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Effects of P_2O_5 Addition and Sintering Temperature on Structural Properties of Silica

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Abstract

Silica (SiO_2) is an essential component of many electronic devices such as MOSFET. The melting point of SiO_2 is quite high which results in an expensive manufacturing process. However, the melting point of SiO_2 can be lowered by altering its crystalline structure to amorphous state. The purpose of this experiment was to add Phosphorus Pentoxide (P_2O_5) to the network structure of SiO_2 to obtain amorphous structure with lower melting point. In this work, P_2O_5 was added at two different weight percentages viz. 5% and 10%. Microstructures of the pellets for each of the addition sintered at different temperatures were investigated by Field Emission Scanning Electron Microscopy (FESEM). Dielectric constant (K) and resistivity were measured as functions of frequency using an impedance analyzer.The structural properties of the sintered pellets were examined by Fourier Transform Infrared (FTIR).Experimental results revealed that addition of P_2O_5 could bring about a partially amorphous structure of Silica and the result was best obtained at sintering temperature 1350°C. The microstructure and dielectric properties of SiO_2 were markedly influenced by the addition of P_2O_5 as well.

Keywords: Silica; Phosphorus Pentoxide addition; Microstructure; Dielectric constant; Resistivity

1. Introduction

Silica forms a major portion of the earth crust. Having a low dielectric constant and loss factor, it also exhibits good chemical inertness and optical qualities [1]. Silicon dioxide films have been an integral part of microelectric devices such as metal-oxide semiconductor field-effect-transistor (MOSFETs) where it is used as gate and field effect oxides. It is also being used as passivation layers, scratch resistant coatings, diffusion and oxidation barriers. Thermally manufactured silicon dioxide films exhibiting a lowest interface trap densities are best insulators [2].

But the major problem encountered with Silica is that, it is very expensive and manufacturing process is stringent. The prices of silica are surprisingly high ranging from $500/kg from tube standard purity to $5000/kg for highly pure material. This is because the melting point of silica is very high melting point as well as high viscosity and volatility. Also it possesses a propensity to dissolve the container [1].

However, additions of some materials have been proved to be a solution to this problem such as phosphorus, rare- earth metals such as Yttrium, Erbium [3,4]. Silica compounds have a varying number of bridging oxygen from 0 to 4. The orthosilicate [SiO_4^{4-}] becomes intermediate silicate structures by the addition of modifiers [5]. Phosphorus works as a nucleating system in glass-ceramics. It has profound influences on microstructure of these glass-ceramics and crystallization behavior and few on melting point and viscosity of glass [6].The characteristics of silicate glasses are influenced by the presence of other oxides in the structure. Phosphorus doped silica glasses bring about excellent structural and optical properties that are suitable for amplifiers, lens, catalysts, drug delivery etc [7]. Phosphorus containing silicate glass has already been a topic of attraction to the researchers as addition of phosphorus to the silicate glass matrix results in creation of non-bridging oxygen, causing and improvement of the spectroscopic properties of the silica glass matrix. Phospho-silicates are better proton conductor as the non-bridging oxygen binds proton more strongly. This causes a rise in conductivity

when relative humidity is >80%. These chemically stable glasses are suitable for hydrogen sensors. [3] These are also very popular as high energy density batteries, medical implant, optical fibers and so on. Therefore, synthesis and characterization of phosphor-silicate glass using different SiO_2:P_2O_5 ratios deserve a great deal of attention [8].

Different methods can be used to add phosphorus in silica such as melting, sintering, sol-gel, VAD etc [1,9]. In this work, we are focusing on sintering process to add phosphorus in silica as it is very cost effective. Direct addition of P_2O_5 is not convenient as researches show that it easily absorbs water molecules that is hygroscopic due to the presence of P=O bond and affinity of phosphorus for oxygen which results in proton in P-OH bond to bind hydrogen strongly. [3] Instead, we are using diammonium hydrogen phosphate as the source of P_2O_5. It gives the following flame-retardant reaction and produces P_2O_5 [10].

$$(NH_4)_2HPO_4 = NH_{3\,(g)} + NH_4H_2PO_{4(s)} \quad \ldots\ldots(1)$$

$$NH_4H_2PO_{4(s)} = NH_{3\,(g)} + HPO_{4\,(l)} \quad \ldots\ldots(2)$$

$$2H_3PO_4 = P_2O_5 + 3H_2O \quad \ldots\ldots(3)$$

This paper focuses on the structure modification of silica after addition of P_2O_5 in its network structure. The microstructure study by Field emission scanning microscopy (FESEM) shows the micrographs of the modified structures of silica for different percentage of addition at different sintering temperatures. The study of Fourier transformation infrared (FTIR) spectroscopies give the structural modification done to silica by the addition and the peak frequencies shift are made related to the structural modification. Also the changes in dielectric constant and resistivity of silica due to the addition of P_2O_5 are reported.

2. Experimental

2.1 Sample Preparation

Highly pure Silica, SiO_2 and Diammonium hydrogen phosphate, $(NH_4)_2HPO_4$ were used as raw materials. SiO_2: P_2O_5 ratios were varied and the amounts of silica and diammonium hydrogen phosphate required were taken for each of the compositions. We conducted our experiment for 5% and 10% addition of P_2O_5. After manually mixing in an agate mortar for 15 minutes, the mixed powders were dissolved into acetone and further homogenized by ball milling by Yttria stabilized zirconia balls in Polyethylene terephthalate (PET) bottle for at least 18 hrs. Then powders of each of the compositions were dried and after taking in silica based crucibles, heated at 500°C for 8 hrs to remove NH_3 from $(NH_4)_2HPO_4$. The powder mixtures of different compositions were grounded again, mixed with little amount of polyvinyl alchohol (PVA) as binder and compacted to form pellets of 13mm diameter and 2 mm thickness. These pellets were sintered at different sintering temperatures such as 1250°C, 1350°C and 1400°C. The sintering cycles consisted of heating the samples at 2°C/min to holding temperature 500°C, again at same heating rate to a seconding holding temperature of 800°C and finally at 3°C/min heated to the sintering temperature, held there for certain period and cooled down at a rate of 3°C/min. These sintered pellets were used for different characterizations.

To examine the morphology of the sintered product, field emission scanning electron microscopy (FESEM: JEOL JSM 7600F) was conducted at different magnifications ranging from 2000 to 10,000. Using IRPrestige-21 Fourier Transform Infrared Spectroscopy the infrared spectra of the sintered pellets of each of the composition were found. Potassium Bromide (KBr) was used as the base material for the measurement. It was found in the 400-4000 cm^{-1} wave number range.

2.2 Dielectric constant and Resistivity measurement

The dielectric constants (K) of the sintered pellets were measure at different frequencies as well as the resistivity using an impedance analyzer.

3. Result and Discussion

3.1 FESEM analysis

Field Emission Scanning Electron Microscopy of samples of each of the composition sintered at 1250°C, 1350°C and 1400°C showed that less porous and dense product were obtained with increasing sintering temperature as shown in fig 1 and fig 2. The samples of 10% P_2O_5 were found to be of more homogenous and large grains than 5% addition. This is due to the fact that, increasing addition of P_2O_5 provides increasing activation energy for softening. This causes lesser grain growth in 5% than in 10% addition. Again, the micrographs showed grain inhomogeneity at lowering sintering temperature with large variation in grain sizes. But with increasing sintering temperature the grains became more homogenous in size.

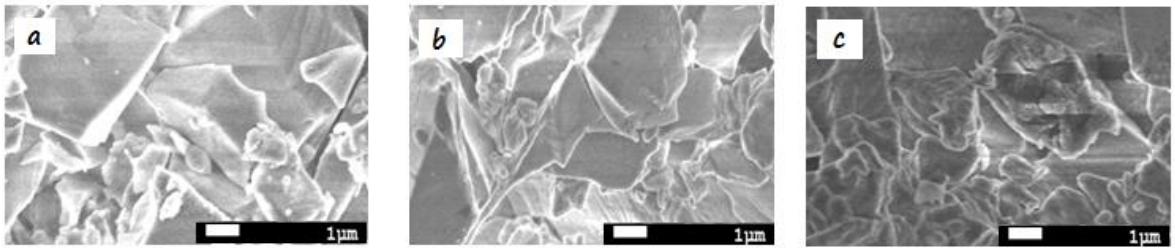

Fig 1: FESEM micrographs of 5% P_2O_5 added Silica sintered at a) 1250°C, b) 1350°C and c) 1400°C

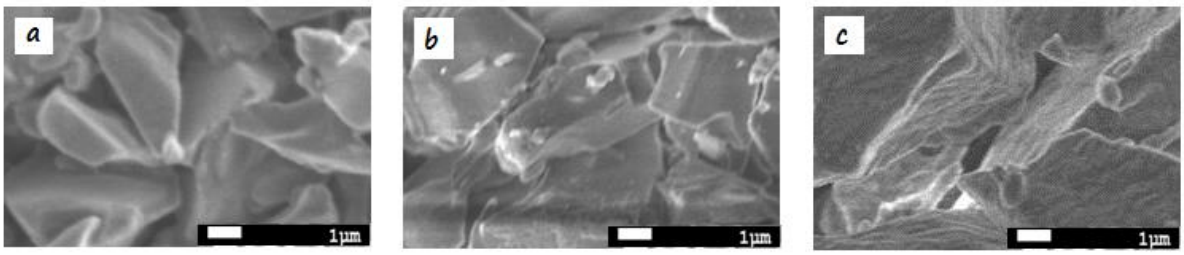

Fig 2: FESEM micrographs of 10% P_2O_5 added Silica sintered at a) 1250°C, b) 1350°C and c) 1400°C

3.2 FTIR analysis

Fourier Transform Infrared Spectroscopy further ensured the newly developed amorphous structure of the sintered pellets and the results found for addition of 5% and 10% are shown in fig 3 and fig 4 respectively. From the spectroscopy of samples sintered at different temperatures, it was found that, wide range of bands from 1000-1170 cm^{-1} were with low transmittance values. Previous works show [5,11], the peaks between 1020-1040 cm^{-1} refers to Si-O-NBO stretching bond modes which causes the breakage of bridging oxygen bond of Si-O-Si stretching transforming it to non bridging oxygen. It results in a crystal distortion which leads to the formation of amorphous phase. Also peaks between 1080 cm^{-1} and 1000-1100cm^{-1} are attributed to Si-O-Si stretching bond [5,12] and PO_4^{-3} asymmetric stretching [13-14] respectively. Peaks between 760-850 cm^{-1} refers to Si-O-Si bend [15] and 450-490 cm^{-1} indicates Si-O-Si rocking [12]. These peaks match with our obtained results as shown in the figures.

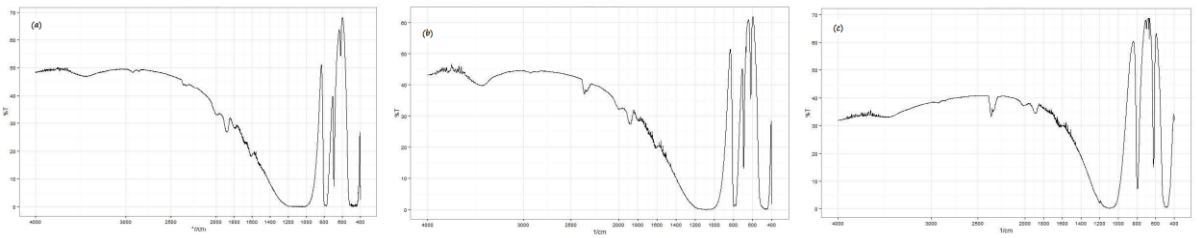

Fig 3: FTIR spectra of 5% P_2O_5 added Silica sintered at a) 1250°C, b) 1350°C and c) 1400°C

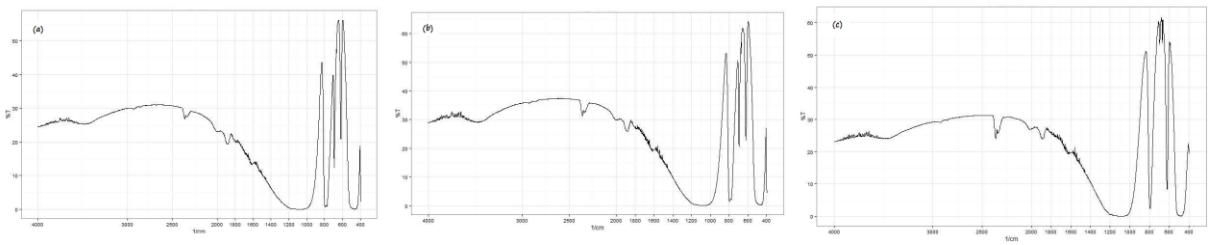

Fig 4: FTIR spectra of 10% P_2O_5 added Silica sintered at a) 1250°C, b) 1350°C and c) 1400°C

3.3 Dielectric constant and Resistivity measurement results

The dielectric constant of pure silica is 15.0 – 25.0 kV/mm and resistivity around 1012-1016 Wm [16]. Even though addition of P_2O_5 and bringing of amorphous structure ease the manufacturing process by lowering the

melting point, it decreases dielectric constant and resistivity of the sintered pellets. So optimization is required. From our result obtained we saw that, dielectric constant and resistivity of both of the compositions decreased. Fig 5 shows the decrease in dielectric constant with increasing frequency and fig 6 shows the decrease in resistivity with respect to increasing frequency.

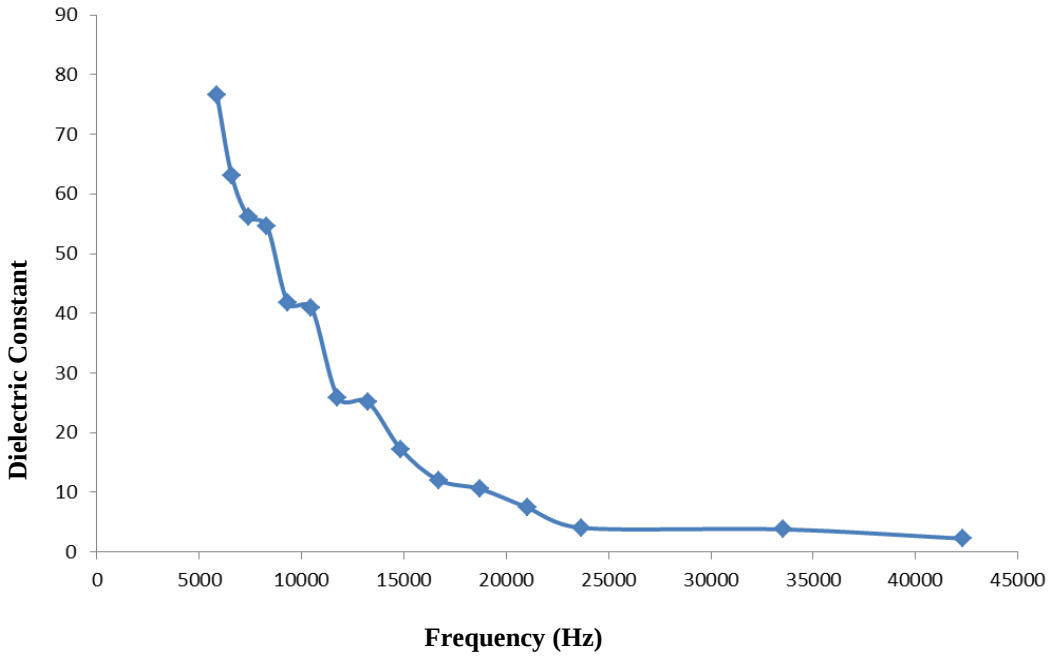

Fig 5: Dielectric Constant vs. Frequency plot showing decrease in dielectric constant due to the addition of P_2O_5 in Silica sintered at 1350°C

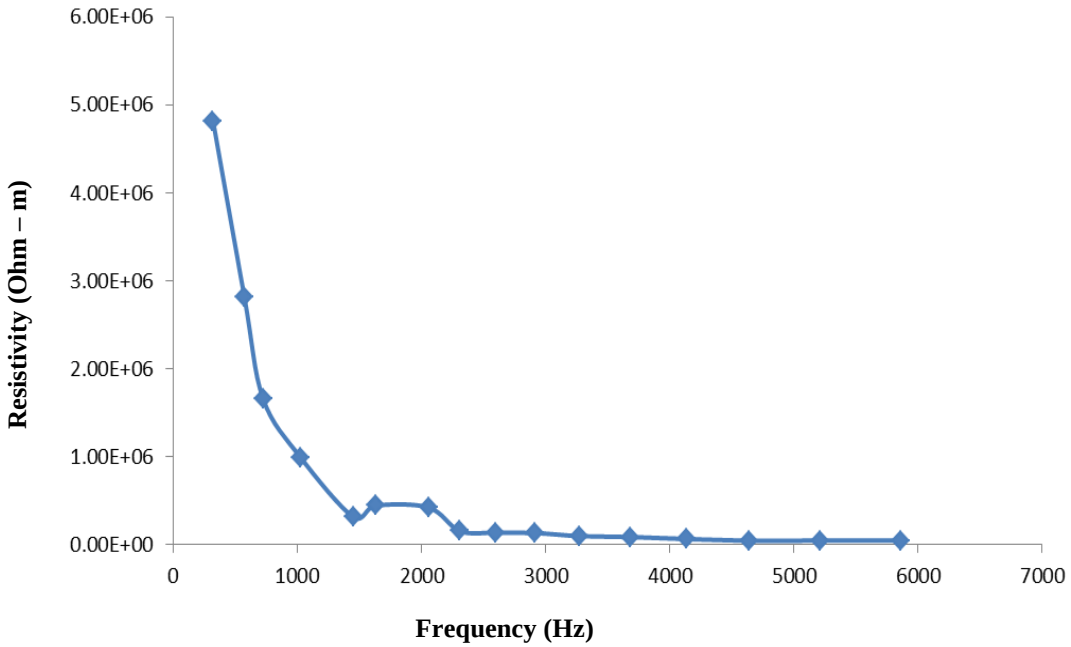

Fig 6: Resistivity vs. Frequency plot showing decrease in resistivity due to the addition of P_2O_5 in Silica sintered at 1350°C

4. Conclusion

The results obtained from FESEM, FTIR and Dielectric constant, Resistivity measurement showed that, addition of P_2O_5 brought about expected change in the crystalline network structure of Silica by altering it to amorphous

structure. Between the additions of 5% and 10% P_2O_5, we observed that, grain growth was higher for later addition as increase in P_2O_5 content lowered the softening temperature and sintering occurred at even lower temperature. Besides, grains were found to be more homogeneous and dense with increasing sintering temperature. The basis of these property manipulations were confirmed by FTIR spectroscopy results where we found significant alteration of bond characteristics of pure Silica due to the addition of P_2O_5. Moreover, we were to keep a notice to the decrease in the dielectric constant and resistivity because of the addition and make this reduction as low as possible. Therefore, by trading off between the amount of P_2O_5 addition and the lowering of dielectric constant and resistivity, we could produce a lower melting point Silica for cost-effective manufacturing process.

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