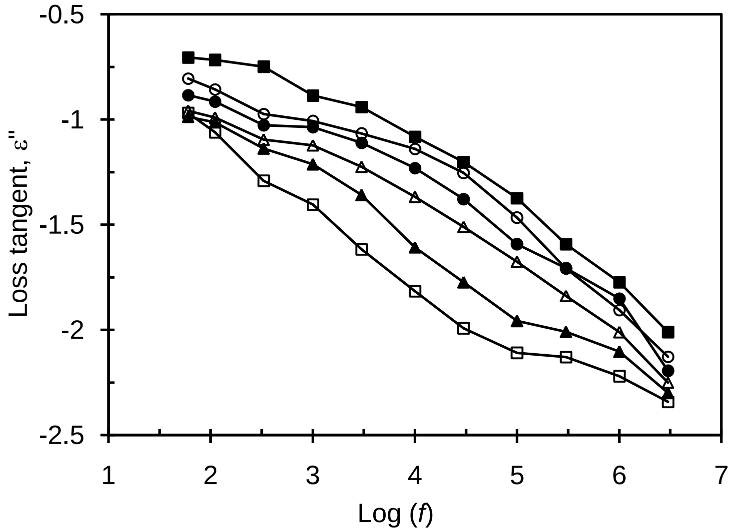

Fig. 5: Frequency dependence dielectric loss tangent as a function of temperature for zirconium dioxide. Symbols are used as in Fig. 1.

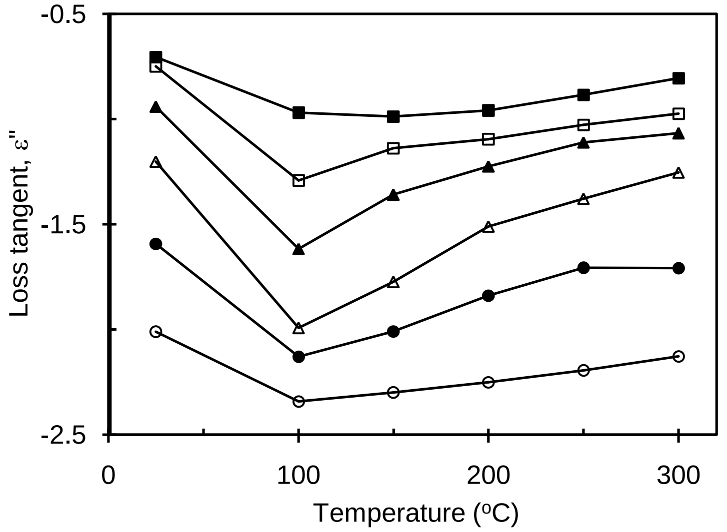

Fig. 6: Temperature dependent loss tangent curve as a function of frequency for zirconium dioxide. Symbols are use as in Fig. 2.

The dielectric losses, a useful parameter of the energy loss as heat, are a combined result of electrical conduction and orientational polarization of the material. Variation of loss tangent as a function of frequency for zirconium dioxide is shown in Fig. 5. The dielectric loss decreases with frequencies at all temperatures. The variation of loss tangent with frequencies and temperatures shows a normal loss without having any α, β, γ peak. The dielectric loss does not shows any significant losses with temperatures as shown in Fig. 6, indicating thermal stability even at high temperature of 300°C.

IV. CONCLUSIONS

Experimental observations suggest that zirconium dioxide exhibits excellent electrical properties, having a range of conductivity, high dielectric constant with normal loss tangent. Zirconium dioxide can be used in the thin film technology, especially for depositing on Si for metal–oxide–semiconductor transistors, where a large range of electrical properties can be tuned with frequencies and temperatures having thermal stability. Details of the optical and structural properties will be another issue for future work.

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