



## Communication

# Effect of trap states and microstructure on charge carrier conduction mechanism through semicrystalline poly(vinyl alcohol) granular film

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## ABSTRACT

We report a comprehensive study on hysteresis behaviour of current-voltage characteristic and impedance spectroscopy of granular semicrystalline poly(vinyl alcohol) (PVA) film. The charge carrier conduction mechanism and charge traps of granular PVA film by measuring and analyzing the temperature dependent current-voltage characteristic indicate a bi-stable electronic state in the film. A sharp transformation of charge carrier conduction mechanism from Poole-Frenkel emission to space charge limited current mechanism has been observed. An anomalous oscillatory behaviour of current has been observed due to electric pulse effect on the molecular chain of the polymer. Effect of microstructure on charge transport mechanism has been investigated from impedance spectroscopy analysis. An equivalent circuit model has been proposed to explain the result.

## 1. Introduction

Recently, semiconducting polymer films have attracted a great attention due to their potential applications such as resistive random access memories (RRAM) [1,2], organic field effect transistor [3], organic light emitting diode [4]. High molecular semicrystalline polymers such as polyvinyl alcohol (PVA), polyvinylidene fluoride (PVDF), polyethyl methacrylate (PEMA), polymethyl methacrylate (PMMA), chitosan etc. [5,6] becomes interesting polymers in the field of electronic devices. Poly (vinyl alcohol) is a semicrystalline, water soluble, synthetic polymer. PVA can be widely used due to its low cost, easy film forming properties and good electrical properties [7–9]. From the concept of polymer stereochemistry, PVA has three alternatives for the relative configuration of stereocenters along the main carbon chain which are isotactic, syndotactic and atactic [10]. For isotactic PVA, hydroxyl groups are arranged in same side of the main carbon chain. For syndotactic PVA, hydroxyl groups are regularly arranged. The hydroxyl groups are randomly placed in left- and right-hand position of main chain for atactic PVA. Yao et al. [11] and Hu et al. [12] used PVA as an electrolyte for super-capacitor application. Gallo et al. [13] used PVA as a binder for battery application. Sun et al. [14] found that the resistive switching behaviour of PVA/graphene oxide blend was significantly improved. To apply semiconducting polymer materials as electronic devices, it is important to understand the basic physics behind the changes of internal

properties of polymer with the application of external electric field and also conduction mechanism of the charge carriers. The permanent electric dipoles in the polymeric materials play an important role for exhibiting multifunctional properties [15–17].

In this work, we have studied the current-voltage (I-V) characteristics and clearly explain the role of the trap states on charge transport mechanism under different experimental condition. We also try to explain how the carrier conductivity changes with the change of inter-molecular distance by successive current-voltage loop study. We also formulate an equivalent circuit to study the grain and grain boundary contribution in semicrystalline PVA film.

## 2. Experimental

PVA (Molecular weight = 89,000–98,000, Sigma-Aldrich) film has been prepared by using solution casting method [18]. First, PVA was dissolved in deionized water at 353 K by continuous magnetic stirring and we find a transparent solution of PVA. The solution poured into a glass Petri dish and dried for 5 days in a controlled environment. After drying, the samples were peeled off from Petridis and take a small portion of 0.12 mm average thickness and  $8 \times 10 \text{ mm}^2$  area. The current-voltage characteristics were recorded using Keithley 2450 SMU equipped with KickStart software in the temperature window of  $300 \leq T \leq 413 \text{ K}$ . For impedance spectroscopy, we used Agilent E 4980A precession LCR meter

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in the frequency range of  $50 \text{ Hz} \leq f \leq 2 \text{ MHz}$ . The details experimental technique is given in the previous work [19].

### 3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern of PVA film which was taken with a PANalytical Xpert Pro MPD diffractometer. The XRD pattern shows a sharp maximum at  $2\theta = 19.6^\circ$ , a shoulder at  $2\theta = 22.9^\circ$  and a small peak at  $2\theta = 40.4^\circ$ ; which indicates the crystalline nature of PVA [20]. According to Bunn [21,22], in the case of PVA, hydroxyl groups may randomly place in left- and right-hand positions without affecting the crystallinity of the polymer. Inset of Fig. 1 shows high-quality field emission SEM (FESEM) images of PVA film at various magnifications. The higher magnified image clearly shows the spheroid shaped grains of PVA and the grains are uniformly distributed. Basically, the presence of humidity takes an important role for crystallization of PVA from the gel. The slow drying process of PVA at ambient humidity and temperature resulting in spheroid shaped grains. The grain diameter distribution histogram shows in inset of Fig. 1. Now we calculate the mean grain diameter by considering a log-normal distribution function:

$$f_D(x) = \frac{1}{\sigma x \sqrt{2\pi}} \exp\left(-\frac{(\ln x/x_c)^2}{2\sigma^2}\right), \quad (1)$$

where  $x_c$  is the median diameter and  $\sigma$  is the corresponding standard deviation. The fit is for median grain diameter  $x_c = 24 \pm 0.5 \text{ nm}$  with standard deviation  $\sigma = 0.26 \pm 0.03$ . The surface roughness of the PVA film is found to be  $46.1 \text{ nm}$  (see supplementary material). The high value of roughness implies the larger grain size within the film. Structural disorder and surface defect are the main origins of trap states within the semicrystalline materials [23]. Large grain size and presence of trap states play an important role in the charge conduction mechanism through the film.

Fig. 2 depicts temperature dependent hysteresis behaviour of PVA film in a voltage sweep circle of  $-60 \text{ V} \rightarrow 0 \rightarrow +60 \text{ V} \rightarrow 0 \rightarrow -60 \text{ V}$ . The area of the hysteresis loop slightly increases with the increase in temperature. This implies an increment of charge storage capacity and bistable electronic states in the film. When we increase the applied voltage, due to spontaneous polarization of PVA molecule the overall current of PVA film increases (low resistance state). But during the decrement of applied voltage, spontaneously polarized molecules are not

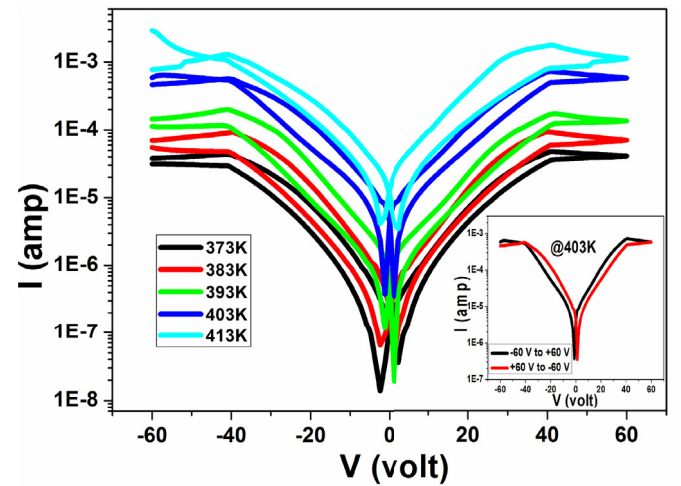


Fig. 2. The current – voltage characteristic of PVA film at different measuring temperature. The inset figure clearly describes the forward and backward current – voltage characteristic at 403 K.

able to back its original state. At this time the viscous force between grain boundaries may hinder the molecular motion, so the conductivity of the film decreases (high resistance state). In both cases the pinpoint of current value is not observed at 0 V due to the induced field within the film, originating from trapped space charge [24]. In order to determine the effect of spontaneous polarization of permanent dipoles within the film, we have studied the variation of polarization with the electric field and find a hysteresis behaviour (see supplementary material).

In our previous work [18], we reported the activation energies ( $E_a = 0.39 \text{ eV}$  for 303–373 K and  $E_a = 0.55 \text{ eV}$  for 373–423 K) of pure PVA film which are within the limit of electronic conduction ( $E_a \leq 0.8 \text{ eV}$ ) suggested by Jonscher [25]. So, for pure PVA film electrons are the dominated charge carriers for transport mechanism. Now with increase in temperature, the phonon density within PVA system increases which can create electron-hole pair that also take part in charge carrier transport [26]. In order to explain the carrier transport mechanism, the nonlinear I-V curves were fitted using different conduction models such as thermionic emission, Poole-Frenkel (PF) emission, Fowler-Nordheim (FN) tunneling and space charge limited conduction (SCLC). In this case, temperature dependent highly symmetric I-V characteristic giving evidence that the charge transport mechanism through the film is not dominated by thermionic emission and Fowler-Nordheim tunneling. The goodness of fitting ( $R^2$ ) is in the range 0.92817–0.99913. The highest goodness of fitting ( $R^2 = 0.99913$ ) is observed only for Poole-Frenkel emission model. So, we take Poole-Frenkel emission model to explain the effect of trap state on the charge transport mechanism. It is observed that in voltage increasing step up to 40 V and in decreasing step, current density follows Poole-Frenkel (PF) model as shown in Figs. 3(a) and 4, respectively. The corresponding PF equation can be expressed as follows [27],

$$J_{PF} = q\mu N_c E \exp\left(-\frac{q(\varphi_T - \sqrt{qE/\pi\epsilon_r\epsilon_0})}{k_B T}\right), \quad (2)$$

where  $q$  is the electronic charge,  $\mu$  is the electronic drift mobility,  $N_c$  is the density of state in the conduction band,  $q\varphi_T$  is the height of trap energy level,  $\epsilon_0$  is the permittivity in vacuum,  $\epsilon_r$  is the optical dielectric constant and  $k_B$  is the Boltzmann's constant. This PF emission involves bulk limited conduction mechanism which depends on the trap energy level and dielectric properties of the film itself. The effect of porosity and effective conjugation length of PVA affect the position of highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit

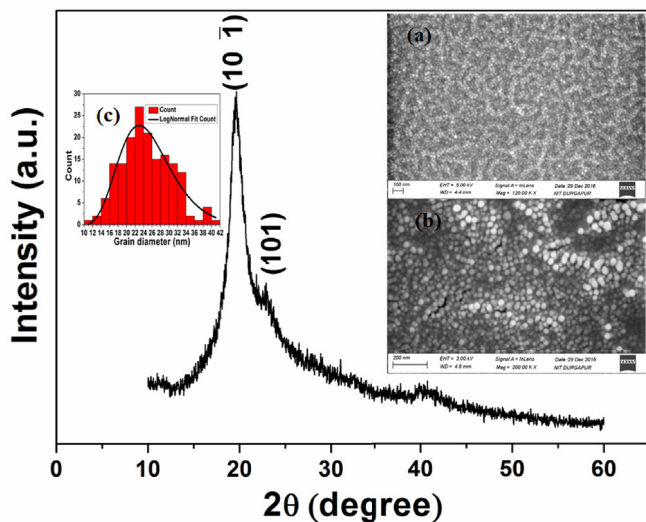


Fig. 1. The X-ray diffraction pattern of pure PVA film. The inset figure (a) and (b) show the FE-SEM images of the film and (c) show the histogram for particle size distribution.

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