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Thermal and Optical properties study of silver nanoparticles doped in silica film on glass substrate as a function of annealing behaviour

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ABSTRACT

Nano-silver doped silica films were deposited on glass slides using a dip coating process and heat treated at different temperatures. The films were characterized by Fourier transformation infrared spectroscopy (FTIR),X-ray diffraction (XRD) and Simultaneous Thermal Analysis (STA) for their optical, chemical and structural properties. FTIR spectrometry has been studied with respect to the microstructure and chemical composition of the film. The transmission peaks of silver colloids were observed after heat treatment. It has been earlier reported that the microstructure depends closely on the solution pH and silver-doping. The present work demonstratesthat the evolution of the system as a function of the sintering temperature is necessary for obtaining a nano-oxide distribution in silica matrix. At temperature 500^0C, the sample was sintered for 30 min and obtained silver nanocrystallites with average size ~19 nm.

Keywords: Nano-silver, sol-gel, silica, heat treatment

Introduction

Nanocomposite materials comprising metal/ oxide particles embedded in a vitreous matrix are of great interest due their interesting physical properties[1]. In particular, silver-silica nanocomposites materials have been obtained by the sol–gel process using diverse methods with different precursor compounds in thin films samples.Due to their linear and nonlinear optical and thermal properties, composite materials formed by metal particles with nanometres dimensions distributed in glasses, also called metal nanoclusters composite glasses, have optical properties useful for applications in photonics[1–3]. For photonic applications, transparent organic/inorganic glasses have gained increased importance. In particular, this material allows the development of optical waveguides or interconnects with a single material and their processing is compatible with conventional thin film processing equipment. They permit the fabrication of electrical and optical interconnects on the same substrate such as optical transmitter and receiver modules, and complex photonic devices such as power splitter, couplings and wavelength demultiplexer/multiplexer[4-6]. Their optical and thermal properties mainly depend on the composition and size of the nanoparticles embedded in the glass substrate. Thus, it is necessary to prepare such composite systems by means of synthesis techniques in which the parameters affecting the optical and thermal properties can be easily and independently varied. The sol–gel technique[7] is a promising low-temperature route that provides good homogeneity for the preparation of metallic nano-particles in thin coatings in a thermally stable dielectric solid oxide matrix such as SiO_2. This process matches the demands of industries in terms of bulk preparation of materials with high density, high mechanical strength and high shock resistance, high specific area, compositional purity and optical grade quality. Nowadays, the sol–gel chemistry provides a means for preparing mixed oxides in which the mixing of two or more metal/ oxide phases can be controlled on both the molecular and the nanoscale. The different reactivity of individual components has been the major problem of the synthesis of mixed oxides, especially in the alkoxides based sol–gel process. The problem can be minimized by controlled pre hydrolysis of the less reactive precursor, by chemical modification of the precursors, by using single-source hetero bimetallic alkoxide precursors or by a non-hydrolytic sol–gel route[8-12]. The aim of this paper is to develop some effective metal nanocluster composite thin films on glass substrate by sol–gel dip coating method.However, Thin composite films have been obtained by thermal treatment at temperatures up to 500^0C.These metal-silica gel coated samples were annealed in air at three temperatures. This may

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lead to development of suitable nano-composite coatings for sensing applications.

1. Experimental procedure

1.1 Preparation of coating films

The films were prepared by the sol–gel method on glass substrates using the dip coating procedure. The sol–gel precursor solution was obtained mixing tetraethoxysilane (TEOS) (Aldrich, 99%) and ethanol with a molar ratio ethanol to TEOS of 4. In another flask the silver nitrate $AgNO_3$ was dissolved in water. Both mixtures were separately subjected to vigorous magnetic stirring for 20 min. Duration. Then, both solutions were mixed and stirred for 40 min, attaining a pH value of 2 and forming a clear grey solution. The molar ratio of water to TEOS was of 11.7. The amount of silver nitrate dissolved into the precursor solution was calculated to obtain a nominal Si to Ag atomic ratio of 2.1. This value assumes that all the silicon in the TEOS is converted into silica and that all the silver is dissolved into the precursor solution. The films were deposited at a withdrawal speed of 20 cm/min. The samples deposited on glass were heat-treated in the temperature range between 100 and 500 ^{0}C for 30 min in air.

2. Characterization

Complementary methods were used to characterize the structure of the doped samples. X-ray diffraction pattern of samples were carried out by a Philips X-ray diffractometer PW/1710; with Ni filter, using mono chromatised CuKα radiation of wavelength 1.5418A^0 at 50KV and 40mA.Chemical composition of the heat treated coating was analyzed using Fourier Transformed Infrared spectroscopy (FTIR) analyses. FTIR spectrum were determined in transmission mode using a FTIR spectrometer (Perkin Elmer) in the range of 4000-400 cm-1 with are solution of 2 cm^{-1} in KBr-diluted medium. In order to determine thermal behaviour of raw coating and optimum temperature for heat treatment, thermal analysis was used. The curves of differential thermal analysis (DTA) and thermogravimetry analysis (TGA) of the dried gels were recorded at a heating rate of 10° C/min using (Perkin Elmer-6000) Differential Scanning Calorimeter in a temperature range of 50-600°C.

3. Results

3.1 FTIR

The infrared transmission spectra of the prepared samples provide some important information about the structural changes. Fig. 1represents the structural evolution of samples annealed at 100 °C for 30 min, 300 °C for 30 min and 500 °C for 30 min with this concentration of silver. FTIR spectra of different sample shows the emergence of absorption peaks centered at2819.6cm $^{-1}$, 1797.3cm $^{-1}$, 1429.2cm^{-1}, 1088.3cm^{-1}, 906.2cm $^{-1}$, 876.7cm $^{-1}$, 790cm $^{-1}$.The peaks observed at 2819.6cm $^{-1}$ and 1797.3 cm^{-1} are identified which appeared at 500^{0}C[13]. A broad band at about 1429.2 cm^{-1} may be due to bending mode of -OH bond on plane. The peak around 1088.3 cm^{-1} corresponds to the TO vibrations mode of Si-O-Si asymmetric bond.[13] The peak at about 906.2 cm^{-1} is due to the asymmetric mode of Si-O-Ag bonds[14].The peak at 876.7 cm^{-1} is attributed to the formation of silver silicate[14]. The peak observed at 790.8 cm^{-1} is associated with symmetric Si-O-Si stretching or vibrational modes of ring structures[15].

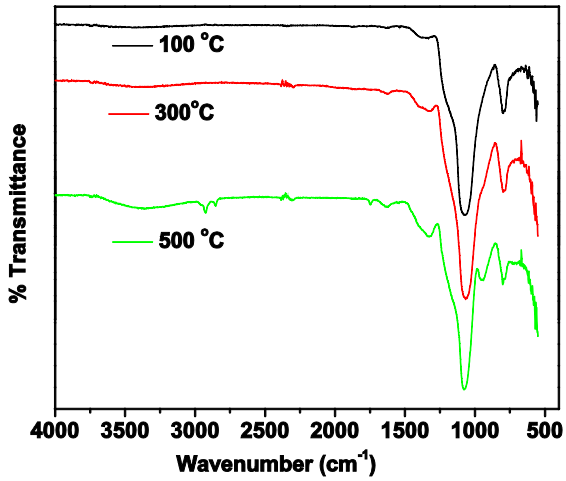

Figure 1 FT-IR spectra for silver nanoparticles in silica matrix annealed at 100° C, 300° C and 500° C.

3.2 Simultaneous Thermal Analysis (STA)

STA (DSC-TGA-DTA) curves of the dried gels at room temperature are displayed in Figures 2 (a), 2 (b) and 2 (c). As it is clear, the absorbed water, residual ethanol and other organic materials in the samples were evaporated at below 150°C with a weight loss of ~10%. A sharp exothermic peak near 100^{0}Cwas observed due to a evaporation of these organic components. Another weight loss area is seen in temperatures between 200-480°C with the amount of about 10% of weight loss attributing to the removal of the OH groups and burning of residual organic materials. Another exothermal peak near 480°C was observed due to a removal of nitrate groups and the weight loss was around 7%.

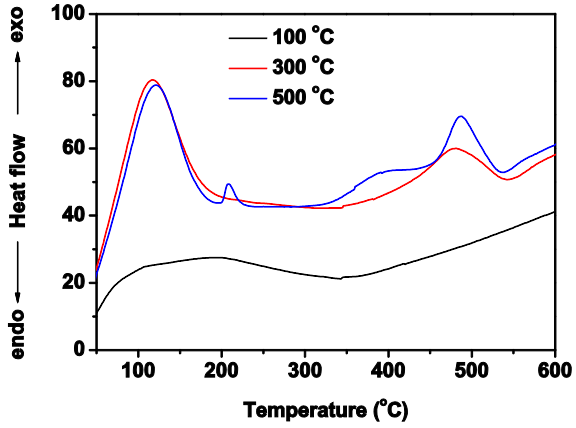

Figure 2 (a) DSC curves of the silver nanoparticles in silica matrix annealed at 100° C, 300° C and 500° C.

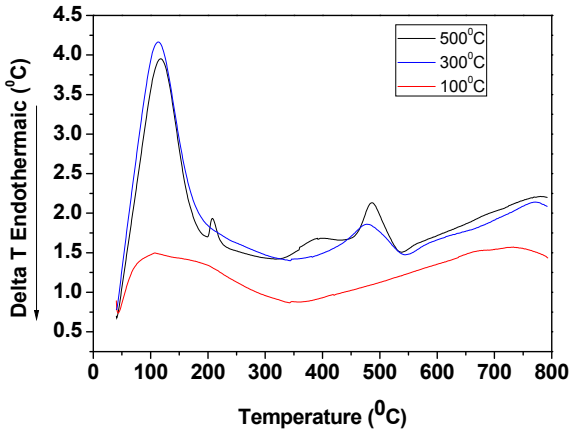

Figure 2 (b) DTA curves of the silver nanoparticles in silica matrix annealed at 100° C, 300° C and 500° C.

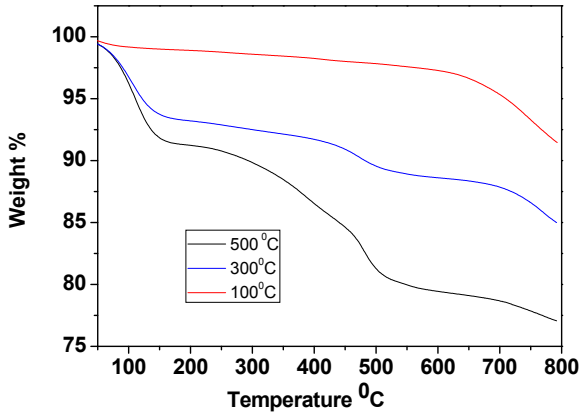

Figure 2 (c) TGA curves of the silver nanoparticles in silica matrix annealed at 100° C, 300° C and 500° C.

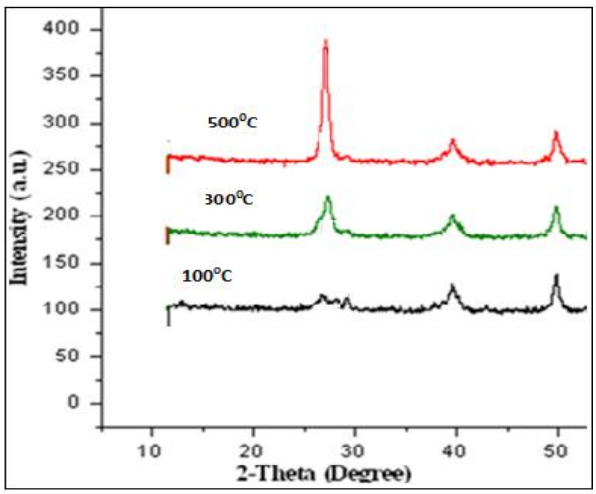

Figure 3: XRD pattern of the Silver doped samples annealed at 100^{0}C, 300^{0}C and 500^{0}C

3.3 XRD

The presence of silver metal in the silica matrix was confirmed by XRD analysis of samples. The XRD pattern of the 1000C dried samples showed a typical amorphous spectrum, and the spectra of all other samples starting from as 3000C and 5000C had sharp peaks that are characteristic of the silver crystals. The average crystalline size was found to be 10-20 nm. For all samples, diffraction peaks matches well with the standard Ag2O3 diffraction pattern and identified structure of Ag2O3 (JCPDS – Joint Committee Pattern of Diffraction System File: No. 40-0909). Structural studies were performed by using XRD technique demonstrated the existence of (111) oriented peak related to Ag2O3 as a dominated one as Polycrystalline in nature. The crystallite size (D) was calculated using the Scherer formula from the full-width at half-maximum (FWHM) (w):

$$D = 0.94\lambda/\beta \cos\theta \quad (1)$$

Where β is full width at half maximum (FWHM) in radians; θ is the Bragg angle at which the peak maximum occurs. λ is the wave length of X-ray radiation used for the study.

Discussion

The mechanism of the formation of silver-silica thin films is clear. In these investigations the authors found that different mechanisms for the interaction between silver and silica phases: Such as substitution of some Si elements in the silica structure by silver elements and physical trapping of elemental silver atoms in the silica matrix.

From these data, it is confirm that the substitution of Si atoms in the silica matrix by silver atoms occurs, but the transformation of silica network due to the Ag^+ ions in the FTIR data was observed. If there were any substitutions of the Si atoms by Ag atoms in the silica structure, a shift (700 cm^{-1} to 795 cm^{-1} at 500^{0}C) in FTIR peaks of Si-O-Si at would have appeared due to the difference in atomic radii of these 2 atoms. Since there is no shift in the pattern annealed at 300^{0}C of the Si-O-Si phase, it seems that the interaction between Si-O-Si and Ag phases is based on the physical trapping of the Ag phase in the Silica matrix. Thermal treatment at high temperature provides metal oxide peaks in this system. Peaks related to the silanol groups of SiOH–which are heat treated at lower temperatures, at 1797.3cm $^{-1}$and 2819 cm $^{-1}$ could be seen in similar systems[1]. It shows that all the SiOH phase is transformed to the SiO_2 phase. There is a peak at 1350 cm $^{-1}$ which is related to the H_2O groups but in some references[1] it also corresponds to Si-O-Si bonds. In similar systems which are heat treated at lower temperatures, there is another value band related to H-O-H deformation which interacts through hydrogen bonds with silanol groups[13]. This means that all of the SiOH phase is also converted to the SiO_2 phase. I.K. Battisha also demonstrated regarding the difference between pure silica and metal /oxide doped silica in their study[13]. It can be seen from their figures that the peak at 790 has appeared in the FTIR of silica due to the Ag doping. In the FTIR (Figure 1) this peak can be seen with higher intensity which is a result of thermal treatment of the coating at higher temperatures.

Looking at simultaneous thermal analysis, it is apparent that nitrate groups, organic components and residual water are removed by a heat-treatment of up to 300°C. The removal of OH group also shows the transformation of the SiOH phase to the Si-O-Si phase. Above 300°C (until 500°C), weight loss is low (<10%) and afterwards a relatively constant weight is achieved above 500°C. These results show that a treatment at temperatures around 300-500°C is suitable for removal of all excess ingredients and achievement of a high crystalline coating. Structural studies have been demonstrated the influence of silver concentration on crystal growth of Ag_2O_3 in their preferred (111) orientation. The humidity sensing of the silver nanoparticles in silica films on glass surfaces analysis are currently being investigated. The results will be published later.

Conclusion

Antibacterial and Hydrophobic coatings of silica on the glass substrates were synthesized by a single step sol-gel process by the dip coating method using TEOS as the precursor and H_2O as a co-solvent. The influence of various synthesis parameters and their effect on the film quality and hydrophobic properties were investigated. Uniform, strongly adherent coatings were obtained for a TEOS:C_2H_5OH:H_2O:$AgNO_3$molar ratio of1:14.14:.3. FTIR spectroscopy confirmed the presence of Si-O-Ag functional groups. Further, the as-deposited films are thermally stable, with only moderate hydrophobicity losses, up to a temperature of 300 ^{0}C. In summary, we have synthesized silver–silica nanocomposites having metal particle diameters in the range of 10 to 20 nm by controlling the microstructure of the crystalline phase grown within the silica matrix. This work nicely demonstrates the advantages of sol–gel methods for the preparation of thin films based on single-pot chemistry with a precursor. A generally useful strategy seems to choose deposition times in pre-gelation regime, where the solution viscosity is such that continuous and uniform films can be obtained. The same methodology could in principle also be used to develop spin coating techniques.

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