ABSTRACT

Chlorine gas sensing characteristics of polypyrrole and Polypyrrole-ZnO nanowire composite thin films have been studied. The composite films were synthesized by drop casting method. The films were characterized for its morphology as well as gas sensing characteristics for different gases such as H₂S, NH₃, CH₄, CO and NO at room temperature. The composite films were found to be more sensitive to chlorine than pure polypyrrole. They were also selective for chlorine gas over other gases. This indicates composite films can be used as room temperature chlorine sensor.

Introduction

Chlorine is a toxic gas with very low toxic limit of 5 ppm in air for 8 hr. It is widely used in various industrial processes as well as to disinfect water. It is desirable to detect chlorine in lower concentrations as it can affect human health. Inorganic materials like semiconducting oxides (SnO₂, ZnO, WO₃) have been used, for sensing of different oxidizing and reducing gases, but the working temperature is generally in the range of 150-400°C [1-3]. It is desirable to develop sensors operable at room temperature. Recently nanostructures in the form of belts, wires and rods have been studied for gas sensing applications [4]. Conducting polymers like polyaniline, polypyrrole and polythiophene are promising candidates for applications in sensor technology [5-7], due to their room temperature operation and easy processing. However, they show lack of selectivity and poor thermal and mechanical stability. Suitably processed organic-inorganic hybrid materials may have advantages of both organic and inorganic materials and need to be investigated for gas sensing and other applications [8-9].

In this paper, we report synthesis and gas sensing characteristics of polypyrrole-ZnO nanowire composite. Results have been compared with that of pristine polypyrrole film. It is seen that composite film shows better sensitivity and selectivity for chlorine than pure polypyrrole.

Experimental

ZnO nanowires were synthesized using carbothermal evaporation method [10] with typical diameter of 80-100 nm and length of several microns.
Polypyrrole-ZnO nanowire composite films were synthesized by drop casting method, using a suspension of polypyrrole and ZnO nanowires in ethanol. The films were deposited on glass substrates of 10 mm X 10 mm size. Pure polypyrrole film was synthesized by using aqueous solution of pure distilled Pyrrole (0.1 M) and Ammonium Persulphate (0.05 M) as an oxidizing agent. The films were drop cast on glass substrates. All the films were dried at room temperature. The composite films were characterized by scanning electron microscopy (SEM) (Vega, MV 2300/T40, Tescan). For gas sensing measurements, two gold pads with 1 mm spacing were thermally evaporated on the films and silver wires were attached, using silver paint for measurement of resistance. In order to record response to different gases, the films were mounted in a SS housing of 250 cc volume and measured quantity of desired gas (at 2000 ppm concentration) was injected through syringe, so as to yield the desired concentration in the housing. All the films were characterized for response to Cl\(_2\), H\(_2\)S, NH\(_3\), CH\(_4\), CO and NO gases by measurement of resistances in air and in the presence of gas. All the measurements were carried out at room temperature.

Results and Discussion

Morphology of the films was determined by SEM. For this purpose, a very thin layer of gold was thermally evaporated on the composite films. Typical micrograph of a film is shown in Fig.1. The image shows formation of island like structure embedding nanowires and polypyrrole. SEM image of ZnO nanowires is also shown in inset of Fig.1.

For gas sensing measurements, composite samples were exposed to 5 ppm concentration of different gases at room temperature. For comparison, gas response of pure polypyrrole film was also studied. It was observed that composite films are more sensitive to chlorine gas, in comparison to polypyrrole. Sensitivity of sensors is defined by:

\[ \text{Sensitivity} = \frac{R_a}{R_g} \]

Typical response and recovery characteristics for composite and polypyrrole films are shown in Fig. 2. The resistance of all the samples is found to decrease after exposure to chlorine gas. This indicates p-type behaviour of all the samples.

Composite films were found to have much higher sensitivity than that of pure polymer films. The response time of composite film was found to be similar to that of pure films (< 1 min) but the recovery time (25 min) was much less. Cross-sensitivity of
composite films for various gases like H\textsubscript{2}S, NH\textsubscript{3}, CH\textsubscript{4}, CO, NO was also measured. The composite films were found to be highly selective towards chlorine as shown in Fig. 3. The higher sensitivity for chlorine gas in composite films, is attributed to localization of electrons on polypyrrole ring from O\textsuperscript{2-} surfaces of ZnO nanowires. It reduces polypyrrole films by donating electrons that makes it insensitive to all reducing gases. Chlorine being highly-oxidizing gas, accepts electrons from composite films, thereby showing more sensitivity than pure polypyrrole.

Conclusion

We have synthesized polypyrrole-ZnO nanowire composite films by drop casting method. The films were characterized by SEM and gas response was studied. Composite films were found to be highly sensitive and selective for chlorine gas at room temperature.

References


ABOUT THE AUTHORS

Dr. D. K. Aswal joined Technical Physics and Prototype Engineering Division through 30\textsuperscript{th} Batch of Training School. He has made several contributions in the field of thin/thick films and single crystals of various high temperature superconductors and colossal magnetoresistive materials. He has investigated various properties of magnesium-di-boride superconductor, metallic multilayer grown by molecular beam epitaxy and thermoelectric materials. Currently he is working on organic/molecular electronics.
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