

High Dielectric Constant SiO₂ Nanoparticles

Sathosh K. Kurni, Pradip Paik*

School of Engineering Sciences and Technology, University of Hyderabad, 500046, India

*Corresponding author, E-mail: pradip.paik@gmail.com; Tel: (+91) 040-2313 4457

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Abstract

SiO₂ nanoparticles of average size 15-20 nm have been synthesized and its dielectric properties have been investigated as a function of frequency (between 20 Hz to 2 MHz). A very high dielectric constant of ca. 14000 at 20 Hz and at room temperature has been observed which is very high compared to the conventional bulk SiO₂ particles (ca. 50-100). For this new SiO₂ the loss value is found to be less than 1. These SiO₂ nanoparticles with high dielectric constant and low loss can be offered its use in constructing high efficient electronic circuit boards and storage devices. Spectra between real and imaginary parts of dielectric constant reveal an inclined line with depressed semicircle. Impedance measurements have been performed to know the electrical properties of the novel SiO₂ nanoparticles. XRD, TEM and FTIR characterizations confirm the solid state network structural, morphological shape and size, and chemical functionality of SiO₂ respectively. Copyright © 2016 VBRI Press

Keywords: SiO₂ NPs, dielectric constant, dielectric loss, impedance, AC conductivity.

Introduction

Materials with high dielectric constant and low loss have potential applications in electronic industry and required new materials on current demands. SiO₂ nanoparticles (NPs) in various forms have wide variety of applications in different fields like electronics, bio imaging, drug delivery [1] and cancer therapy [2] etc. SiO₂ NPs are used as coatings in photovoltaic devices to reduce the reflectance [3]. Due to the development of Very Large Scale Integration technology (VLSI), use of low dielectric constant materials (low k) and high dielectric constant materials became mandatory. SiO₂ films can be used as low k material as well as high k material in the form of interlayer dielectric in transistors depending on its dielectric constant. Its dielectric constant can be increased/decreased by doping with carbon or fluorine and imparting porosity to it [4-6].

The common high k materials being used in electronic industry are SiO₂, Hafnium silicate (HfSiO₄), and Zirconium silicate (ZrSiO₄) [7]. Interlayer dielectric should be in the form of films by requirement. Polymer dispersed with high k materials also can be used for the same followed by composite film formation [8]. The SiO₂ being used as gate oxide material in transistors encounters problems like leakage current and diffusion of metal layers and less gate capacitance for its lesser thickness (less than 2nm) [9]. Therefore a high k material is required which avoids such problems in the device. There has been a search for new high k materials with fewer inconveniences for the past decade. In this work a

new ultra-fine SiO₂ NPs has been synthesized and its dielectric properties have been investigated as a function of frequency and temperature. The present material discussed in this article has very high dielectric constant when compared to conventional SiO₂ films (3.9) deposited through PECVD [10] and which can be used for increase in the efficiencies of the future generation electronic devices.

Experimental

Materials details

TEOS (99.9%, Sigma Aldrich), Ethanol (99.3%, Merck) and NH₄OH (99.9%, Sigma Aldrich) were used in their pure form for synthesis.

Material synthesis

Synthesis of SiO₂ NPs: The synthesis of SiO₂ NPs was done using sol-gel technique with a little modification. The detailed procedure of the method is as follows. Ethanol 30 ml was taken in a flask and 2 ml TEOS was added after 10 minutes under vigorous stirring. After 10 minutes 1 ml water was added to the reaction mixture. Stirring continued for 20 minutes then 3 ml NH₄OH was added to it. Gel was formed after few minutes and was dried in a furnace at 80°C for overnight. A white powder of SiO₂ NPs was obtained.

Characterizations

High resolution transmission electron microscopy (HRTEM) (Model: FEI TECHNAI G2 200 kV S-twin) was used to find out the shape, size and

morphology of the SiO_2 NPs. Chemical characteristics of SiO_2 NPs were identified by Fourier transform infrared (FT-IR) (Nicolet model Impact-410) studies. The SiO_2 NPs were mixed with dry and pellets were made using the hydraulic press with a load of 9 tons. Advanced X-ray diffractometer (Bruker AXS Model D8) with a $\text{Cu K}\alpha$ source ($\lambda = 1.54 \text{ \AA}$) was used study the crystal structure of SiO_2 NPs. For dielectric measurements, pellets of SiO_2 were prepared (8 mm dia. and 2 mm thickness). All the pellets were coated on both the sides with conducting silver paste. Drying of pellets was done before measurements to remove volatile materials in it. Dielectric measurements were conducted with in the frequency range of 20 Hz-2 MHz at RT and at temperatures between 200-400°C using AGILENT LCR Meter (Model E4980A Precession Impedance Analyzer). The dielectric measurements were executed using parallel plate capacitor method.

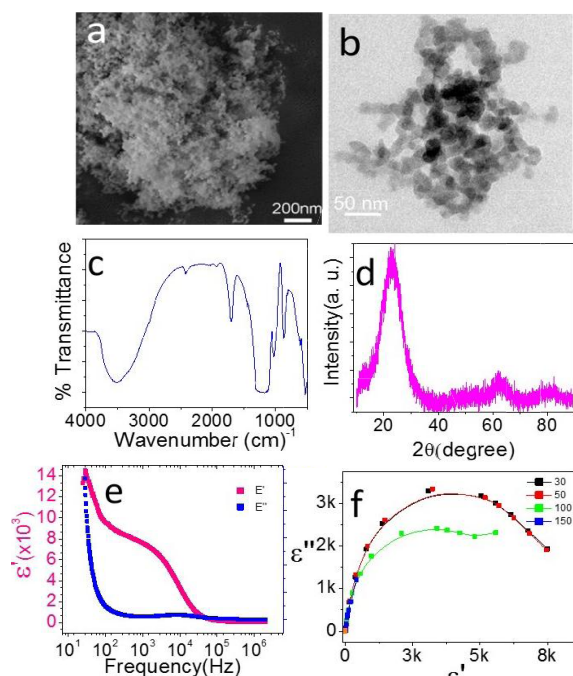


Fig. 1. (a) FESEM (b) TEM micrographs (c) FTIR (d) XRD spectra (e) real (ϵ') and imaginary (ϵ'') parts of dielectric constant of with frequency (f) Cole-Cole plot between ϵ' and ϵ'' of SiO_2 NPs.

Results and discussion

Fig. 1(a) shows FESEM micrograph of SiO_2 NPs. From this the particle size is 15-30 nm. To confirm particle size and morphology TEM was done. Particle size from the **Fig. 1(b)** is matching well with results obtained from FESEM result. Both FESEM and TEM confirm the morphology of the particles is nearly spherical. **Fig. 1(c)** shows FTIR spectra of SiO_2 NPs and the bands at 1080 cm^{-1} indicates Si-O-Si stretching vibrations along with other standard bands confirm the formation SiO_2 NPs. The structural analysis for these particles was done using XRD. The

results are shown in **Fig. 1(d)**. It is giving short range order yielding broad peak at $2\theta = 25^\circ$ indicates amorphous nature of the SiO_2 NPs. The real (ϵ') and imaginary (ϵ'') parts of dielectric constant of SiO_2 NPs was measured within the frequency range 20 Hz to 2 MHz and temperature range 27-200°C and shown in **Fig. 1(e)**. A very high dielectric constant ~ 14000 has been observed at 20 Hz and the value of ϵ'' is also high. At 100 Hz, the values of ϵ' (9569) and ϵ'' both are same. A sudden decrease in ϵ' value has been observed between 20 Hz and 100 Hz. There has been a gradual decrement in the value of ϵ' from 101 Hz to 3116 Hz. Even at 1 KHz, ϵ' is 7614 which is very high [11] while ϵ'' is 2224 which is very low when compared to ϵ' . After this, again a sudden decrease of ϵ' has been observed up to 44 KHz.

A plot between ϵ' and ϵ'' at various temperatures has been drawn and shown in **Fig. 1(f)**. The depressed semicircle with center above x axis indicates non Debye type of relaxation [12]. The dielectric constant of SiO_2 NPs was measured with increasing temperature (27-200°C) to know its behaviour so that it can be used even at different temperature ranges. The real (ϵ') and imaginary (ϵ'') parts of dielectric constant with temperature is shown in **Fig. 2** at various constant frequencies (1 KHz - 2 MHz). From the **Fig. 2** it is clear that at RT (27°C), the ϵ' value is 7000 even at 1 KHz. And slight increment in this is observed up to 75°C. The same trend has been found for all other frequencies. But there is a downshift in this temperature as the frequency increases.

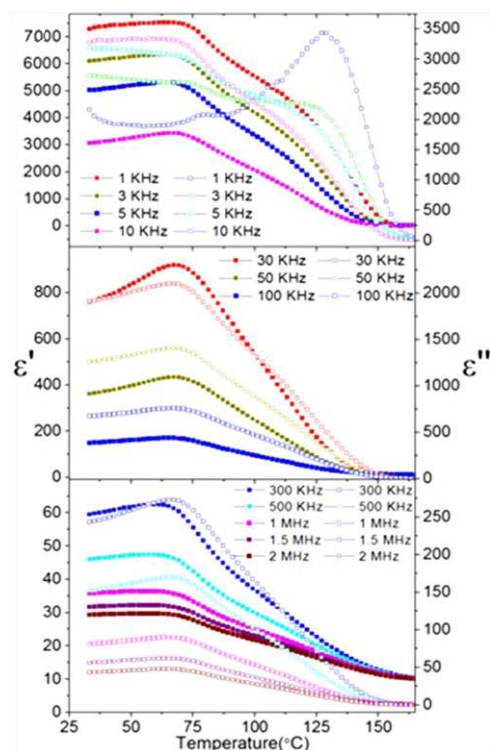


Fig. 2. Variation of ϵ' and ϵ'' with temperature of SiO_2 NPs.

After that there is a gradual decreasing trend is observed with temperature for all frequencies. The decrease in the ϵ' value has been observed with the increase in the frequency (at RT, 2 MHz ϵ' is 29). Further, except for 1 KHz, for all other frequencies, similar behaviour with increase in temperature has been observed even for ϵ'' also. For 1 KHz frequency, peak at 125°C has been observed for ϵ'' . The dispersion of ϵ' as a function of frequency was studied at different temperatures (27-200°C) and results are shown in **Fig. 3**. From the **Fig. 3**, it is evident that ϵ' is high at lower frequencies and low at high frequencies.

This is due to the general frequency dispersion of any system with an application of AC field (seizing of various polarization mechanisms orientational, ionic and atomic with increasing frequency).

The effect of temperature on ϵ' is clearly shown in the **Fig. 3**. The dielectric loss ($\tan \delta$) with varying frequency at different temperature was measured (**Fig. 4(a)**). With the increase in temperature decrease of its value has been observed. The reason for the decrement with increasing temperature is, at higher temperature, the thermal vibrations of atomics causes non-cope up of the atomic/molecular dipoles with change in the applied electric field.

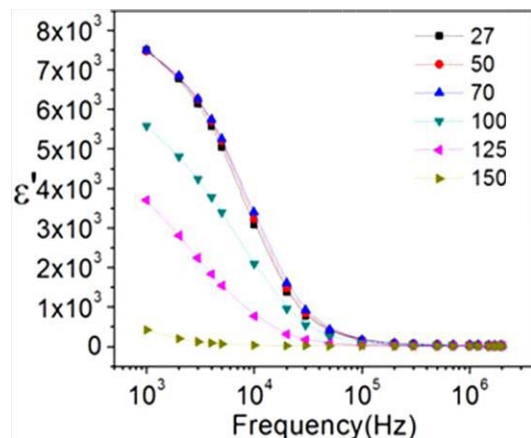


Fig. 3 Dispersion of ϵ' as a function of frequency at different temperatures of the SiO_2 NPs.

From the figure it is clear that a dielectric loss peak has been observed for all the temperatures up to 125°C. Above that temperature the loss peak has been disappeared. Below 100°C, there is no much peak shifting and some loss peak value change is observed. The loss peak is shifting towards low frequency for 125°C and 150°C temperatures with no change in loss value. The dispersion of $\tan \delta$ at 1 KHz is evident with temperature. At 1 KHz, except for 150°C, the loss value is less than 1. The $\tan \delta$ with varying temperature at different frequencies has been measured and is shown in **Fig. 4(b)**.

The loss value at RT is increasing with frequency for 1, 3, 5, 10, 30, 50 and 100 KHz. For these frequencies, with increase in temperature a slight

variation is observed up to 100°C and a loss peak is observed. Within this range of frequency, the value of peak is maximum for low frequency and minimum for high frequency and shifting towards lower temperatures.

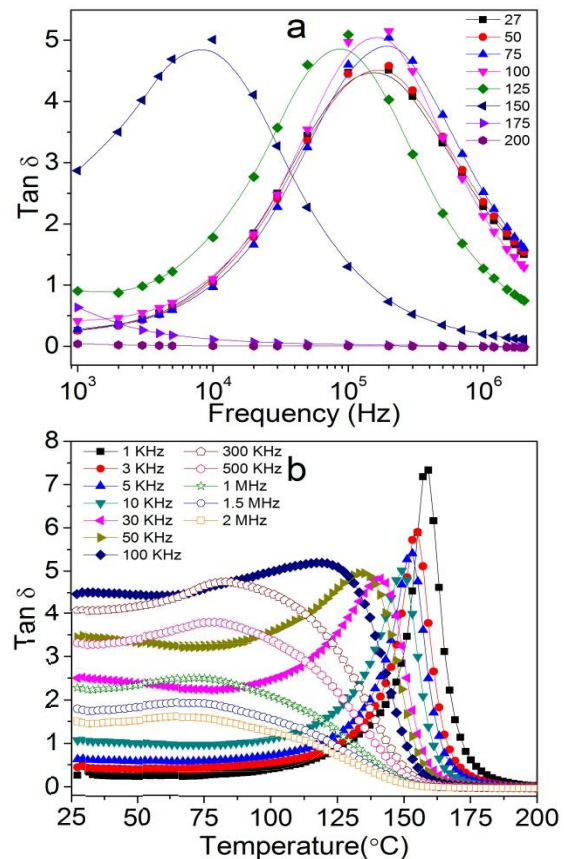


Fig. 4. Frequency versus $\tan \delta$ at various temperatures (a), and temperature versus $\tan \delta$ at various frequencies (b) of the SiO_2 NPs.

After that for 300, 500 KHz, 1, 1.5 and 2 MHz, at RT, loss value is decreasing with increase in frequency. As the frequency increases the loss peak for these particular frequencies becoming broader and the peak value for $\tan \delta$ is decreasing and shifting towards the lower temperatures.

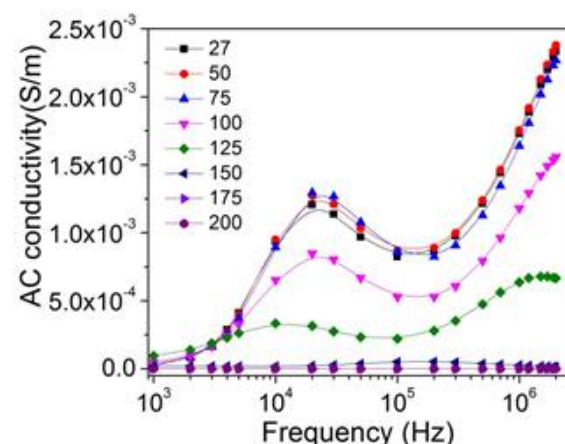


Fig. 5 Dispersion of ac conductivity with frequency at different temperatures.

Impedance measurements with frequency and temperature were executed to know the conducting behavior of SiO₂ NPs. From this data AC conductivity was calculated and is shown in **Fig. 5** at different temperatures. As the frequency increases the AC conductivity is increasing. This may be due to the moment of the dipoles with alternating field. This trend is followed at all other temperatures also. There is a peak observed between 10 KHz to 100 KHz at all temperatures except for 175 and 200°C. Comprehensively, with the temperature the AC conductivity is decreasing.

Conclusion

SiO₂ NPs with fine particle size were synthesized and the dielectric properties were studied in the frequency range 20 Hz to 2 MHz and temperature range 27-200°C. The real part of dielectric constant ϵ' has been found to very high at 20 Hz and RT. This value is 7000 even at 1 KHz which is very high when compared to previous SiO₂ particles and films. The dielectric loss is also less at 1 KHz. The optimized synthesis process that leads to the fine particle size and it might be the reason for the high value of dielectric constant. The temperature dispersion of dielectric constant was also being studied and found that with increase in temperature dielectric constant is decreasing. Impedance measurements were also done to know its conducting behavior with frequency and temperature. AC conductivity of the synthesized material was found to be strongly dependent on frequency and temperature. These findings for SiO₂ NPs with high dielectric constant can offer its use in electronic circuit boards and storage devices. These particles can further be deposited in the form of films and one can study their behaviour for various applications.

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Author's contributions

Conceived the plan: Paik; Performed the experiments: Kurni; Data analysis: Kurni; Wrote the paper: Kurni and Paik. Authors have no competing financial interests.

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