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Role of silver nanotube on conductivity, dielectric permittivity and current voltage characteristics of polyvinyl alcohol-silver nanocomposite film

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ABSTRACT

A comprehensive study on the prevailing conduction mechanism, dielectric relaxation and current voltage behaviour of Polyvinyl alcohol (PVA) – Silver (Ag) nanotube composite film has been reported. Introduction of Ag nanotubes enhances the conductivity and dielectric permittivity of film. Film shows semiconducting behaviour with two activation energies. The dc conductivity of the nanocomposite film obeys the adiabatic small polaron model. The dielectric permittivity can be analysed by modified Cole-Cole model. A non-Debye type asymmetric behaviour has been observed in the sample. The back to back Schottky diode concept has been used to describe the current-voltage characteristic of the composite film.

1. Introduction

Recently the synthesis of metallic nanoparticles embedded in insulating polymeric matrices has attracted much interest due to their potential application in electronic industries [1]. Electrical and optical properties of this polymer are controlled by proper doping with suitable dopants [2]. They are widely used in rechargeable batteries, electrodes, electromagnetic interference shielding (EMI), sensors, corrosion protection coatings, microwave absorption, LED, biomedical materials etc [3–7]. Through a careful examination we have selected PVA among different conducting polymers due to its simple synthesis procedure, thermal stability, low cost price, high mechanical strength, water-solubility, good environmental stability and dopant dependent electrical conductivity, good magnetic, chemical and optical properties [8–10]. The development of nanotechnology has allowed us to create new nanosized materials having unique electronic and optical properties [11]. The collective properties of nanoparticles are controlled by different research groups [12,13]. In recent years, there has been an immense interest in research area where metal nanoparticles are injected in a dielectric medium because of their novel characteristics. Polymers are very good host materials for metal and semiconductor [14] nanoparticles. Application of metal polymer nanocomposite has been discussed in many articles. Faupel et al. [15] have discussed the functional application of metal polymer nanocomposite. They have discussed about the dramatic change in the electronic properties, antibacterial coating and enhanced chemical potential due to large surface of nanoparticles. They have also discussed several approaches of preparation of metal polymer nanocomposite. Torrisis et al. [16] give a review on preparation of metal-polymer nanocomposite by co-evaporation and co-sputtering approaches and ultimately explain the electrical properties. Based on microscopic mechanism of different properties author correlates them with structure properties. Finally they have discussed the technological applications such as photovoltaic cells, sensor, energy conversion, flexible electronics and optoelectronics of those materials. Sanchez et al. [17,18] describe the critical review on applications of hybrid organic-inorganic nonmaterial. They have discussed general synthesis routes of hybrid materials for different applications like protective and decorative coatings, energy application like fuel cells, Li-batteries, photovoltaic device, optical sensors, human health care like cancer therapy, drug delivery, body care and cosmetics etc. Silver nanoparticles as filler are of current importance because of their good conductivity [19–21], unique optical, thermal, electrical properties, easy preparation process etc. Silver nanoparticles are widely applicable in surface Plasmon optics, photonics, photography, Raman scattering, catalysis, data storage device etc. So the study of PVA-Ag nanoparticles is necessary.

Many methods such as chemical reduction and radiolysis method have been applied for the synthesis of Ag-NPS [22,23]. Khanna et al. [24]. had prepared polyaniline-silver nanocomposite via in situ reduction of silver salt in aniline by mild photolysis and Choudhury [25] had also synthesized this type of sample by in situ chemical oxidation polymerization method. Fievet et al. [26] was first proposed Polyol process for the synthesis of submicrometer-sized metallic nanoparticles. Xia et al.

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[27] successfully developed this method to prepare single-crystal Ag nanoparticles with uniform size and shape by reducing silver nitrate with ethylene glycol (EG) in the presence of polyvinylpyrrolidone (PVP). Sun et al. [28] have also developed the polyol process to synthesize Ag nanotubes. Yu et al. [29] reported the synthesis of PVA-Ag nanocomposite films by in-situ reduction method. They have also reported that the films can be used as surface enhanced Raman scattering (SERS) active substrates. Mahendia et al. [30] have reported the electrical conductivity and dielectric constant of PVA-Ag nanocomposite films prepared by soft chemical route. They studied the effect of concentration of Ag nanoparticles in PVA matrix on conductivity and dielectric relaxation behaviour. Vimala et al. [31] have studied the application of chitosan-PVA-Ag nanocomposite films as anti-microbial packaging, wound dressing and antibacterial materials. They have reported that these films are potentially useful in preventing infections. But in this paper, we have prepared PVA-Ag nanocomposite film from PVA solution at 160 °C by chemical process.

In this work, we report the preparation and characterization of silver nanotubes and electrical transport properties of PVA-Ag nanotube composite film. The sample is characterized by XRD and FESEM. In this communication, we have studied the DC conductivity, temperature and frequency variation of dielectric constant and loss tangent, current density-voltage characteristic of PVA-Ag nanotube composite in the temperature range 303 $\leq$ T $\leq$ 423 K and in the frequency(f) range 20 Hz $\leq$ f $\leq$ 1 MHz.

2. Experimental details

2.1. Materials

Silver nitrate ($AgNO_3$, 99%), ethylene glycol (EG, 99.8%, molecular weight = 62.07), polyvinylpyrrolidone (PVP, molecular weight = 10,000) and polyvinyl alcohol (PVA, molecular weight = 89,000–98,000) were purchased from Sigma-Aldrich. All these materials and de-ionized water were used as received from market.

2.2. Materials preparation

At first, 10 mL EG was reflux in a two neck flask at 160 °C. After few minutes EG-$AgNO_3$ solution and EG-PVP solution in the molar ratio 1:6 were added simultaneously. The solution become gray in colour and reaction continued for 90 min at 160 °C. After that the solution was cooled to room temperature and centrifuged several times and dried to obtain Ag nanotubes [32]. In this case, $AgNO_3$ and PVP serve as the salt precursor and polymeric capping agent, respectively. EG acts as both solvent and reducing agent to generate metal colloids. Ag nanotubes are generated using a self-seeding process. In this type of Polyol process, initially silver ions are reduced to atoms, which in turn come together to form nuclei. As nuclei grow there is a possibility to form variety of seeds such as multiply twinned, singly-twinned, and single-crystal seeds [33]. According to Wiley et al. multiply twinned seeds grow to form nanorods and nanowires [34]. In this synthesis, once PVP and silver nitrate were simultaneously added into the reaction the chemical potential of silver ion would decrease and during the nucleation period the silver seeds generated more easily. After that multiply twinned nanoparticles (MTPs) of Ag are formed through homogenous nucleation with the assistance of PVP. The corresponding chemical reactions:

$$2HOCH_2{-}CH_2OH \rightarrow 2CH_3CHO + 2H_2O;$$

$$2CH_3CHO + 2AgNO_3 \rightarrow CH_3CO{-}COCH_3 + 2Ag + 2HNO_3.$$

These MTPs could serve as seeds for the subsequent growth of silver nanotubes. Immediately after formation of MTPs, PVP would selectively adsorb onto the side surfaces, as a result that side surfaces are become completely passivated, while end surfaces are still quite active [35]. Hence, the reduced silver atoms are preferentially deposited onto end surfaces of MTPs, leading to the 1D growth of silver nanotubes [32,36].

In the next step 1.2 gm of PVA was dissolved in deionized water at 353 K with continuous magnetic stirring. Then Ag nanoparticle (2 wt%) was dispersed in 10 ml deionized water and added drop wise into PVA solution under continuous stirring at room temperature. After that the PVA-Ag solution was poured on a Petridis and dried at room temperature for 5 days. A gray colour film of average thickness 0.11 mm was obtained.

2.3. Characterization technique

The crystalline behaviour of the sample was analysed with X-ray diffraction (XRD) study using Philips X-ray generator (PW 1830). The XRD data were collected in the scan range (2θ) of 30° - 90° at room temperature with copper K_α radiation source (λ = 0.1541 nm). Field emission electron microscope (FE-SEM, Carl Zeiss Sigma) was used to analyse the morphology of the synthesized silver nanoparticles and nanotubes. Thermogravimetric analysis (TGA) data for the polymer films were collected using Simultaneous Thermal Analyzer (STA 6000); under nitrogen flow at a heating rate of 10 °C/min. The FTIR spectra of the film were recorded on a Thermo Nicolet iS10 spectrometer in the range 4000–400 cm^{-1}.

To study the electrical properties of the film, take a small portion of the film of thickness 80 μm–170 μm and area (10 × 10) mm^2 and silver paste contact was applied to the opposite face of the samples and it behaves like a capacitor. Using Keithley 6514 electrometer we measure DC conductivity. To study dielectric properties we use Agilent E 4980A precision LCR metre. From the LCR meter we can directly obtain the parallel plate capacitance (C_p) and the loss tangent (tanδ) values. If 'd' is the sample thickness and 'A' is the electrode area, then the real ($\varepsilon^{/}$) and imaginary ($\varepsilon^{//}$) part of the dielectric permittivity can be expressed as $\varepsilon^{/} = \frac{C_p d}{\varepsilon_0 A}$ and $\varepsilon^{//} = \varepsilon^{/} \times \tan\delta$ respectively. ε_0 is the permittivity of free space.

The current-voltage characteristic is recorded using Keithley 2450 SMU equipped with KickStart software. Temperature variation of conductivity and dielectric response is done by high temperature cryostat in the temperature range 303–423 K.

3. Results and discussions

3.1. Characterization

The X-ray diffraction pattern of Ag nanoparticle is shown in Fig. 1, and matches with JCPDS file no. 98-002-1923. The five sharp peaks (2θ = 38.2°, 44.4°, 64.5°, 77.5° and 81.6°) in XRD patterns could be indexed to (111), (002), (022), (113), and (222) reflection lines of a cubic crystal of silver. The average crystallite size of Ag nanoparticles were estimated using Debye–Scherrer formula given by, $D = \frac{k\lambda}{\beta \cos(\theta)}$, where D is crystallite size, k is a dimensionless shape factor, β is FWHM and θ is the Bragg's angle. The average crystallite size of Ag nanoparticles found to be 20.26 nm. We have performed the Rietveld refinements of these X-ray diffractograms and the refined XRD pattern is shown as solid line in Fig. 1. The fitted curve matched well with the experimentally observed data and "goodness of fit" was observed as 1.3368 for the sample. Analysing the XRD pattern, it is observed that the lattice constant (a) of Ag is 4.094 Å which is very close to the reported data (a = 4.0860 Å, JCPDS = 98-002-1923).

Morphology of Ag has been obtained from FESEM micrograph. Fig. 2(a) represents FE-SEM image of Ag particles just after complete of addition of PVP and Fig. 2(b) shows FE-SEM image after 90 min reaction. It is observed from the figure that due to this synthesis procedure Ag nanotube of different aspect ratio (length: diameter = 14:1 to 44:1) has been obtained. When we add $AgNO_3$ into EG at 160 °C, Ag nanoparticles has been formed. However, simultaneous addition of PVP solution leads to uniaxial elongation into nanotubes [37]. Inset of Fig. 2(b) shows EDS micrograph which suggests that the nanotubes are made by Ag. The