Studies of Nanocomposite of Polyaniline with Gold Nanoparticles and Schottky Junction with Aluminium for Electrical and CO₂ Gas Sensing Properties

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Abstract — Gold nanocomposite of Polyaniline was prepared by chemical synthesis method and its thin film was made by drop casting. The Schottky junction of thin film was fabricated with aluminium metal. TGA analysis of the sample showed good stability. Current density-voltage characteristics of the junction showed good rectifying nature. The diode ideality factor is greater than unity. The junction showed good sensitivity to CO₂ gas with decrease of forward current. The response time of the junction to CO₂ showed good repeatability and recovery time is about 52 s.

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INTRODUCTION

Conducting polymers are interesting materials and have special importance due to change of physical and chemical properties in various forms. Nanocomposites of these polymers were new class of material with novel properties [1–3]. They are the important candidates for device application in organic materials. Due to their technological importance in various fields like, microelectronics, optoelectronics, sensors etc. [4–5], research interest has been grown tremendously in the recent years. It has been shown that mechanical and electrical properties of conducting polymer can be largely improved by incorporation of metal nanoparticles [6–7]. Moreover, the presence of metal nanoparticle increases the active surface area and improves gas diffusion inside the film. Polyaniline is one of the important conducting polymers due to its good environment stability, easy to prepare and inexpensive compared to other polymeric material. It can undergo reversible control of conductivity both by charge transfer doping and protonation [8]. Thus, adding nanoparticles of inorganic material to the polyaniline forms a matrix which can considerably change the electrical properties [9]. It has been reported that incorporation of Au particle to polyaniline enhances the conductivity by two order of magnitude [10]. There are various processes by which nanocomposite of polyaniline are prepared. However, chemical synthesis technique is mostly used for polyaniline using AuCl₄, KAuCl₄ and AuBr₄ compound for incorporation of gold nanoparticles. The chemical synthesis of polyaniline using AuCl₄ is similar to the chemical synthesis of polyaniline using a more common oxidizing agent such as peroxidisulphate. Schottky junction of polymer is another important subject and has drawn much attention in recent years. Although some informations relating to the Schottky junction of polyaniline with some metals are found in literature, its junction in nanocomposite form is yet to be fully studied. In this paper we have reported the production of gold nanocomposite film of Polyaniline and fabrication of Schottky junction with aluminum metal. Electrical characteristics and sensing effect of the Schottky junction to CO₂ gas has been discussed. In this process of study, the optical and TGA analysis of gold nanocomposite of polyaniline are also investigated.

EXPERIMENTAL

Preparation of Gold Nanocomposite Material

Nanocomposite of polyaniline was synthesized by oxidation polymerization of aniline hydrochloride using ammonium persulfate as an oxidant. Freshly distilled aniline (8 mL) in 200 mL of 1 M HCl solution at 3°C (keeping in ice chamber) was stirred for 15 minutes and subsequently 1 M APS solution (50 mL) was added to it at the rate of 5 drops per minute. After adding complete solution of APS, the gold solution (AuCl₄, 50 mL) is added freely (not drop wise) by opening the burette to the main solution. The
weight percentage of gold in the preparation was estimated to be on the order of 40% of polyaniline. Then the stirring of solution was continued for about 2 hours as before and the resulting solution was kept overnight for allowing complete polymerization. The precipitate was washed out by using first tetrahydrofuran (3 mL tetrahydrofuran in 15 mL distilled water) and secondly by sodium hydroxide (NaOH) solution to eliminate any oligomers and dried in oven at 50°C for 20–24 h. Thus the powdered sample had been obtained.

Film Casting and Junction Preparation

The powder of polyaniline nanocomposite was mixed in 25 mL of dimethylsulphoxide (DMSO) or 1-methyl-2-pyrrolidinone (NMP) solution and was stirred in the magnetic stirrer for about 4 hours. The filtered solution was drop coated on the chemically cleaned glass substrate with the help of a syringe and was dried in a vacuum chamber at 45°C for about 5 h. This process was continued till the film was dried and suitable for use. In a cycle, four sets of sample were prepared. Two samples of identical nature were taken for analysis.

For the fabrication of junction, the film was prepared on Indium Tin Oxide coated glass substrate. For this purpose, the ITO substrate was chemically cleaned before use. Pure aluminium metal (99.99% purity) was vacuum evaporated onto the film using suitable mask. Disc shaped electrodes were made on the film for making junction with electrode area of 5.7 × 10⁻² cm².

Arrangement for Measurement

IR spectra of the samples were recorded by a Fourier transformed spectrometer (Perkin Elmer System 2000). The absorption spectra of the samples were analyzed by UV–VIS spectrophotometer (Shimadzu, Model-UV-1800). The samples were kept in a specially designed vacuum chamber fitted with inlet and outlet pipe and a temperature controller for keeping the temperature at 45°C. The sample was connected to DC power supply (Specific Electronics PS-25) and the current produced in the sample was recorded by a digital multimeter (Fluke). The chamber could be evacuated up to 10⁻⁴ torr by a rotary pump for measurement in vacuum and to introduce gases to the chamber. Since the sensitivity of the film is affected by humidity, special care was taken to keep the humidity at 50% RH. Two probe methods were used to study the change of electrical parameters. Pure carbon dioxide gas was taken from a gas cylinder with regulator and was connected to the chamber by a pipe.

At first, the current density J at various voltages V was measured for the junction in air, then the chamber was evacuated and the J–V characteristics in vacuum were studied. The difference in readings was recorded. For J–V curve in CO₂ gas, the chamber was evacuated first to about 10⁻⁴ torr and then carbon dioxide gas was slowly introduced at a small rate to occupy the space and the corresponding current–voltage characteristic of the sample was measured. The detailed process of measurement was discussed in our earlier paper on polyaniline Schottky junction [11]. For the measurement of response and recovery time of the junction for gas, the initial value of conductivity in air inside the chamber was taken. The chamber was evacuated and the gas was quickly introduced to the chamber. The stable value of conductivity at full gas atmosphere was noted. The chamber was then evacuated and air was introduced to the chamber. The time taken to get the original value in both the cases were recorded.

RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of gold nanocomposite of polyaniline. It has been observed that all the peaks corresponding to polyaniline are also seen here with slight shifting of peaks. The peak around 1483 and 1581 cm⁻¹ are attributed to Benzoid and Quinoid units. The shift of about 5–10 cm⁻¹ is thought to be due to the incorporation of gold nanoparticles. The peak at 1120 cm⁻¹ may be due to in plane valence oscillation of C–N oscillation [11]. UV–VIS spectra of the sample (Fig. 2) shows the peak at 330 nm corresponds to π–π* transition [11]. The peak at 510 nm may be attributed to the transition from polaron to π. The plateau may be due to the complex formation arising out of gold nanocomposite and PANI matrix. The SEM spectra (Fig. 3) of the film show almost spherical nature of gold nanoparticles present. The estimated average size of the nanoparticles obtained from the spectra is 10 nm.

TGA measurement of gold nanocomposite of polyaniline (recorded by SDT Q 600 V 20.9 Build 20) is shown in Fig. 4. The curve indicates the degradation of the composite (8.3840 mg of sample) in three steps. The degradation up to 120°C is thought to be due to the evaporation of moisture, which is about 19%. The second and third are attributed to organic solvent (NMP) and structural decomposition of the polymeric nanocomposite. The degradation of sample was observed beyond 280°C. However, it has been found that the rapid degradation of polyaniline which are generally observed beyond 250°C was not seen in this nanocomposite structure. This may be due to the incorporation of Au particles to polyaniline [12].