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Pt Embedded Porous Aluminum based Gas Sensor

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Abstract

A simple and cost-effective chemical bath deposition (CBD) technique was employed to prepare thin film of platinum embedded on porous aluminum substrates from aqueous solutions of platinum chloride at 50 ^{o}C. The effects of Pt modified porous aluminum on structural, morphological, and gas-sensing properties of films were examined. The X-ray diffraction patterns of the Pt-Al_2O_3 films showed the polycrystalline nature. Scanning electron microscopy (SEM) images of pure and Pt modified porous Al_2O_3 films revealed the uniform distribution of the various spherical grains of ~10 - 100 nm size. Tiny Pt nanoparticles are clearly visualized in the SEM of Pt-Al_2O_3 films. The investigation of the effect of Pt on the gas-sensing properties of the Pt modified porous Al_2O_3 film revealed that the Pt-Al_2O_3 sample has the highest gas sensitivity (~ SF = 4.5 X 10^5) at an optimum operating temperature of 35 ^{o}C and at higher temperature the sensitivity is almost constant (~ SF = 2.0 X 10^5). A possible mechanism of Pt-Al_2O_3-based sensor sensitivity to the target gas is also proposed.

Keywords: Porous aluminium; Platinum; Gas sensor; Chemical bath deposition.

Introduction

Ethanol is flammable and hazardous. The largest single use of ethanol is as a motor fuel and fuel additive. Increasing concerns on health and environmental protection has driven a continuous expansion of sensor development from last few decades. An extensive research in the past few decades has revealed that the chemical sensor is effective to sense the toxic pollutants and combustible gases [1]. For chemical sensors, the key requirements are not only high sensitivity and good selectivity to a trace targeted gas but also the abilities of working in a continuous mode at room temperature. A lot of efforts have been exerted on the research toward new materials and techniques to solve the problems related to the commercial sensors. Recently, growing interests have been observed in the developing gas sensors that could work at room temperature, which is probably motivated by the development and advances in material fabrication and nanotechnology [2] as well as some novel concepts of sensing mechanisms, such as gas sensing based on the variation in resistance response [3]. Particularly, the metal oxide gas sensors have very important applications in industrial safety, environmental monitoring, chemical process controlling and safety [4 - 13]. They offer a simple and cost-effective route for detection of the harmful volatile gases as compared to other methods. Additionally, they exhibit high sensitivity under ambient conditions, low power consumption and are easy to integrate in devices.

Among the various physical and chemical deposition techniques [5-13], chemical bath deposition technique (CBD) is a low cost, safe, easily scalable, versatile technique for deposition of resistive materials and can be implemented in a standard laboratory. It offers a most attractive way for the formation of thin films due to the simplicity of the apparatus and good productivity of this technique on a large scale. As the gas sensing properties are related to some critical factors therefore, it is necessary that morphology, surface-to-volume ratio, and active center of the material should be further optimized to improve gas-sensing properties. At present, we use to modify the material preparation method to improve the properties of semiconductors.

In this work, the CBD technique was utilized to grow Pt thin films on porous aluminum substrate. The structural, morphological, compositional properties of thin films are investigated and presented in this manuscript. The main objective of this study is to see the effect of Pt embedded porous aluminum on the ethanol gas sensing performance of Pt-Al_2O_3 thin films and to derive the correlation between the Pt-Al_2O_3 and gas-sensing property.

Experimental Work

The porous alumina (PoAl) thick layer was prepared in dark on cleaned aluminum substrate (size = 5 mm x 5 mm) by electrochemical anodization method. The solution of hydrogen fluoride (40 wt %) and ethanol (60 wt %) in the ratio 2:3 was used as an electrolyte with current density of 50 mA/cm^2 and anodization time of 30 min. After anodization, PoAl samples were rinsed thoroughly with de-ionized water. Finally, these samples were dried at 50 ^{0}C. Thin semitransparent platinum (Pt) film was deposited on PoAl samples by using chemical bath deposition (CBD) method at ambient conditions. Pt nanoparticles coated PoAl samples were dried under infrared (IR) lamp for 10 min. and identified as Pt-PoAl. The resultant films were characterized by X-Ray diffraction (XRD) and scanning electron microscopy (SEM) and gas sensing properties.

Results and Discussions

The gas sensing characteristics of these films were measured using in home built gas sensor characterization system at 1000 ppm concentration of gas at ambient atmospheric conditions. The gas sensing properties: sensitivity factor (S.F.), response time, recovery time and repeatability of the films were measured at optimum temperature. The changes in the resistance in air ambient and in presence of gas were recorded by half bridge method [4, 12-13]. The sensitivity factor (S.F.) was obtained by using equation (1).

$$S.F. = \frac{(R_a - R_g)}{R_g} \times 100 \qquad \text{--- (1)}$$

Where, R_a = resistance of film in air and R_g = resistance of film in air + ethanol gas atmosphere. The ethanol gas sensing behavior of Pt deposited porous alumina (Pt-PoAl) composite film were evaluated by measuring the relative change in resistance of the film with and without exposure of gas. Using the similar approach, the change in the resistance of the sensing film as a function of temperature was recorded in order to analyze the gas sensing behavior of the nano-composite film sample. Figure 1 gives the variation of sensitivity factor for Pt-PoAl films obtained at 1000 ppm concentration of ethanol gas. The maximum value of S.F was found to be SF = 4.5 X 10^5 with the response time 2 - 3 second at optimum operating temperature of T_{opt} = 35 ^oC. The observed response time in the present investigation was found to be significantly higher as compared to the other sensors reported in the literatures [1-13]. Further, the measurement of ethanol gas sensing properties of Pt-PoAl film for three cycles at 1000 ppm concentration of ethanol gas clearly indicated the repeatability of gas sensing response of the films. On exposure of ethanol gas (1000 ppm) to the Pt-PoAl film, a sudden increase in resistance was observed.

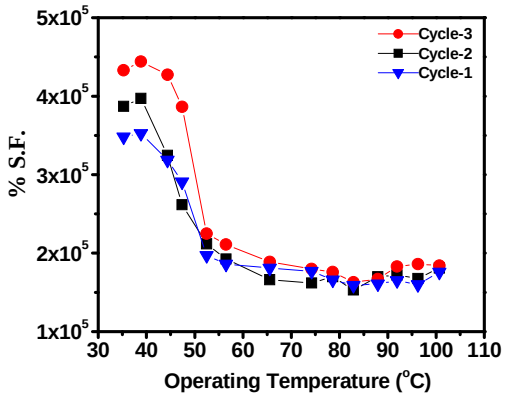


Figure 1. Variation of SF with the operating temperature for 1000 ppm of Ethanol

The original resistance was regained after the introduction of fresh air into the test chamber. The observed change in resistance of film sample was due to the physical adsorption of ethanol gas on surface of nano-composite Pt-PoAl film. The interaction of ethanol gas with Pt-PoAl network captures the electron from the Pt, which decreases the resistance of the probe. Since Pt-PoAl is junction semiconductor, it will create a spatially charged region at the junction interface. Upon ethanol gas adsorption, a high conductivity in the sensing probe was achieved because of the reduction in spatially charged region. Introduction of fresh air in the test chamber removes the adsorbed gas molecules from the probe's surface to regain the original current. The interface gives a high range of sensitivity for ethanol gas and hence the sample can operate at comparatively low temperature. In the present case, the Pt-PoAl contact is an ohmic, so there is no possibility of the current rectification. The junction between Al and the porous layer has the resistance in the tune of few tens of kilo-ohms. Therefore, the current rectification

may be the result of the Schottkey effect at the interface of the Pt film and the PoAl layer. The rectification, therefore, appears to be consistent with the formation of the Schottkey barrier at the junction between Pt and PoAl layer. The observed result indicate significant potential of Pt coated PoAl for ethanol gas sensing application in diverse areas. Figure 2 provides the XRD patterns for PoAl and Pt-PoAl films.

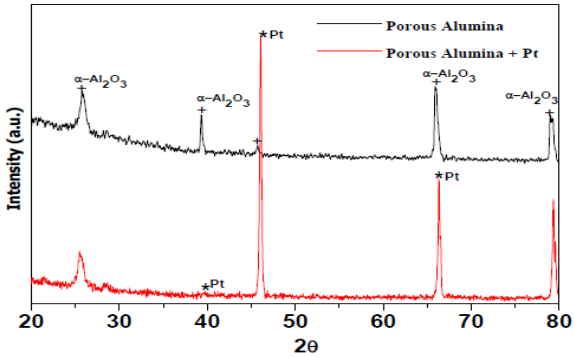
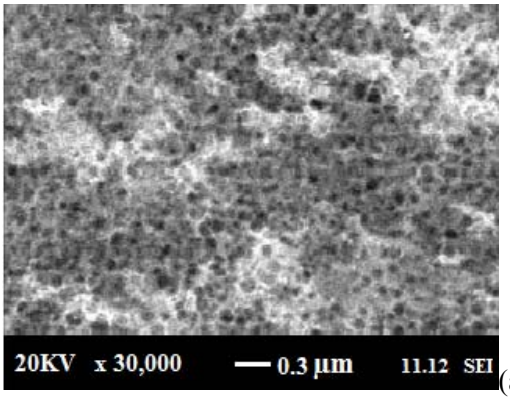


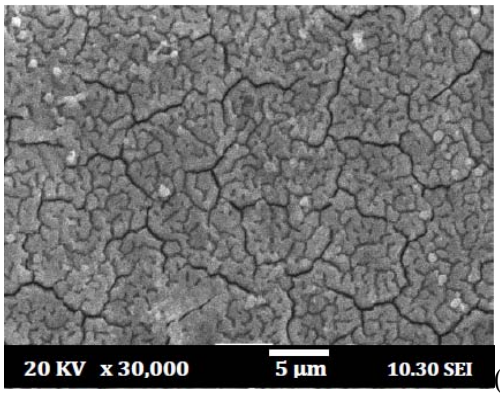
Figure 2. XRD patterns for PoAl and Pt-PoAl films

The XRD confirmed the purity of both PoAl and Pt-PoAl films due to the presence of the only peaks corresponding to Al_2O_3 and Pt in the respective XRD patterns. In these cases, 4 peaks of porous alumina film are observed in all modified and sintered samples. All these peaks correspond to the alpha phase of porous alumina film. The reflection at $2\theta = 39.74^o$ corresponding to Pt (111) was observed in Pt-PoAl film. In addition, reflections at $2\theta = 46.28^o$, and 66.76^o (JCPDS No. 65-2868) corresponding to Pt are also observed in case of Pt modified porous alumina system and remaining all the peak corresponds to α-Al_2O_3 [ASTM card no. 10 -173].

The surface study of the films was done using scanning electron microscopy (SEM). Figure 3 (a) and (b) give the surface topology of PoAl and Pt-PoAl films respectively. The surface of PoAl thick film was found to be porous with spherical pores of 0.25 to 0.50 µm in diameter. The size distribution of pores was found to be uniform.



(a)



(b)

Figure 3. SEM microphotographs (a) PoAl and (b) Pt-PoAl samples

In case of Pt-PoAl film, the particles on the surface of film were found to be spherical, uniformly distributed with the average particle size of ~ 100 nm. The densification at the surface of film was good. This might be due to the high deposition time of 20 min. When the Pt-Al_2O_3 film is surrounded by air, oxygen molecules adsorb on the exposed surface of Pt-Al_2O_3 to generate chemisorbed oxygen species (O_2, O^{2-}, and O^-) by extracting an electrons from the Pt-Al_2O_3 conduction band. The reactive oxygen species such as O_2, O^{2-}, and O^- are adsorbed on the Pt-Al_2O_3 surface at elevated temperature. At low temperatures O_2 is commonly chemisorbed. At high temperatures, however, O^- and O^{2-} are commonly chemisorbed, while O_2 disappear rapidly. Consequently, depletion layers are formed in the surface as well as in the grain-boundary regions of Pt-Al_2O_3, causing the carrier concentration and electron mobility to decrease. Thus, Pt-Al_2O_3 thin film becomes more electrically resistive [1-8]. When the film is exposed to a reducing gas, such as ethanol, the reaction between the ethanol vapour and the adsorbed oxygen on the film surface can be expressed by [8].

$$CH_3CH_2OH(adsorbed) + 6O^-(adsorbed) \rightarrow 2CO_2 + 3H_2O + 6e^-$$

The above chemical reactions need OH^- groups on the surface. It can be noted that as a result of reactions, negative charge is moved from the surface to the bulk, decreasing the negative charge on the surface. Therefore, this ethanol sensing mechanism justifies our experimental measurements and it can be concluded that the sensing mechanism reported in the present investigation is different to that reported in the previous literature, which means an opposite behavior of both work function and resistance variations are operable in the present study. The surface generated electrons migrate to the solid surface, where they interact with the chemical adsorbed species leading to an increase of the hydroxyl group's (OH^-) concentration on the surface. The surface activation phenomenon influences, not only the possibility of sensing at relatively low temperature, but also the kinetics and desorption of chemical species present on the surfaces. Without surface generated electrons, the chemical reactions are not reversible and the electrical signal does not recover the base line.

Conclusions

The chemical bath deposition method was also found to be very simple and effective method for deposition of Pt thin film on PoAl. This combined experimentation leads to a nano-composite film sensor with high sensitivity (S.F. = 4.5 X 10^5). The present study promises a significant potential of Pt coated porous alumina (Pt-PoAl) film for ethanol gas sensing applications in diverse areas.

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