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Influence of thin layer of silver nanoparticles on optical and dielectric properties of poly(vinyl alcohol) composite films

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ABSTRACT

A thin interlayer of silver nanoparticles (Ag-NPs) is embedded in a matrix of poly(vinyl alcohol)(PVA)films, and its influence on the microstructural, optical, and dielectric properties of 'Ag/PVA' thin films is investigated. As evidenced from atomic force microscopy studies, size of the deposited Ag-NPs clusters and surface roughness of the films decreased with an increase of annealing temperature. Optical and structural properties of 'Ag/PVA' nanocomposites were studied using UV-Visible spectroscopy and Confocal Raman spectroscope. The PVA/Ag nanocomposite films demonstrated lower optical band gap values than pure PVA films and the estimated optical band values of 'Ag/PVA' nanocomposite films decreased from 3.66 eV to 3.57 eV with the increase of temperature from 20 °C to 200 °C, respectively. The multi-layered 'PVA/Ag-NPs/PVA' films (MLTs) were fabricated and studied their dielectric properties as a function of frequency. The presence of Ag-NPs inter layer shows significant influence on dielectric and conductivity properties of MLTs. At room temperature in comparison to pure PVA, MLTs exhibited three times higher dielectric permittivity value at 1 kHz and observed to increase 5 times with an increase in temperature to the higher value of 200 °C. The evaluated dc conductivity value of MLTs increased from −11.72 to −10.38 S/cm on a logarithmic scale with an increase in temperature from 20 °C to 200 °C, respectively.

1. Introduction

In the current science and technology, metal – polymer nanocomposites (MPNCs) have been recognized as potential candidates in the both academia and industry [1–3]. In comparison to intrinsic metal oxide/noble metal multi-layers, MPNCs are of current interest due to their characteristic properties such as exceptional multi-functionality, potential for large-scale manufacturing, significantly lighter than metals and ease of synthesis [4–6]. MPNCs demonstrate combined organic and inorganic materials properties, which make them as suitable novel materials to employ in future based sensors, charge storage capacitor systems, electromagnetic shielding and microelectronic devices [7–13]. To fabricate MPNCs, the polymeric materials have been recognized as a promising host matrices for the incorporation of metal nanoparticles [14–16]. It is worth to mention that, preparing nanocomposite polymeric thin films with homogeneous dispersion of metal nano particles is the key challenge. Because metal nano particles easily agglomerate with each other due to their high surface free energy and this phenomenon of agglomeration leads to degrade the characteristic properties of MPNCs [17,18]. Nanoscale metal particles such as silver nano particles (Ag-NPs) signify the promising functional fillers due to their specific electronic, optical, magnetic, catalytic, and antimicrobial properties. Among the various polymers, polyvinyl alcohol (PVA) is a promising material due to its high dielectric strength, easy film formation, adhesiveness and whose properties can be controlled by dopant concentrations [19–21]. In addition, PVA is highly soluble in water, biologically friendly and the carbon chain backbone with hydroxyl groups has the ability to form a polymer nanocomposites by the incorporation of inorganic nanoparticles in the matrix of PVA [22,23]. Significantly, silver nano particles (Ag-NPs) doped PVA nanocomposites have been identified as potential candidates for electromagnetic shielding and charge storage capacitor systems [24–28].

The performance of MPNCs predominantly depends on size, concentration and distribution of additive nano particles through the matrix of polymers and type of preparation method [29–35]. The interface between the matrix of the polymer and embedded

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metal nanoparticles plays a prominent role to modify the frequency and temperature dependent response of dielectric properties of the host matrix. As a result of inclusion of metal nano sized fillers can enhance the effective dielectric constant of the polymer matrix due to occurrence of interfacial polarization [36]. In the present investigation, instead of following *in situ* synthesis of metal nanoparticles in the host of polymer matrix, a thin inter layer of Ag-NPs is introduced in inside of PVA matrix and studied its influence on microstructural, optical and dielectric properties of PVA matrix as a function of temperature. Pure PVA thin films were deposited on ITO coated glass substrates using conventional spin coating technique and a layer of Ag-NPs of thickness 200 nm was deposited on pre-deposited PVA thin film by using cold plasma polymerization process to prepare 'Ag-NPs/PVA' composite thin films. In the following sections, we discuss about the effect of embedded thin layer of Ag-NPs on microstructural, optical and dielectric properties of PVA film in the temperature range 20 °C–200 °C and in the frequency window of 10 mHz–10 kHz.

2. Experimental

The PVA powder of molecular weight of 89,000 to 98,000 and spherical shaped silver nanoparticles (100 nm–150 nm) were purchased from Sigma Aldrich and Plasma Chem GmbH (Berlin), respectively. In the present study, 5 g of PVA powder was dissolved in 100 ml of distilled water at 70 °C and followed by continuous mechanical stirring for 3 h to form a viscous solution. The 0.09% concentration of aqueous solution of silver nanoparticles was prepared using deionised water as a solvent. The pure PVA films were spin coated on ITO layer (of thickness 25 nm) coated glass substrates using spin coater at 2000 rpm and resultant thickness of PVA films was found to be 10 µm. A thin layer of Ag-NPs of thickness 200 nm was deposited on pre-deposited PVA films by using a home-built cold plasma polymerization (CPP) technique to prepare 'Ag-NPs/PVA' composite films. Cold plasma polymerization process was carried out in a cylindrical shaped plasma discharge chamber (5 cm diameter and 20 cm length), which was coupled to a container (which contains 0.09% concentration of aqueous solution of silver nanoparticles) through standard manifold with flux adjusted by a vacuum cock and mechanical atomizer. The discharge chamber consists of anode (Rogowski electrode) and hollow cylindrical cathode (negative Rogowski shape) and the diameter of the cathode is twice the diameter of anode, which were separated at a distance of 10 cm (as shown in Fig. 1). The DC source was connected across the two electrodes for the generation of plasma in the chamber and plasma discharge was initiated in argon atmosphere. During the deposition process, the optimized working pressure of 1×10^{-1} Torr and glow power of 30 W were maintained to deposit 200 nm thickness of thin layer of silver nano particles on "PVA/ITO/glass" substrates by introducing them at exit of the cathode in downstream plasma to obtain 'Ag-NPs/PVA' composites films. As described in Fig. 2, the resultant two 'Ag-NPs/PVA' composites films were attached with each other to prepare 'ITO/PVA/Ag-NPs/PVA/ITO' cells, which are employed for impedance measurements. The temperature of the resultant composite films was varied from 20 °C to 200 °C to understand the influence of thin layer of Ag-NPs on their microstructural and optical properties.

To study the surface morphological features of the films as a function of temperature, atomic force microscopic studies were carried out in non-contact mode (AFM, Nano Focus, MOD-1 M Plus) with tip size of 10 nm. Raman spectra of the samples were recorded in the wavenumber range 200–2000 cm^{-1} using Horiba Jobin Yvon, Lab Ram HR-800 Confocal Raman spectrometer and source of ND: YAG laser (1064 nm). The optical absorption spectra were recorded in the wavelength range 300–1000 nm using

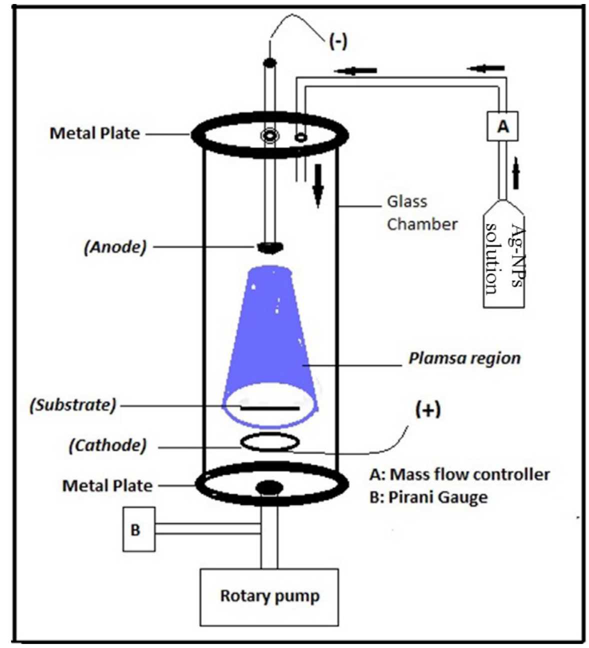

Fig. 1. Schematic representation of cold plasma polymerization deposition system.

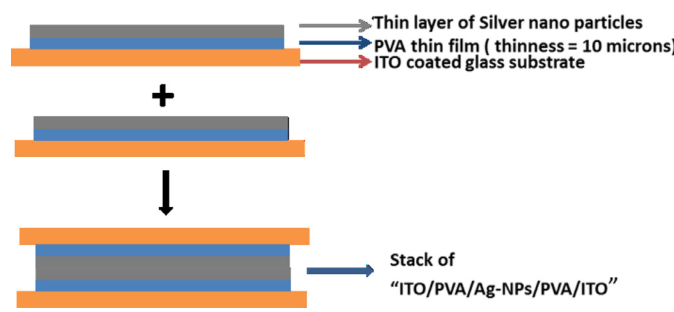

Fig. 2. The schematic illustration of fabrication of stack of "ITO/PVA/Ag-NPs/PVA/ITO".

a Cary 5 UV–VIS-NIR double beam spectrophotometer by Varian. The Ag-NPs/PVA composite films were sandwiched between two ITO electrodes of sheet resistance 100 Ω/Square to make a "ITO/PVA/Ag-NPs/PVA/ITO" structured cell (MLTs) (as illustrated in Fig. 2) and EG&G 273A galvanostat-potentiostat/impedentiometer controlled by the impedance software M398 was used to measure the real and imaginary parts of impedance in the frequency range of 10 mHz–10 kHz with a maximum applied voltage of 1.4 V (RMS). The dielectric measurements were performed as a function of temperature by placing resultant cell in a CaLCTec FB150 programmable temperature hot stage by varying the temperature in the range 20 °C–200 °C. The Havriliak–Negami (H-N) relation in addition to the power law [37] is adapted to fit the dielectric spectroscopy data to understand the influence of inter layer of Ag-NPs as a function of temperature on frequency dependent dielectric parameters of PVA matrix such as dielectric strength, relaxation time and conductivity values.

3. Results and discussion

3.1. Microstructural properties

Fig. 3 illustrates the modifications in surface morphological features of 'Ag-NPs/PVA' composite films as a function of annealing temperatures. The formation of large number of clusters of silver