Available online at www.sciencedirect.com

Materials Letters 60 (2006) 1099 – 1105

materials letters

www.elsevier.com/locate/matlet

Comparison of solid state studies and electrochemical behavior of poly (dimethylsilane) and poly (dimethylstannum) film electrodes

M. Elangovan, A. Muthukumaran, M. Anbu Kulandainathan *

Electro Organic Division, Central Electrochemical Research Institute, Karaikudi-630 006, India

Received 6 August 2005; accepted 24 October 2005
Available online 15 November 2005

Abstract

Poly(dimethylsilane) (M. Wt. 2175) and poly(dimethylstannum) (M. Wt. 2650) have been successfully synthesized by electrochemical polymerization of dichloro-dimethylsilane and dichlorodimethylstannane, respectively, in a single-compartment cell equipped with aluminium electrodes in tetrabutylammonium tetrafluoroborate in dimethoxyethane as the supporting electrolyte. Thin films of the above polymers with a thickness of about 50–60 μm were prepared by physical vapor deposition technique. Si–Si and Sn–Sn catenations have been determined using Fourier Transform-Infrared spectroscopy, Nuclear Magnetic resonance spectroscopy and Ultraviolet-visible spectroscopic studies. Cyclic voltammetric measurements of the polymer thin film electrodes show the reduction peak of the polymers and give reversible response for the Fe^{3+} /Fe^{2+} redox couple. Impedance studies at different cathodic potentials clearly indicate that both the polymers behave like capacitive nature at less negative potentials and behave like a charge transfer carriers at more negative potentials. Mott–Schottky plot for these polymers reveal that the polymers are semi conducting nature of narrow band gap with high carrier densities and are p-type carriers.

Keywords: Electrochemical synthesis; Polysilanes; Polystannane; Physical vapour deposition; Impedance study

1. Introduction

Polysilanes consisting of Si–Si σ bonds are synthesized using the most general method, the Wurtz coupling reaction of organo dichlorosilanes with alkali metals [1]. However this approach has several disadvantages such as controlling the unit-structure, molecular weight, polymerisation of monomers possessing functional groups and difficulty in controlling the dispersity of the polymers [2]. The yield of polymers is also usually low and alkali metal reduction does not seem to be easily industrialized on a large scale because of the risk of involvement of alkali-metals and high reaction temperature in the case of Na and K. To circumvent various setbacks mentioned in the Wurtz type synthesis, several novel methods have opened new approaches to the synthesis of structure-ordered polysilanes, which are essential to the further development in the polysilane chemistry [3]. Recently, it has been demonstrated that compound with Si–Si bonds are produced in good yields by the electrolytic reduction of dichlorosilanes in an undivided cell using a sacrificial metal anode such as mercury, aluminium, magnesium, silver and copper or using hydrogen electrodes [4–6]. Poly(methylsilane) and poly(cyclohexylsilane–co–methylsilane) network copolymers were prepared by the electrochemical reduction of methyltrichlorosilane, or a mixture of the monomers methyltrichlorosilane and cyclohexyltrichlorosilane, utilizing copper electrodes. This poly methylsilane is proposed as potential soluble precursor for SiC [7]. Polygermane and Germane-silane copolymers also were prepared electrochemically using magnesium electrodes. These polymeric materials have promising physical properties such as semiconductivity, photoconductivity, photoluminescence and third order non-linear effects [8].

There has been a great deal of interest in the synthesis and application of various luminescent compounds of silicon, particularly polysilanes because of their unique aspects regarding spatial confinement and dimensionality [9–13]. Organosilicon polymers comprising Si–Si bonds have attracted much attention because their potential applications as functional polymers

---

* Corresponding author.
E-mail address: manbu123@yahoo.com (M. Anbu Kulandainathan).

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.10.083

and their unusual electric and photo electronic properties, which have been attributed to the delocalization of σ-electrons [14]. Yamabe and co-workers [15] have investigated theoretically the relationship between the structure of organosilicon polymers and the band gap energy. They predicted that a hypothetical polymer consisting of Si–Si single bonds and C–C double bonds alternately would have the lowest band gap energy. Therefore, many types of organosilicon polymers comprising Si–Si bonds have been prepared, and their potential as conducting polymers has been investigated [16–19].

Increasing attention has also been directed towards synthesizing organosilicon compounds and their photo luminescence as well as the possibility of making efficient room-temperature light emitting devices [12]. Photo luminescence is important not only to understand the origin but also to make efficient opto-electronic devices [20]. The polysilane polymers will be more promising in view of their ease with which uniform films with good mechanical and electronic properties can be fabricated in large area. The development of such polymer is technologically important for a variety of application such as flat screen, full color displays, light emitting diodes, color-based chemical sensors etc. [21].

Till recent times, many physical properties have been reported for the organo polysilanes. For example, they are considered to be direct-allowed-gap semiconductors, and show an efficient photoluminescence. Organo functional polysilanes like Poly (dimethylsilane) have one dimensional silicon backbones and hence has the future for application in electronic and optical devices. However, only few papers have reported data for this material [22–25]. Wilson et al., [26] have studied the pyrolysed silicon-containing polymer film electrodes as high capacity anodes for lithium–ion batteries.

Poly (dimethylsilane) has the smallest side group among polysilane groups and all-trans rigid conformation at room temperature. Moreover, the crystal and electronic structures have also been known [27]. Poly (dimethylsilane) has been considered to be the most suitable material for investigations on oriented polymer materials. Evaporated films have been used as electrodes as there is no good solvent for the polysilane polymers [25] and hence physical properties of poly (dimethylsilane) have not been well examined.

Similarly, polystannanes have attracted much attention of many researchers [28], because heavier atoms in the backbone of σ-conjugated polymers are expected to give larger σ-conjugation, narrower band gaps and more metallic characters [29]. Polystannanes are used as antifouling paints on ships and offshore oil platforms. Poly (dimethylsilane) and Poly (dimethylstannum) are the most fundamental materials of organo metallic polymers.

The present work deals with the systematic study involving the electrochemical synthesis of poly(dimethylsilane) and poly (dimethylstannum), and their characterization towards optical and electrochemical properties. The films of the above materials have been prepared on ITO glass by physical vapour deposition technique and they have been characterized using spectral and electrochemical methods [30–32].

2. Experimental

2.1. Electrochemical synthesis of polymers

Constant current electrolysis was performed in a 30 ml single compartment cell equipped with spectroscopically pure aluminium rods as the cathode and anode. 0.4 M tetrabutylammonium tetrafluoroborate in dimethoxyethane was used as the supporting electrolyte. Before adding the starting material to the supporting electrolyte (0.08 M dichlorodimethylsilane for polysilane and 0.08 M dichloro-dimethylstannane for polystannum) dry nitrogen gas was purged into the cell to eliminate the dissolved oxygen. The current density for electroploymerisation was 4.5 mA/cm^2 and the charge consumed for the reaction was 2F/mol. After electrolysis, the solution was concentrated to half the original volume under reduced pressure and poured in to 300 ml of methanol. The polymer was precipitated in methanol leaving TBATFB in solution. The separated polymer was re-dissolved in 50 ml of toluene and again precipitated by adding methanol. Such a dissolution and precipitation procedure was repeated thrice. Finally the collected polymer was dried in vacuum. The resulting polymers were characterized by Gel permeation chromatograph (GPC), UV-Vis, FTIR and ^{1}H-NMR spectroscopic analysis [33].

2.2. Polymer film preparation

The molecular weight of the poly (dimethylsilane) and poly (dimethylstannum) powder using GPC analysis were found to be 3556, 4280, respectively. The polymer thin film was prepared by physical vapor deposition (PVD) method. First, the source powder and various substrates (tin oxide coated glasses and slide glasses) were set on a molybdenum evaporator and a substrate holder, respectively, in the vacuum chamber. Then, the chamber evacuated to about 10^{-6} torr using rotary pump and diffusion pump. After evacuation, the substrates were heated from 300 to 670 K and by applying an AC current of tens of amperes the powder was evaporated. The thickness of the obtained film was about 50–60 μm. The similar procedure was followed for the preparation of poly (dimethylstannum) film [34].

2.3. Spectral and electrochemical analysis

Identification of polymers was carried out by comparing their properties with the reported values. Poly(dimethylsilane) and poly(dimethylstannum) were identified using GPC(Shimadzu, LC-6A,Japan), UV (Hitachi,V-3400,Japan), FT-IR (PerkinElmer,Paragon-500,England) and 1H-NMR (BRUCKER,350 MHz,Japan) spectral techniques. UV spectra were measured in tetrahydrofuran unless otherwise noted because it dissolves variety of polysilanes. FT-IR spectra were measured after mixing with KBr. 1H-NMR spectra were measured in $CDCl_3$. Molecular weights were determined by gel-permeation chromatography relative to polystyrene standard. Films were characterized electrochemically using cyclic voltammetry and impedance techniques. Mott–Schottky analysis was carried out for measuring flat band potential and band gap energy. For all electrochemical studies, a three-electrode configuration was followed. The film-working electrode was inserted into the solution only so far as to cover the disk region. A platinum foil was used as an auxiliary electrode and a saturated calomel electrode was used as the reference. All electrochemical measurements were carried out using BAS-ZAHNER make, IM6 model electrochemical analyser. The electrolyte was 0.1 N KNO_3 aqueous solution except in the case of redox response where 0.1 N KNO_3 aq. solution containing 2mM $K_3[Fe(CN)_6]$ was used. Nitrogen gas was purged before starting each experiment. Complex impedance analysis of the film was measured under different potentials from OCP to cathodic potential in the frequency range of 1 mHz to 100 kHz with an ac amplitude of 5 mV.

3. Results and discussion

3.1. Polymer characterisation

A typical spectrum of poly(dimethylsilane) is shown in Fig. 1a. It exhibits absorption band at 2962 and 2872 cm^{-1}, which can be attributed to CH_3 group stretching. The peak at 1412 cm^{-1} is characteristic of the asymmetric bending mode of CH_3 bonded to silicon. The peak at 882 cm^{-1} is due to Si–CH_3 vibration. Peaks at low wave numbers 697 cm^{-1} for Si–C stretching and 525 cm^{-1} are typical for Si–Si in plane vibration for these polysilanes. The absorption at 3410 cm^{-1} may be due to the moisture absorption by the starting material. In the spectrum Si–Cl (662 cm^{-1}) is completely absent (which was very well present in the monomer) and it clearly indicates that the formation of Si–Si catenation in the main chain of the poly(dimethylsilane).

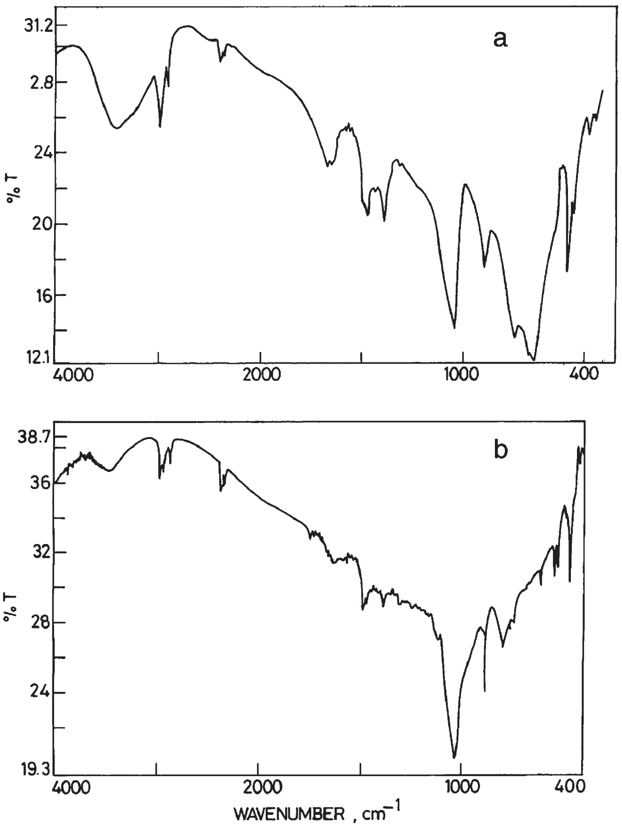

Fig. 1. FTIR spectra of the powder samples of a) poly (dimethylsilane) b) poly (dimethylstannum).

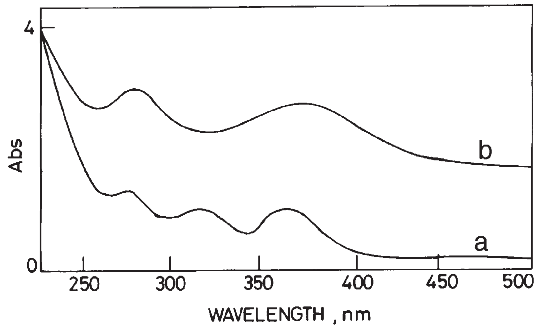

Fig. 2. UV-Vis absorption spectra of the powder samples of a) poly (dimethylsilane) b) poly (dimethylstannum).

Similarly Fig. 1b shows that the poly(dimethylstannum), it exhibits absorption bands at 2960 and 2874 cm^{-1} which are attributed to CH_3 group stretching. A characteristic band at 1860 cm^{-1} is attributed to Sn–H. Peaks at 1482 and 1362 cm^{-1} are characteristics of the asymmetric and symmetric bending modes, respectively, of the CH_3 bonded to stannum in the polymer backbone. The absorption band at 740 cm^{-1} is attributed to Sn–C stretching and at 598 cm^{-1} it exhibits presence of Sn–Sn main chain in the polymer backbone. Poly(dimethylstannum) is extremely sensitive to air, so the peak at 3432 cm^{-1} may be due to the absorption of moisture. Sn–Cl (671 cm^{-1}) absorption band is completely absent (which very well present in the monomer) and it clearly indicates the formation of Sn–Sn main chain in the poly(dimethylstannum) [20,35].

Polysilanes are different from all other high molecular weight polymers, which exhibit sigma electron delocalisation. It is observed that polysilanes show UV-visible absorption maxima ranged between 280–350 nm, due to the electrons excitation from ó valence band to σ^* conduction band [36–39]. The electronic spectra of poly (dimethylsilane) in THF (Fig. 2a) exhibits two absorption peaks at 315 and 375 nm. The absorption peak at 315 and 375 nm are attributed to the presence of Si–Si main chain of trans and gauche states, respectively [38].

Similarly the electronic spectra of poly(dimethylstannum) (Fig. 2b) exhibits two absorption peaks at 370 and 290 nm. The absorption peak at 370 nm is attributed to presence of Sn–Sn main chain in the polystannane polymer backbone. The absorption peak at 290 nm indicates the presence of fewer amounts of oligomers formed in this procedure [35].

^{1}H-NMR spectra (Fig. 3a), poly(dimethylsilane) shows characteristic chemical shifts (CDCl3) near δ 0.04,1.09, 1.4, and 3.5 ppm. These chemical shifts have been predicted for the above polymer (Si–CH_3, methyl proton, Si–Si Chain and Si–CH–). The results of the ^{1}H-NMR are consistent with this prediction. Since ^{1}H-NMR chemical shifts for silicon with methyl substituents, can be observed in the range of 0–0.4 ppm, the peak observed near δ 0.04 ppm is assigned to Si–CH_3 group. The peak observed near δ 1.09 ppm, δ 1.4 ppm and δ 3.5 ppm are assigned to methyl proton, Si–Si catenation and Si–CH-groups, respectively [4,42–44].

Similarly ^{1}H-NMR spectrum (Fig. 3b) of poly(dimethylstannum) shows chemical shifts ($CDCl_3$) near δ 0.04 ppm is assigned to Sn–CH_3 group. The peaks observed near δ 1.03, 1.148, 1.807 and 3.23 ppm are assigned to the methyl proton, Sn–Sn catenation, Sn–H, and Sn–CH groups, respectively.

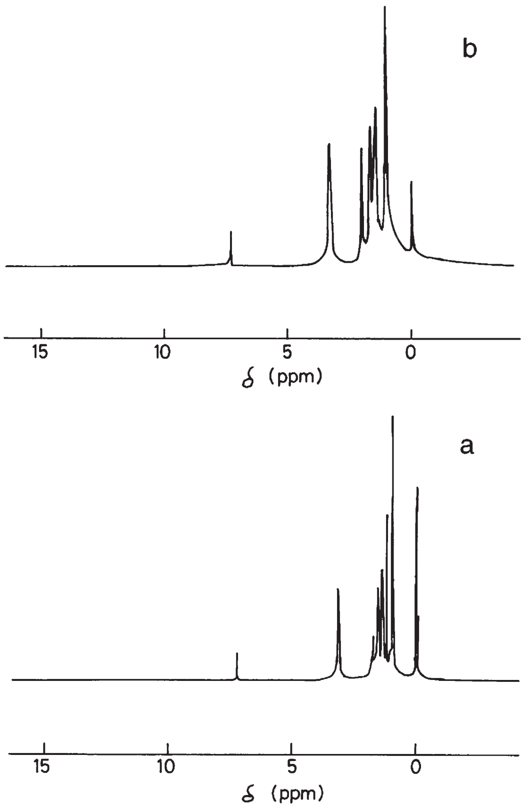

Fig. 3. H[1] NMR spectra of the powder samples of a) poly (dimethylsilane) b) poly (dimethylstannum).

3.2. Polymer film characterization

Fig. 4a shows the Uv-vis-NIR absorption spectra of poly (dimethylsilane) film prepared by PVD method. The band at 562 nm is attributed to the presence of Si–C main chain in the polymer backbone. The longer absorption band at 942 nm is attributed to the presence of Si–Si main chain in the polymer backbone. Similarly the poly (dimethylstannum) film (Fig. 4b) was analysed between the same region which shows the peak at 516 nm is attributed to the presence of Sn–CH_3 in the polymer backbone. The longer absorption band at 898 nm in the NIR region, may be due to σ–σ^* electron transition in Sn–Sn main chain in the polymer backbone [30,33,35,39–41].

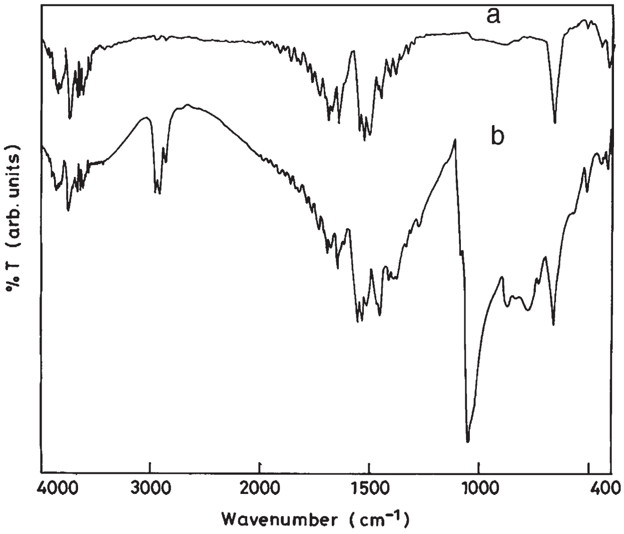

Fig. 5. FTIR spectra of the film electrodes of a) poly (dimethylsilane) b) poly (dimethylstannum).

Fourier Transform Infra Red Spectral measurements for poly (dimethylsilane) film prepared by the PVD method is presented in Fig. 5a. It shows specific absorption bands at 475 cm^{-1} implies the presence of Si–Si catenation in the main chain and at 943 cm^{-1} corresponds to the presence of Si–CH_3 bond. The peak at 625 cm^{-1} (Si–Cl) is completely absent which results in the formation of Si–Si catenation [35]. Similarly Fig. 5b shows the FTIR spectrum of poly (dimethylstannum), it can be seen from the figure that the absorption at 492 cm^{-1} is attributed to Sn–Sn main chain in the polymer backbone. The absorption band at 533 cm^{-1} is attributed to presence of Sn–CH_3 in the polymer backbone. Absorption band at 671 cm^{-1} (Sn–Cl) is absent which clearly indicates the formation of Sn–Sn catenation [20].

XRD — profile of poly (dimethylsilane) film is shown in Fig. 6a. From the pattern, it is clear that the polymer has a semi crystalline nature, whereas poly (dimethylstannum) (Fig. 6b) is more crystalline in nature. It indicates the uniaxially oriented thin film of poly (dimethylsilane) has an all-trans conformation. In that case, the diffraction peaks, related to the trans period, do not appear on the small-angle side, because the trans period is relatively small [25].

Scanning electron micrographs of poly(dimethylsilane) and poly (dimethylstannum) films clearly show that poly(dimethylsilane) film has uniform crystalline particles over the surface with an increasing

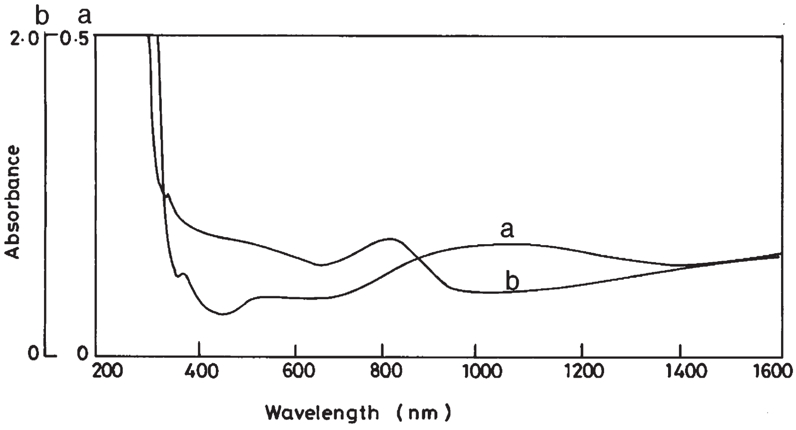

Fig. 4. UV-Vis absorption spectra of the film electrodes of a) poly (dimethylsilane) b) poly (dimethylstannum).

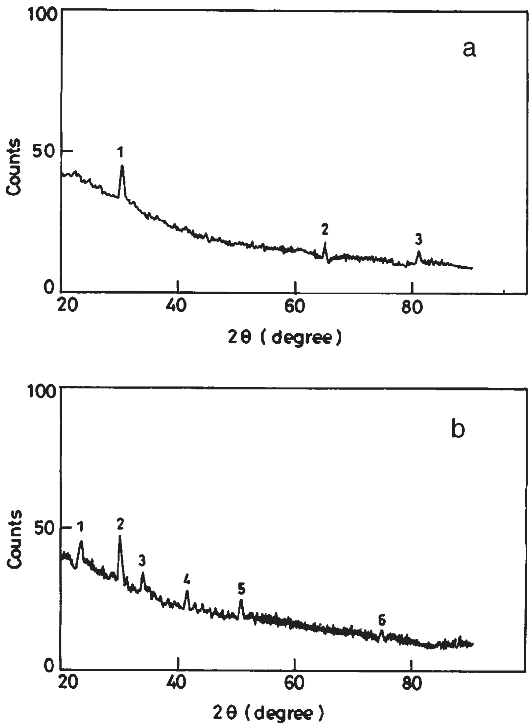

Fig. 6. XRD diffraction spectra of the film surface a) poly (dimethylsilane) b) poly (dimethylstannum).

deposition rate and are homogeneously distributed over the polymer, whereas in the case of poly(dimethylstannum) film, crystalline particles are randomly oriented and are highly adsorbed on the surface of the substrate [45,46].

3.3. Electrochemical characterisation of the films cyclic voltammetry

In deaerated 0.1 N KNO_3 aqueous solution, cyclic voltammogram at poly (dimethylsilane) film electrode (Fig. 7A) shows a reduction peak at −0.65 V vs SCE, which may be due the reduction of silicon present in the polymer film. Fig. 7B shows voltammograms of the ferri-/ferrocyanide couple in 0.1 N KNO_3 at the above film electrode. It clearly indicates a more reversible peak for the ferri/ferrous redox couple with almost 60 mV peak differences for the anodic and cathodic peaks. This result clearly indicates that the carrier density at the polysilane film is fairly high and is in general, accord with the conductivity of the electrode surface [24,25]. Similarly, Fig. 8A shows the cyclic voltammogram of the poly (dimethylstannum) film electrode, which clearly indicates the reduction peak at −0.8 V vs SCE and anodic peak at −0.43 V vs SCE. This may due the phase formation at the film surface [4]. This electrode also shows very similar behavior for the ferri/ferrous redox couple (Fig. 8B).

3.4. Impedance measurements

Poly (dimethylsilane) film was subjected to impedance measurements at various applied potentials in 0.1 N KNO_3 aq. solutions under deaerated condition. Potentials were fixed as a) open circuit potential (−50 mV vs SCE) b) −400, c) −600 and d) −800 mV vs SCE. It can be seen from the Fig. 7C, at OCP and less negative potentials the electrode behaves capacitive in nature by showing the very high increase in parallel to imaginary axis. But at higher negative potentials viz., −800 mV vs SCE a semi-circle behavior can be seen. This behavior corresponds to a charge-transfer controlled process [47]. This similar behavior is seen in the cyclic voltammetry response of the poly (dimethylsilane) film electrode. Fig. 8C shows impedance spectrum of poly (dimethylstannum), which also shows very similar response to poly (dimethylsilane)

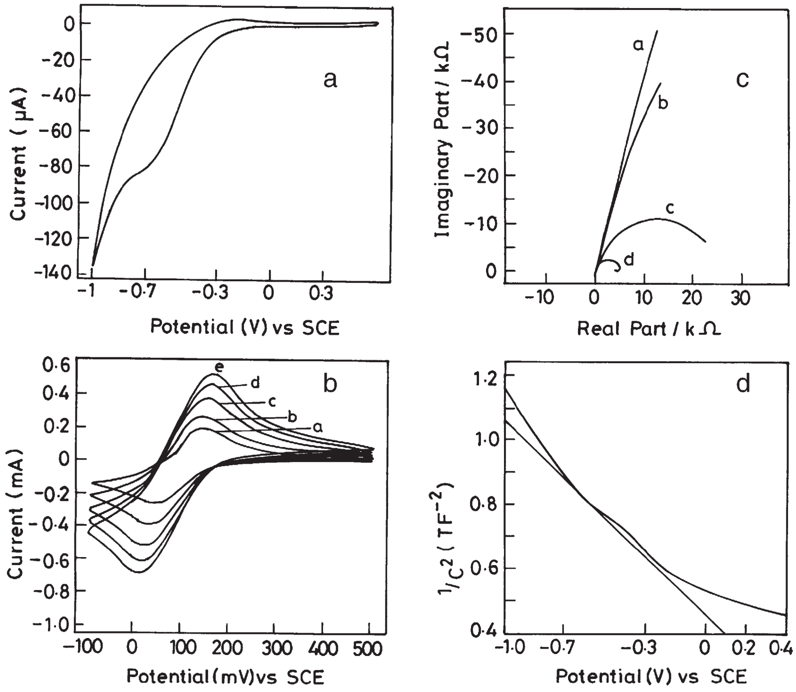

Fig. 7. a) Typical cyclic voltammetric response of poly (dimethylsilane) film electrode in 0.1 N KNO_3 solution at a scan rate 25 mV/s. b) Cyclic voltammogram of poly (dimethylsilane) film electrode in 0.1N KNO_3 solution containing 2 mM $K_4[Fe(CN)_6]$ at different scan rates a) 10 b) 25 c) 50 d) 75 e) 100 mV/s. c) Nyquist impedance spectra of poly (dimethylsilane) film electrode in 0.1 N KNO_3 solution a) OCP b) −0.400 c) −0.600 d) −0.800 V vs SCE. d) Mott–Schottky plot of poly (dimethylsilane) film electrode in 0.1N KNO_3 solution.

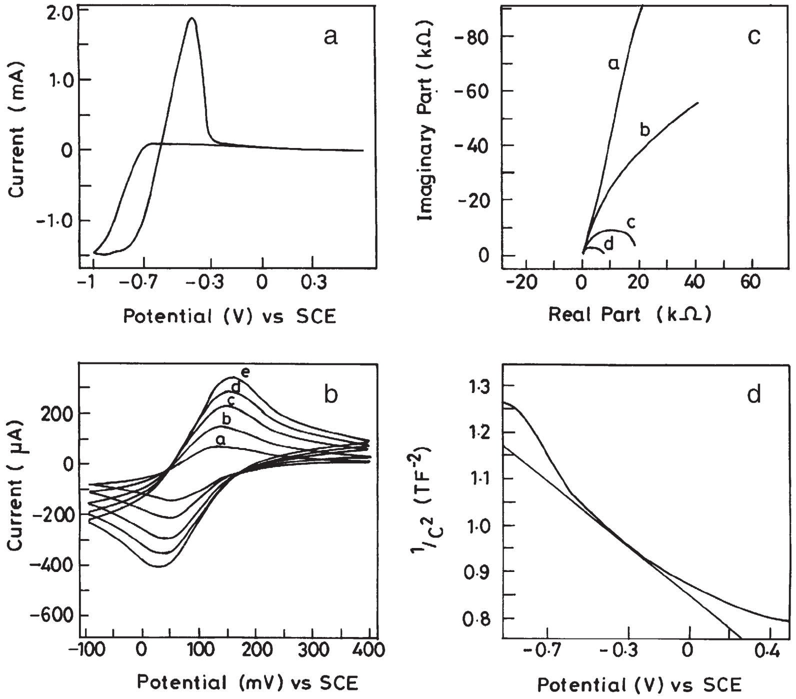

Fig. 8. a) Typical cyclic voltammetric response of the poly (dimethyl stannum) film electrode in 0.1 N KNO_3 solution at a scan rate 25 mV/s. b) Cyclic voltammogram of poly (dimethylstannum) film electrode in 0.1 N KNO_3 solution containing 2 mM $K_4[Fe(CN)_6]$ at different scan rates a) 10 b) 25 c) 50 d) 75 e) 100 mV/s. c) Nyquist impedance spectra of poly (dimethylstannum) film electrode in 0.1N KNO_3 solution a) OCP b) −0.400 c) −0.600 d) −0.800 V vs SCE. d) Mott–Schottky plot of poly (dimethylstannum) film electrode in 0.1N KNO_3 solution.

indicating the charge transfer for the reaction of metal ion present in the polymer.

3.5. Capacitance measurement

The flat-band potential using the Mott–Schottky relation [48,49] was determined for the system of poly(dimethylsilane) film electrode in 0.1 N KNO_3 aq. solution, by plotting the reciprocal of the square of the semiconductor–electrolyte interface capacitance vs the biased potential of the semiconductor calculated against the SCE (frequency 1 Hz). It was shown that the interfacial double layer capacitance at any low frequency (~ 1Hz) on the tail (spike) as frequency dependent capacitance [50]. The potential was between −1.0 to 0.6 V vs SCE. The intercept of the linear plot ($1/C^2=0$) was considered as the electrode potential of the semiconductor at which the band bending is zero. This potential is known as flat-band potential and is equal to 0.63 V (SCE) (Fig. 7D). The negative slope of the Mott–Schottky plot confirms the p-type conductivity of the poly (dimethylsilane) film. The depletion layer width (W) was calculated from the value of N_D using the equation $W=(2\varepsilon\varepsilon_o V_b/eN_D)^{1/2}$ Where V_b is the built in voltage or the band bending and the depletion layer width (W) was 1.969 μm that for the poly (dimethylsilane) film. Semiconductor materials parameters of the poly (dimethylsilane) thin film obtained from the MS plot are given in the Table 1.

It can be seen from Fig. 8D that the flat band potential for poly (dimethylstannum) is 2.35 V vs SCE. The depletion width W for the above polymer is calculated as 5.944 μm. Mott–Schottky plot also confirms the p-type conductivity of the polymer film. The semiconductor material parameters of the poly (dimethylstannum) thin films obtained from the plot are given in Table1. From the above values it can be seen that the density of states is very high for the above film and this may be responsible for the redox response at the electrode surface of the polymer films [49].

Table 1
Semi-conductor material parameters obtained from Mott–Schottky plot for poly (dimethylsilane) and poly (dimethylstannum) film electrodes

Physical parameter	Polysilane	Polystannum
Electrolyte used	KNO_3	KNO_3
Fermi level of the electrolyte E_F	0.803 V SCE	0.803 V SCE
Flat band potential V_{FB}	0.63 V SCE	2.35 V SCE
Density of states in valance band N_V	$1.081\times10^{28}cm^{-3}$	$47.402\times10^{28}cm^{-3}$
Built in voltage (band bending)Vb	0.173 V	−1.55 V vs SCE
Depletion width W	1.96 μm	5.95 μm
Carrier type	P	P

4. Conclusions

The above experiments exhibit the following conclusions: (1)FTIR, NMR and UV-Vis studies reveal that the polymers contain Si–Si and Sn–Sn catenation. (2) CV measurements show the reduction peak of the polymers and gives reversible response for the Fe^{3+} /Fe^{2+} redox couple. (3) Impedance study at different cathodic potentials clearly indicate that both the polymers at less negative potentials behave like capacitive in nature and at more negative potentials behave like charge transfer carrier. Mott–Schottky plot for these polymers reveal that the polymers are semi-conducting materials of narrow band gap with high carrier densities and are p-type carriers.

References

[1] H.K. Kim, K. Matyjaszewski, J. Am. Chem. Soc. 110 (1988) 3321.
[2] Y. Kimata, H. Suzuki, S. Satoh, A. Kuriyama, Organometallics 28 (1995) 59.
[3] K. Tamao, G.-R. Sun, A. Kawachi, S. Yamaguchi, Organometallics 16 (1997) 780.
[4] S. Kashimura, M. Ishifune, N. Yamashita, H. Bu, M. Takebayashi, S. Kitajima, D. Yoshiwara, T. Kataoka, R. Nishida, S. Kawasaki, H. Murase, T. Shono, J. Org. Chem. 64 (1999) 6615.
[5] X. Wang, Y. Yaun, I. Cabasso, Electrochemical Soc., Extended Abs., 99 (2) Abstract No.3.
[6] C. Jammegg, S. Graschy, E. Hengge, Organometallics 13 (1994) 2397.
[7] L.A. Vermeulen, K. Haung, Polymer 41 (2000) 441.
[8] T. Shono, S. Kashimura, H. Murase, Chem. Commun. (1992) 896.
[9] L.T. Canhan, Appl. Phys. Lett. 57 (1991) 104.
[10] C. Zyhik, V.P. Koch, Angew. Chem., Int. Ed. Engl. 32 (1993) 845.
[11] T. Shono, S. Kashimura, M. Ishifune, R. Nishida, Chem. Commun. (1990) 1160.
[12] J.L. Heinrich, C.L. Curtis, G.M. Gredo, K.L. Kavanagh, M.J. Sailor, Science 255 (1992) 66.
[13] L.T. Canhan, A.G. Cullis, C. Pickering, O.B. Dosser, T.I. Lyuch, Nature 368 (1994) 133.
[14] R. Miller, J. Michl, Chem. Rev. 89 (1989) 1359.
[15] K. Tanaka, K. Nagajima, M. Okada, T. Yambe, Organometallics 10 (1991) 2679.
[16] R. West, L.D. David, P.I. Djurovich, K.L. Stearley, K.S.V. Srinivasan, H. Yu, J. Am. Chem. Soc. 103 (1981) 7352.
[17] R.J.P. Corriu, W.E. Douglas, Z.X. Yang, F. Garnier, A. Yassar, J. Organomet. Chem. 417 (1991) C50.
[18] M. Ishikawa, T. Hatano, Y. Hasegawa, T. Horio, A. Kunai, A. Miyai, T. Ishida, T. Tsukihara, T. Yamanaka, T. Koike, J. Shioya, Organometallics 11 (1992) 1640.
[19] A. Ohshita, K. Matsnguchi, Furumori, R.F. Hong, M. Ishikawa, T. Yamanaka, T. Koike, J. Shioya, Macromolecules 25 (1992) 2134.
[20] Y. Kimita, H. Suzuki, S. Satoh, A. Kuriyama, Chem. Lett. (1994) 1163.
[21] M. Erkan Kose, Recent Advances in Metal-Containing Polymers, University of Florida, Nov. 20, 2001.
[22] S. Furukawa, K. Takeuchi, T. Nomura, T. Yasuda, M. Tamura, J. Phys., Condens. Matter 5 (1993) 4729.
[23] S. Furukawa, T. Koga, J. Phys., Condens. Matter 9 (1997) L99.
[24] H. Tachikawa, L.R. Faulknev, J. Am. Chem. Soc. 100 (1978) 4379.
[25] Fu-Ren Fan, L.R. Faulknev, J. Am. Chem. Soc. 101 (1979) 4779.
[26] A.M. Wilson, G. Zank, K. Eguchi, W. Xing, J.R. Dahn, J. Power Sources 68 (1997) 195.
[27] Y. Majima, K. Kawata, Y. Nakano, H. Hayase, J. Polym. Sci., Polym. Chem. 223 (1995) 2456.
[28] T. Imori, V. Lu, H. Cai, T.D. Tilley, J. Am. Chem. Soc. 117 (1995) 9931.
[29] K. Takeda, K. Shriraishi, Chem. Phys. Lett. 195 (1992) 121.
[30] R. West, J. Organomet. Chem. 300 (1986) 327.
[31] T. Imorin, T.D. Tilley, J. Chem. Soc., Chem. Commun. (1993) 1607.
[32] M. Okano, H. Fukai, M. Arakawa, H. Hamano, Electrochem. Commun. 1 (1999) 223.
[33] M. Elangovan, M. Phil. Dissertation, Alagappa Univeristy, India (2000).
[34] P. Vinod, K. Vijayamohan, Appl. Phys. Lett. 68 (1996) 1.
[35] M. Okano, N. Matsumoto, M. Arakawa, T. Tsuruta, H. Hamano, Chem. Commun. (1998) 1799.
[36] S. Hayase, Recent Trends in Polymerisation, vol. 3, 1995, p. 304.
[37] H. Bock, W. Ensslin, Angew. Chem., Int. Ed. Engl. 10 (1971) 404.
[38] P. Trefonas III, R. Damewood Jr., R. West, R.D. Miller, Organometallics 4 (1985) 1318.
[39] P. Trefonas, R. West, J. Polym. Lett. Ed. 23 (1985) 469.
[40] T. Shono, S. Kashimura, H. Murase, J. Chem. Soc., Chem. Commun. (1992) 327.
[41] M. Okano, K. Watanabe, Electrochem. Commun. 2 (2000) 471.
[42] K. Ebata, K. Furukawa, N. Matsumoto, J. Am. Chem. Soc. 120 (1998) 7367.
[43] A. Kunai, E. Toyode, T. Kawakami, M. Ishikawa, Electrochim. Acta 39 (1994) 2089.
[44] P. Roux, J. Paul Pillot, M. Birot, J. Dunogues, P. Lapouyade, J. Organomet. Chem. 499 (1995) 199.
[45] Y. Matsuura, K. Matsukawa, R. Kawaba, N. Higashi, M. Niwa, H. Inoue, Polymer 43 (2002) 1549.
[46] H. Nagai, Y. Nakata, M. Suzuki, T. Okutani, J. Mater. Sci. 33 (1998) 1897.
[47] N. Yoskiike, M. Ayusawa, S. Kondo, J. Electrochem. Soc. 131 (1984) 2600.
[48] M. Sharon, K. Basavaswaran, Sol. Cells 20 (1987) 323.
[49] B. Subramanian, C. Sanjeevaraja, M. Jeyachandran, Mater. Chem. Phys. 71 (2001) 40.
[50] M.D. Levi, D. Aurbach, J. Power Sources 146 (2005) 727.