A UGC SPONSORED MINOR RESEARCH PROJECT ON

IRON OXIDE THIN FILM SENSORS (II PHASE)

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THE EXECUTIVE SUMMARY OF THE REPORT

Introduction

Iron oxide is one of the most important transition metal oxides of technological importance. There are 16 phases of iron oxide forms i.e., pure oxides, hydroxides, and oxy-hydroxides. Characteristics of these oxide compounds include mostly the trivalent state of the iron, low solubility and brilliant colors. Heamtite (α Fe_2O_3) the most stable iron oxide with n-type semiconducting properties under ambient conditions, is widely used as catalysts, pigments, gas sensors, and electrode material, owing to its low cost, high resistance to corrosion and environment friendly properties.

Most of the traditional gas sensors are thick film sensors or sintered type sensors made by metal oxides, e.g. tin oxide, zinc oxide, and ferric oxide. In comparison with those sensors, thin film sensors have attracted much attention due to their high sensitivity, low working temperature and good selectivity. In recent years, ferric oxide thin films have been prepared by liquid phase deposition method (LPD), plasma enhanced chemical vapor deposition (PECVD), ion sputtering, and ultrasonic spray pyrolysis. The working temperature of these films is higher than100˚C.There are seldom reports on the preparation of α Fe_2O_3 thin films with good sensing properties at room temperature by chemical bath deposition technique. In the present work chemical bath deposition technique is employed for producing iron oxide thin films.

Brief objective of the project

This project is the second phase of our previous study. We could successfully prepare films which were highly sensitive to humidity.We require further investigations regarding composition and sensitivity to other gases.The main objectives of our present study are

- To prepare and characterize iron oxide thin film synthesized by chemical bath deposition technique
- To systematically analyze the composition of the film
- To study the effect of annealing on the humidity sensitivity of iron oxide film
- To study the sensitivity of this material to other gases like methane, carbon dioxide etc.

Experimental procedure

`Thin films of iron oxide were deposited onto well-cleaned glass substrates by chemical bath deposition method at different bath temperature conditions (60°C, and 80°C). These as-deposited films were subjected to air annealing at 300°C for one hour. Its characterization was done using techniques like SEM, XRD, FTIR and EDAX.

In the present study the response of iron oxide thin films to relative humidity of surrounding air was made by noting the variation in its sheet resistance. The study was made on films prepared at 60C and 80C as well as on corresponding annealed films.The resistance of the film was measured using a two probe setup. The set-up consists of a probe arrangement, high voltage power supplyEHT-11 and digital pico ammeterDPM-111.Samples were of one sq. cm area and contacts were made by attaching silver stickers.

Relative humidity of surrounding air was controlled by chemical method. For this a small amount of fused calcium chloride, which is a good absorber of water vapour, was kept at the bottom of the vessel in which the film was suspended. Relative humidity (R.H) was noted using Racer Electronic Hygrometer (model-HT.02)

Results and Discussion

Iron oxide thin film was prepared by Chemical Bath Deposition technique The SEM images of annealed films showed the presence of micro cracks. Structural characterization of the film by XRD revealed the amorphous nature of as-prepared films and its transformation into crystalline γ Fe_2O_3 phase with tetragonal structure on annealing. FTIR analysis revealed the presence of bands corresponding to O-H, - FeOOH, γ-FeOOH and Fe_2O_3. Composition of the films was thus confirmed to be a mixed phase of - FeOOH, γ-FeOOH and Fe_2O_3. The O-H peak intensity increased with increase in bath temperature and decreased on annealing. The intensity of - FeOOH and Fe_2O_3 peaks showed the predominance of these phases in as-prepared films. The higher deposition temperature favoured the -FeOOH phase than Fe_2O_3.

To confirm the composition of the material of the film, the composition of the precipitate from the chemical bath was analyzed and compared with the standard iron oxide nano powder . The FTIR analysis of as-prepared precipitate revealed the presence of bands corresponding to Fe_2O_3, -FeOOH and β- FeOOH with some residual thiourea in it. But annealing to 300˚C removed the peaks corresponding to residual thiourea and FTIR spectra showed only the presence of bands corresponding to γ Fe_2O_3 and β FeOOH.

Further annealing of the precipitate to 800˚C showed the transformation of the material in to pure -Fe_2O_3 phase. The FTIR spectra of the precipitate from the chemical bath annealed to 800˚C was in agreement with the FTIR spectra of standard iron oxide nano powder. From these studies composition of the chemical bath precipitate was confirmed as iron oxide and the presence of any iron complex was ruled out. EDAX pattern confirmed the same results in the thin film also.

An investigation on the humidity sensitivity of the film revealed that the room temperature sheet resistance of as prepared films is sensitive to moisture, indicating its potential applicability in moisture sensing systems. The sheet resistance was found to increase as humidity decreased. Humidity sensitivity decreased with deposition temperature due to the predominance of -FeOOH phase in the thin film. This is probably because the first layer of water adsorbed on -FeOOH is more hydrogen bonded than in the case of Fe_2O_3, due to the presence of structural proton in -FeOOH. Hence removal of water from -FeOOH is difficult and therefore 80C films seem to be less sensitive to humidity. High sensitivity of 60Cfilm is probably due to the high intensity of -Fe_2O_3 phase in the film, as the dissociation of Fe_2O_3 on adsorption of water is a reversible process responsible for humidity sensing property of the film. At low levels of humidity, the sensitivity is found to be almost independent of deposition parameters. On annealing the humidity sensitivity decreased due to the phase change occurring in the material and also due to the micro cracks developed. The material of the film is found to be insensitive to other gases like cooking gas and carbon dioxide at room temperature.

Summary and Conclusion.

Iron oxide is one of the cheapest and easily available materials which have got a number of technological applications. Composition of the thin film prepared by chemical bath deposition technique in this study is confirmed to be a mixed phase of - FeOOH, γ-FeOOH and Fe_2O_3. The as-prepared films are found to be in amorphous nature and annealing transforms the material into crystalline γ Fe_2O_3 phase.

A study on the humidity sensitivity of the film, revealed that as prepared films are sensitive to moisture, where as annealing decreased the humidity sensitivity. Humidity sensitivity decreased with increase in deposition temperature due to the predominance of FeOOH phase in the thin film. The high intensity of Fe_2O_3 phase is favoured for higher humidity sensitivity , as the dissociation of Fe_2O_3 on adsorption of water is a reversible process, responsible for humidity sensing property of the film. At low levels of humidity, the sensitivity is found to be almost independent of deposition parameters. The material of the film is found to be insensitive to other gases like cooking gas and carbon dioxide at room temperature. Further investigation is to be carried out about the sensitivity of the material to cooking gas and carbon dioxide at high temperature.

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