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Trace Level Gas Sensing Characteristics of Nano-Crystalline Silver Decamolybdate

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ABSTRACT

A soft-chemical method has been developed for the synthesis of nano-crystalline powders of silver decamolybdate. Gas sensing characteristics of this composition both in porous pellet and thin film configurations were investigated. The compound $Ag_6Mo_{10}O_{33}$ was found to sense selectively ammonia at 503 K. Above 503 K it has significant cross sensitivity to petroleum gas (PG). Spin coated thin films exhibited selective sensing towards PG.

Keywords: Soft-Chemical Method; Silver Decamolybdate Nano Crystals; Spin Coated Thin Film; Interdigitated Platinum Electrode; Gas Sensor

1. Introduction

Ammonia is one of the important raw materials used in many industries. For instance, in fertilizer plants, heavy water plants, etc., where large quantities of ammonia at high pressures are used, leakage of ammonia into air can lead to very undesirable consequences. It is also an explosive gas, which makes an explosive mixture with air. Its lower and upper explosive limit values are between 16% and 27% respectively. In addition to being explosive, TLV[1] of ammonia is around 25 ppm. Hence, its incipient detection is mandatory [1]. Usage of nano-scaled advanced materials and their thick/thin films would make the gas sensors more sensitive, selective, compact and reliable, ensuring the safety aspects and pollution control in industrial environment [1-3].

Silver decamolybdate ($Ag_6Mo_{10}O_{33}$) is known to be a good material for gas sensing applications [4,5]. In thick film form, it senses ammonia down to 2 ppm by volume in air [6]. Nano-crystalline thin film configuration may enhance its gas sensing characteristics further. In this present work, the gas sensing behaviour of both porous pellet and the spin coated nanocrystalline thin films of silver decamolybdate prepared by solution chemistry route were investigated.

[1]TLV is nothing but the maximum concentration of the species to which people can be exposed continuously 8 hours a day without causing any health hazards.

2. Experimental Methodology

Silver decamolybdate was prepared by mixing appropriate quantities of aqueous solutions of $AgNO_3$ and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ with ammonia solution. The resulting precipitate was heated to 573 K for 5 h [7-10]. The resulting nano-crystalline $Ag_6Mo_{10}O_{33}$ was made in the form of porous pellets and its gas sensing characteristics were evaluated as mentioned in the previous studies [8]. The test gases used for this study were 100 ppm of NH_3, H_2, NO_x and petroleum gas (PG) by volume. The sensitivity for a given concentration of analyte gas was calculated as follows:

$$\%\text{Sensitivity} = \left[\left(R_a - R_g\right)/R_a\right] \times 100$$

where R_a = resistance of the pellet in air and R_g = resistance of the pellet in air containing the analyte gas.

A Photo Resist Spinner (M/s Ducom, India) was used to spin coat the ammoniacal solutions of $AgNO_3$ and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ over polycrystalline alumina substrate of 0.5 mm thickness at a rate of 1000 revolutions per minute followed by drying it in an oven. This process was repeated several times and then the films were slowly heated at a rate of 1 K/min to 773 for half an hour to get $Ag_6Mo_{10}O_{33}$ phase [7,9]. Prior to the fabrication of this thin film, a serpentine shaped platinum heater pattern was screen printed on the rear side of the substrate for heating the sensor film. The resistance of the Pt-heater was calibrated for various temperatures. Gold contact pads with interdigitated platinum electrodes were screen printed on the front side of substrate for measuring the electrical signal of the thin film. Gas sensing characteristics of nano-crystalline thin film of $Ag_6Mo_{10}O_{33}$ mounted in a sensor chamber made of quartz were investigated at various temperatures by injecting 100 vppm of NH_3, H_2 and petroleum gas (PG) each. Acquisition of data was carried out as mentioned in the earlier publications [4,6,8].

3. Results and Discussion

3.1. Gas Sensing Characteristics of Porous Pellet Sample

Both the nano-cyrstalline powder and thin film samples of $Ag_6Mo_{10}O_{33}$ were characterized by a variety of physicochemical techniques and the results were presented elsewhere [7-9]. Gas sensing characteristics of the porous pellets comprising nano-crystalline $Ag_6Mo_{10}O_{33}$ powders were investigated at various operating temperatures towards four different analyte species.

Figure 1 reveals a sensitivity of ~45% to 100 vppm ammonia at 503 K. At this temperature it is found that this film is selective to ammonia while the sensitivities to PG, H_2 and NO_x are less than 10%. But, above this temperature this compound shows significant cross sensitivity to PG and sensitivity value reaches about 75% in the temperature range 570 to 625 K. And it shows lower sensitivities towards H_2 and NO_x above 503 K. The sensing behaviour of this compound prepared by solid-state route is reported by Sunu *et al.* [5] where it senses ammonia (500 vppm) selectively with a higher sensitivity of ~80% and lower sensitivity (~25%) towards 500 vppm of PG and H_2 between the temperatures 573 to 673 K. This difference may be attributed to the presence of modified surface states when the compound is prepared by soft-chemical method.

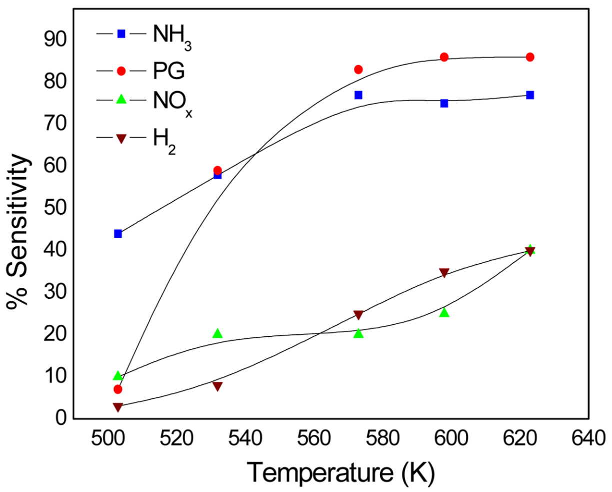

Figure 1. Typical sensitivity values of nano-crystalline $Ag^6Mo^{10}O^{33}$ porous pellet towards 100 vppm of four different analytes.

3.2. Gas Sensing Characteristics of Thin Films

The gas sensing characteristics of the spin coated $Ag_6Mo_{10}O_{33}$ thin film over polycrystalline alumina substrate with interdigitated platinum electrode were investigated towards trace (ppm) level of different toxic and flammable gas analytes at various temperatures. **Figure 2** shows the typical response pattern of this film towards various analytes at 573 K. The signal is stable and reproducible with sensitivity of 13% towards 100 vppm ammonia and 32% towards 100 vppm petroleum gas at 573 K. The response time of the sensor at this temperature towards ammonia is around 10 min and the retrace time is ~40 min whereas for petroleum gas the corresponding values are around 8 and 25 min respectively. It showed negligible sensitivity towards 100 vppm of hydrogen gas.

The mechanism for this ammonia sensing action for bulk $Ag_6Mo_{10}O_{33}$ had been investigated and reported by Sunu *et al.* [5]. Similar mechanism for petroleum gas sensing can be proposed. On reaction with petroleum gas, molybdenum carbide could form along with silver and both products have good electrical conductivity. At this optimised temperature this causes abrupt drop in resistivity value of the material from its stable baseline. However, more experiments are required to support the mechanism proposed. Once the reducing analyte gas is consumed the original baseline is retraced in presence of fresh air (oxygen) reforming the sensor base material ($Ag_6Mo_{10}O_{33}$). The chemical equations for this mecha-

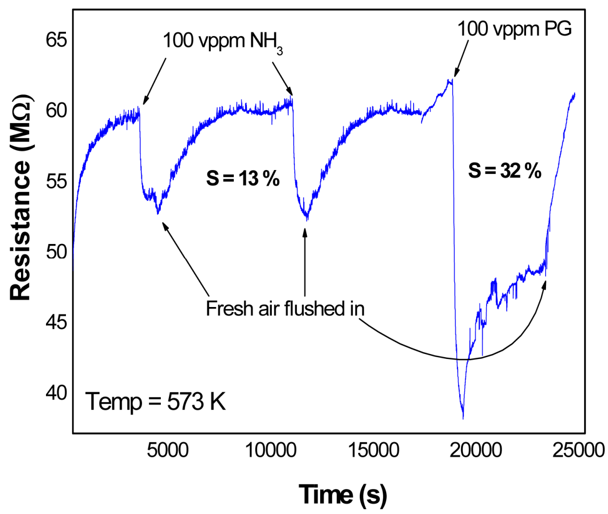

Figure 2. Typical response of nano-crystalline $Ag_6Mo_{10}O_{33}$ thin film with Pt-IDE towards 100 vppm of analyte gas at 573 K.

nism in presence of PG are proposed below.

$$\mathrm{Ag_6Mo_{10}O_{33}} \underset{[\mathrm{Air}]}{\overset{\mathrm{PG}}{\rightleftarrows}} \mathrm{6Ag + 5Mo_2C + 11CO_2 + 11H_2O + 12NH_3}$$

$$\mathrm{Ag_6Mo_{10}O_{33}} \underset{[\mathrm{Air}]}{\rightleftarrows} \mathrm{6Ag + 2}\gamma\mathrm{\text{-}Mo_2N + 2MoO_2 + Mo_4O_{11} + 18H_2O + 5N_2}$$

At 673 K the sensitivity of the film towards 100 vppm ammonia remained unaltered whereas towards 100 vppm petroleum gas the sensitivity decreased to 15%, which is almost equivalent to that of ammonia (**Figure 3**). The response and recovery of the film towards analytes are also relatively fast at this temperature viz. 1.5 and 7 min for ammonia and for PG these values are 5 and 4 min respectively (**Table 1**). The results also showed almost no sensitivity towards hydrogen. Typical sensitivity values of $Ag_6Mo_{10}O_{33}$ thin film towards 100 vppm of different gas analytes at temperatures 573, 598 and 673 K are clearly depicted in **Figure 3**. At 573 K, it showed 13% and 32% sensitivities towards 100 vppm of NH_3 and PG respectively with negligible sensitivity to hydrogen. On comparing this thin film study with its bulk, it is inferred that at an optimum temperature of 573 K, pellet has also similar trend, but higher sensitivity of 77% towards 100 vppm ammonia and 83% towards 100 vppm petroleum gas.

Table 1. Response and recovery time for $Ag_6Mo_{10}O_{33}$ thin film towards 100 vppm of NH_3 and PG each at 573 and 673 K.

Time in min	At 573 K		At 673 K	
	NH_3 (100 vppm)	PG (100 vppm)	NH_3 (100 vppm)	PG (100 vppm)
Response	10	8	1.5	5
Recovery	40	25	7	4

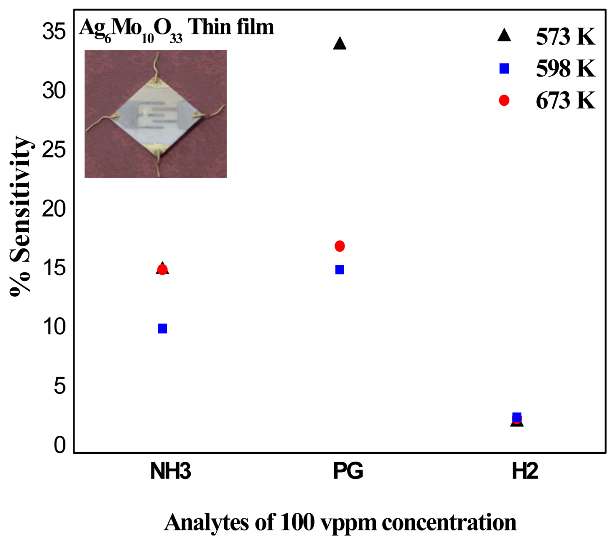

Figure 3. Typical sensitivity values of nano-crystalline $Ag_6Mo_{10}O_{33}$ thin film towards 100 vppm of different gas analytes at T = 573, 598 and 673 K.

4. Conclusion

Using the present soft-chemical method we could successfully synthesize nano-crystalline powders as well as thin films of $Ag_6Mo_{10}O_{33}$ on polycrystalline alumina substrate. The nano-crystalline $Ag_6Mo_{10}O_{33}$ is found to sense selectively ammonia at 503 K. But, above 503 K this compound has high cross sensitivity towards petroleum gas (PG). $Ag_6Mo_{10}O_{33}$ thin film sensor with IDE showed 13% sensitivity towards 100 vppm ammonia, 32% towards 100 vppm petroleum gas and negligible sensitivity towards 100 vppm hydrogen at an optimum temperature of 573 K. Thus, for ammonia and petroleum gas sensing applications, fabrication of compact device with $Ag_6Mo_{10}O_{33}$ thin film on substrate patterned with interdigitated Pt-electrodes can be recommended where there is no interference from each other between the two analytes. The exact sensing mechanism for PG is not known.

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