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Investigation of Polyaniline Thin Film and Schottky Junction with Aluminium for Electrical and Optical Characterization

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ABSTRACT

Polyaniline Powdered sample was chemically synthesized using aniline and doped with HCl. Ultra thin film and Schottky junction with Al metal have been fabricated from this powdered sample Ultrathin film of polyaniline shows amorphous nature of the film. Two activation energies of these films at two different temperatures regions within 25 - 120˚*C have been observed. Schottky Junction with Al metal shows that the diode ideality factor is much higher than unity. Barrier height of this Schottky junction is estimated to be around* 0.61 *eV. C-V plot of the junction indicates that the carrier concentration is about* 10^{15} cm^{-3}*. There are various factors found to affect the junction to deviate from ideal Schottky behaviour.*

Keywords: *Aniline, Activation Energy, Diode Ideality Factor, Barrier Height*

1. Introduction

Among all conducting polymers, polyaniline (PANI) and its derivatives have attracted much interest worldwide. Because of chemical stability, simple polymerization, high conductivity, polyaniline has been used in various application, like, optoelectronics, bio-sensors, gas sensors, microelectronics etc. [1-5]. Several methods of preparation of PANI film such as, spin coating, drop coating, electrochemical deposition, thermal evaporation, emulsion polymerization, Langmuir-Blodgett (L-B) technique etc. [6-11] have been reported by various workers. Polyaniline may be doped by protonic acid and oxidative doping [12]. It has been reported that the conductivity of film cast from solution of polyaniline camphor sulphonate in m-cresol is of about 2 order of magnitude higher than that of polyaniline protonated with mineral acid and organic acid [13]. Different inorganic and organic acids of different concentration have been used in the synthesis of PANI and this protonated products of polyaniline differs in stability and conductivity [14]. The effect on property and growth of polyaniline produced by ionic sputtering in presence of electric and magnetic field was studied by P. Stakhria *et al.* [15]. Nanocomposite of PANI is an important candidate for device application in biosensor, gas sensors, optoelectronics etc. [16-19].

Schottky junction of polyaniline with metal is another important subject and have great technological importance [20]. This is recently gaining momentum for device application. Electrical and optical properties of polyaniline and its composite is however dependent on preparation techniques and matrix material used [21]. The aim of this study is to see the various properties of the ultra thin film and Schottky junction of HCl doped PANI and to improve the quality for device fabrication. In the process, we have prepared powered polyaniline by chemical synthesis method and produced ultra thin films by simple technique. Electrical and optical properties of these films and Schottky junctions with Al metal have been investigated.

2. Experimental

2.1. Preparation of Polyaniline Powder

Chemical Synthesis of polyaniline in the form of emaraldine salt was done by the general procedure using redox polymerization of aniline in presence of an oxidant, ammonium peroxidisulphate (APS) and using HCl as dopant. Freshly distilled aniline (4 ml) in 50 ml of 1M HCl solution at 2 to 3˚C was stirred for 20 minutes and subsequently added 1M APS solution (25 ml) drop wise at a rate of 5 drops/minutes. The process continued till the whole quantity was added and the solution turned green. Stirring of the compound continued for about 3 hours after which the solution was kept for overnight. The precipitate was treated with Tetrahydroforen to eliminate other oligomers and was filtered using funnel. The product was dried in an oven for 24 hours at 45˚C to get the powder.

2.2. Preparation of the Film and Junction

The powdered sample of PANI was dissolved in Dimethyl Sulfoxide (DMSO) in a beaker with continuous stirring for about 4 hours. The solution was filtered and drops of it were placed over a glass slide already cleaned by chemical wash and subsequently in ultrasonic bath. The drops were spread over by small glass spoon to make in the form of film. For fabrication of junction, ITO coated glass substrate were used after proper cleaning. This was dried in a specially made vacuum chamber which was fitted with a heater and a temperature controller. The temperature was maintained at 45˚C for drying in vacuum for about 5 hours. Four sets of ultrathin films in the ranges from 200 Å to 400 Å were produced in a cycle to study various parameters. One set of film so produced was taken to the thermal evaporation unit for deposition of electrodes. Gap type sample was made by using two co-planer electrodes separated by a gap to study electrical properties. Two electrodes of pure silver were deposited onto the film keeping a gap of 1 mm using a mask. For fabrication of junction, high purity Al foil (99.99% purity) was vacuum deposited onto the film that was already prepared over the ITO coated glass slide in the form of small disc shaped electrodes. The schematic diagrams of gap type and sandwich type structure are shown in **Figure 1**.

2.3. Experimental Arrangement

The samples of polyaniline film and junction so prepared were kept in a departmentally designed vacuum chamber for studying different characteristics. It is a glass cylindrical chamber of 35 cm length and 14 cm in diameter. It is fitted with some electrical feedthroughs for electrical and temperature controlling arrangement and a has gas inlet valve. The chamber could be evacuated by a rotary pump. All measurements were carried out in this chamber keeping the sample in vacuum.

The structural investigation of the powered Polyaniline and film so prepared was done by XRD spectrometer (JDX-IIP3A). Absorption spectra was taken by a UV-Vis spectrometer (Specord-200). IR absorption was recorded by a fourier Transform spectrometer (Perkin Elmer System 2000). Electrical characteristics were measured by a electrometer amplifier using two probe method. The temperature effect was measured in the chamber as mentioned above at a vacuum of 10^{-4} torr.

3. Results and Discussions

3.1. For the Films

XRD spectra of the powdered and thin film samples show nearly amorphous nature of the samples (Curve A of **Figure 2**). However, with increase of thickness, the film grows in grains and at higher thickness, the films tends to be polycrystalline in nature. The PANI peak at around $2\theta = 9.5˚$ has been indicted in the curve B of **Figure 2**. Similar observation has also been reported by other workers [22] in PANI film. **Figure 3** shows the FT-IR spectra of PANI film. As is seen from the figure, the peaks around 1563 cm^{-1} and 1476 cm^{-1} correspond to the absorption upon quinoid ring and is closed to that corresponding to the absorption of benzene ring (1502 cm^{-1}). The peak around 1470 cm^{-1} can be attributed to torsion C-N oscillation in Alkyl chain and peak at 1301 $cm^{-1}$to torsion oscillation C-N in the Benzene ring. The peak at 1119 cm^{-1} can be attributed to in plane valance oscillation C-H. UV-Vis spectra (**Figure 4**) indicates the absorption peaks at 3.8 eV and 4.1 eV of doped polyanilene and these can be attributed to the transition from lower polaron to upper polaron and to the conduction band respectively [23].

A plot of conductivity σ versus 10^3/T for the film in the range of 25˚C to 120˚C (**Figure 5**) of a typical sample shows that conductivity increases with temperature within this range.

The conductivity may be express as :

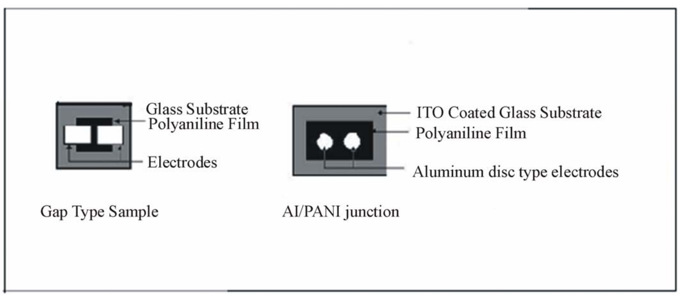

Figure 1. Sample for measurement.

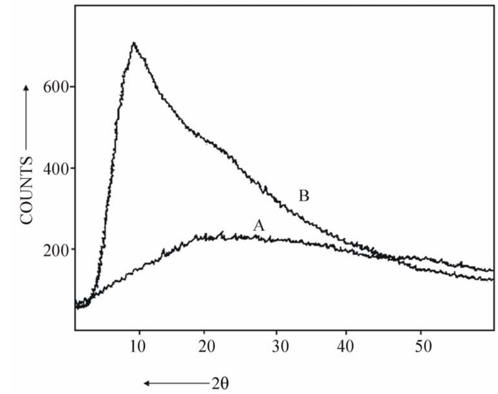

Figure 2. XRD spectra of HCl doped PANI film. (A) Thin film of PANI (B) Thick film of PANI.

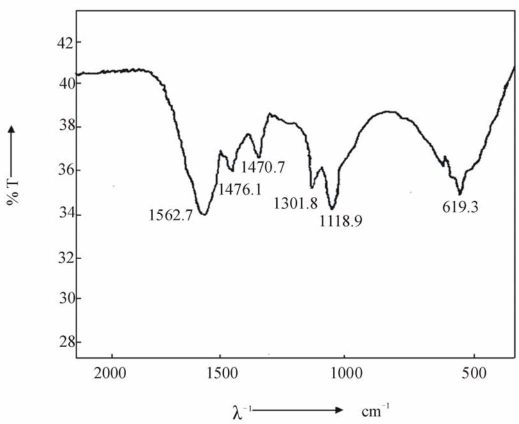

Figure 3. FTIR spectra of a typical doped film of PANI.

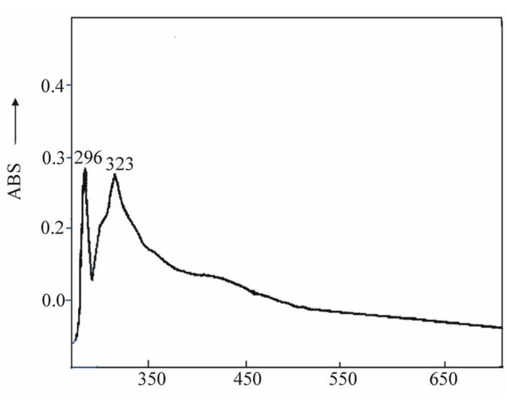

Figure 4. UV-Vis spectra of the doped film of PANI.

$$\sigma = \sigma_0 \,\mathrm{Exp}\,(-E_a/kT) \quad (1)$$

where, σ_0 is pre exponential factor, **k**, **T** and E_a are the Boltzmann constant, absolute temperature and activation energy respectively. The conductivity may be attributed to hopping conduction model where two types of conductivity components are combined such that **σ** can be written as:

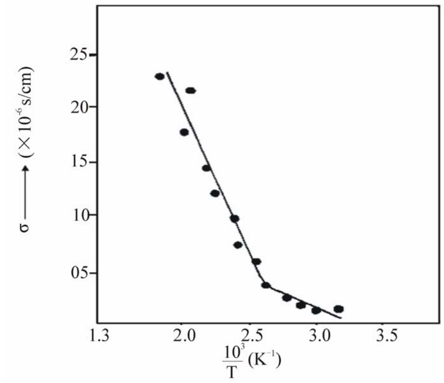

Figure 5. The Temperature versus Conductivity pl ot of typical doped PANI film.

$$\sigma = \sigma_1 + \sigma_2 \quad (2)$$

where, σ_1 and σ_2 are inter chain and intra chain respectively. Activation energy estimated in the lower temperature range is about 0.5 eV and at higher temperature is about 3.5 eV. Similar observations in polyaniline film have been reported by previous workers [24-25]. Yakuphanoglu *et al*. [26] have reported three regions for temperature variation of resistivity in polyaniline film.

3.2. For the Junction

Al/PANI/ITO junction was fabricated as mentioned above for studying various parameters. The junction produced by Al on doped PANI film shows rectifying nature of the junction (**Figure 6**). ITO with high work function make ohmic contact to PANI (p-type). The current density **J** and voltage **V** can be expressed by the Richardson's equation as,

$$J = J_o \,\mathrm{Exp}\,(qV/kT) \quad (3)$$

where J_o is the saturation current density and can be written as :

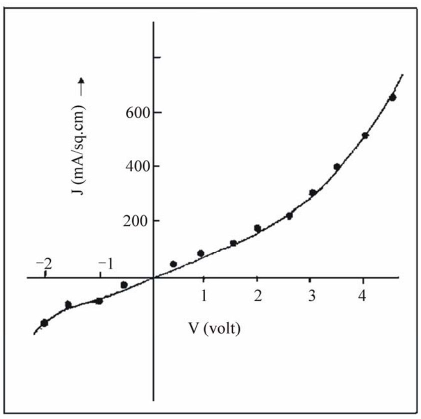

Figure 6. Current density versus Voltage characteristics of the Al/PANI/ITO structure.

$$\mathbf{J_o} = \mathbf{A^*}\ \mathbf{T^2}\ \mathrm{Exp}\ (-\mathbf{Ø_b/kT}) \quad (4)$$

where $\mathbf{A^*}$ and $\mathbf{Ø_b}$ are the Richardson constant and effective barrier height respectively. The saturation current density is estimated to be around 5.4 × 10^{-3} A/sq·cm. $\mathbf{C^{-2}}$**-V** plot under reverse bias condition at 10KHz has been shown in **Figure 7**. The plot of the junction shows almost a linear relationship indicating the average uniform charge distribution in the space charge region. The carrier concentration estimated from the slope is found to be around 10^{15} cm^{-3}. The diffusion potential $\mathbf{V_0}$ obtained from the graph is around 0.58 eV. Barrier height estimated from the saturation current density J_o using $\mathbf{A^*}$ value as 120 $AK^{-2}\cdot cm^{-2}$ is found to be 0.61 eV. This value is however almost agree with the value of 0.6 eV derived from the diffusion potential after necessary correction. Wei-chih chen *et al*. have also reported similar barrier height for Al/PANI junction [27]. The barrier height above 1.5 eV for boron trifloride doped PANI with Al metal has been also reported [28].

The diode ideality factor **n** of these junctions are higher than unity. An estimate of diode ideality factor shows to be around 8. The various factors responsible for diode ideality factor greater than unity are, presence of an interfacial layer, recombination of charges, migration of electrode materials etc. One possible cause is the presence of the aggregation of primary and secondary particles arising during polymerization giving rise to two different transport mechanisms [29]. Recombination in the depletion region is another possible cause. This also contributes to the fact that reverse current is not showing saturation. Presence of a very thin interfacial layer is not ruled out. This is formed while transferring the film to a vacuum evaporation chamber for depositing the counter electrode. Similar affect of interfacial layer and effect on diode ideality factor have been reported by earlier worker in metal/polymer junction [30]. Since the carrier concentration is moderate, the current transport is mainly dominated by the thermionic emission process. Similar observations on Al/PANI junction have also reported by previous workers [31].

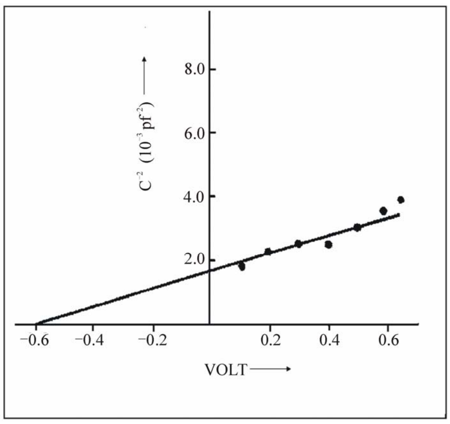

Figure 7. Voltage versus Capacitance plot of the junction of figure 6.

4. Conclusions

Thin film of HCl doped PANI and Schottky junction with Al have been fabricated. Ultra thin film of PANI produced in this process is amorphous in nature. The UV-Vis spectra indicate the two transitions peaks. The film shows two activation energies at 0.5 eV and 3.5 eV at two temperatures regions respectively. PANI film makes Schottky junction with Al and has high ideality factor. The barrier height obtained for the junction is around 0.6 eV. The current transport is believed to be mainly dominated by thermionics emission process.

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