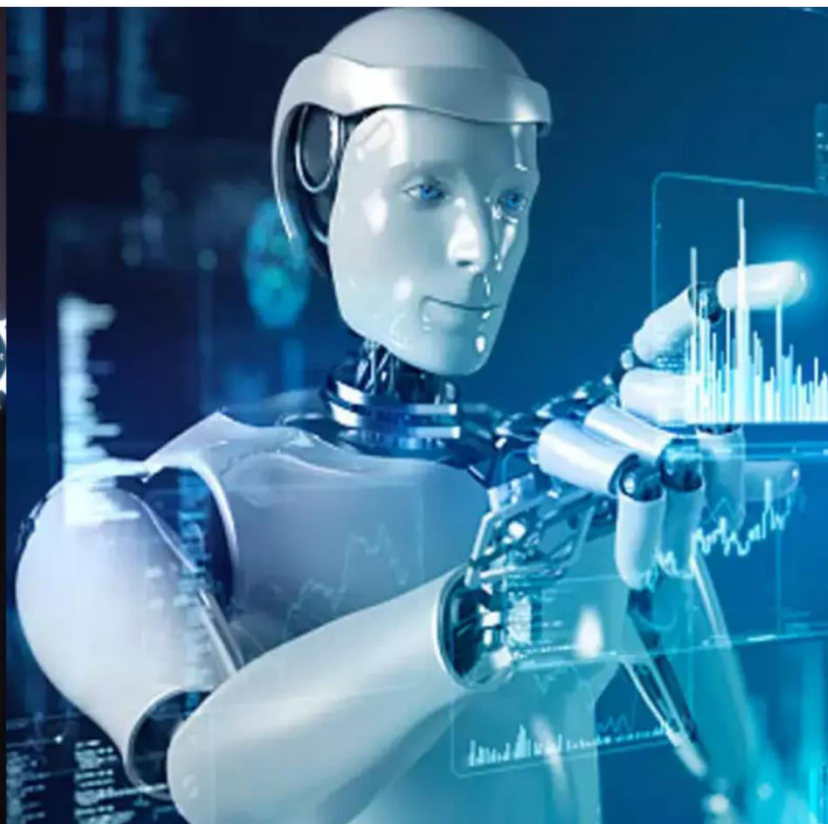




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Study of CuO-TiO₂ Composite Thick Film as an Ammonia Gas (NH₃) Sensor

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ABSTRACT: The present research was to prepare composites of Copper oxide (CuO) and titanium oxide (TiO₂) and their properties. The CuO-TiO₂ composites were prepared by mixing these oxides in different molar ratios using a mortar and pestle. These composites then subjected to sintering in the furnace at 800°C for 5 hrs in air. CuO-TiO₂ thick films were prepared on the glass substrate using screen printing technique. The prepared thick film were investigated by scanning electron microscope (SEM). This shows the composition is uniform throughout the mixture and CuO-TiO₂ composites are porous with varying crystal size. These thick films were further employed for NH₃ gas sensing at different temperatures and gas concentrations ranging from 10 to 200 ppm. Among the investigated composites, the mixed-oxide sample containing 45 mol% CuO and 65 mol% TiO₂ demonstrated the highest sensitivity at room temperature compared to other CuO-TiO₂ compositions. The response time and recovery times were also reported for optimizing the sensor in the present research.

KEYWORDS: Mixed Oxide Composites, Thick Film Sensor, NH₃ sensor, CuO-TiO₂, SEM

I. INTRODUCTION

One of the major challenges facing humanity is meeting the increasing energy demands driven by population growth, while sustaining economic development without causing irreversible harm to the environment. The constant emission of chemical pollutants such as NO_x, NH₃, CH₄, SO_x, CO, and fluorocarbons from industrial activities, vehicle exhaust, and household waste leads to several environmental issues, including acid rain, global warming, sick building syndrome, and ozone layer depletion [1,2]. To mitigate the environmental damage caused by air pollution, it is essential to have monitoring and control systems that can promptly detect these pollutants and accurately identify them within the limits of established standards. The first decade of the 21st century has been referred to by some as the “Sensor Decade” [4]. Historically, concerns about air pollution date back to as early as 1273, when the use of coal was banned in London due to its harmful effects on health. In 1863, the first “Alkali Works Regulation Act” was introduced to reduce the harmful emissions from industrial alkaline processes. Notably, in 1876, the UK established its first emission limit, setting a maximum allowable hydrogen chloride concentration at 0.446 g/m³ [5]. Since then, a wide range of technologically advanced sensors has been developed to detect and control environmental pollutants, as well as to ensure compliance with environmental regulations [4,5].

The manufacture of small-size cheap, functional at lower temperatures, high sensitivity, best selectivity, long-term stability, fast response/ lesser recovery times, lower detection limits, reliable gas sensors with high energy efficiency and enhanced performances have attracted wider interest due to growing global concern on environmental monitoring, domestic/public safety and automotive applications [6-8]. Gas sensors using semiconductor oxides have numerous advantages, such as low-cost, easy fabrication method and miniaturization, durability, and lower detection limits [9,10]. P-type semiconducting metal oxides such as NiO, CuO, and Cr₂O₃, and its n-type counterparts like TiO₂, SnO₂, and ZnO are recognized as promising sensing materials due to their potent chemical and physical stability [11-15]. Semiconductor oxides-based p-type and n-type gas sensors show interesting responses with oxidizing (e.g., NO₂, NO, CO₂) and reducing (e.g., CO, NH₃, CH₄, SO₂) gases. In our day-to-day life, ammonia gas (NH₃) is found its applications in dairy plants, frozen dessert plants, wineries, breweries, petrochemical industry, fruit crush, vegetable juice and beverage processing facilities [16].

In this study we prepared CuO-TiO₂ mixed oxide composites as sensors for NH₃ gas detection at ppm level. Also focuses on understanding the potential mechanism for detecting NH₃ species using Semiconductor oxides-based composites.

II. MATERIALS & METHODS

A) Preparation of CuO-TiO₂ mixed oxide composites

Commercial CuO (Merck AR Grade, 99%) and rutile-TiO₂ (Merck AR Grade, 99+%) were thoroughly mixed in different mole ratios to prepare CuO-TiO₂ composites. Acetone was added drop wise to the initial mixture placed in a crucible and grinded uniformly using a mortar and pestle. The resulting composite powder was first dried at 100 °C in a convection oven, then finely ground. This powder was subsequently calcined at 800 °C for 5 hours in air with a ramp rate of 10 °C/min. After calcination, the powder was re-ground using a mortar and pestle. The well-dried composite powders were then used for the fabrication of thick films. The prepared metal oxide composite samples were coded as listed in Table 1.

Sample	Composition in Mole %
S ₁	PureTiO ₂
S ₂	30CuO-70TiO ₂
S ₃	40CuO-60TiO ₂
S ₄	45CuO-55TiO ₂
S ₅	50CuO-50TiO ₂
S ₆	55CuO-65TiO ₂
S ₇	60CuO-40TiO ₂
S ₈	70CuO-30TiO ₂
S ₉	Pure CuO

Table1: Sample code for different composition

B)Preparation of CuO-TiO₂ Mixed Oxide composite Thick Film

Thick films of semiconductor sensors were fabricated using the standard screen-printing technique. For the preparation of these films, inorganic metal oxides were mixed with an organic binder solution in a 70:30 ratio. Binder solution was prepared by using Butyl carbitol acetate (BCA) and ethyl cellulose (EC) in fixed ratio of 8:92. Metal oxides and binder solution were mixed meticulously for 30 minutes using mortar and pestle. This gave us stoichiometric slurry to make stable thick films over glass substrates.

Further small amount of BCA was mixed to above slurry drop wise to get gel like paste. This jelly paste is applied as thick film with dimension of 1 X 0.5 cm over clean and dry glass substrate. After the application of composite coat on glass, these films were dried in air for 20 minutes and subsequently under IR light for 30 minutes. Afterward these composite loaded glass plates were heated in muffle furnace at 100⁰ C for approximately 2hrs. After cooling these thick films were used for the study of its electrical properties using screen printed silver electrode for electrical contact with the circuit.

C) Gas Sensing System

Performance of the prepared composite sensors was tested using ‘static gas sensing system’ [9-11]. Thick films were connected to D.C. voltage supply using two silver electrodes and varying voltage was measured by digital micro voltmeter. Heater was mounted at the base plate in order to maintain required temperature. Thermocouple was connected to digital thermometer for measuring temperature and inlet valve was fitted at one of the ports of base plate for the entry of the required amount of ammonia gas through injecting syringe. After every gas exposure cycle air was passes through glass dome.

III. RESULT AND DISCUSSION

A. Morphological characterization:

Scanning Electron Microscopy (SEM) is often used to examine the surface morphology of materials. SEM analysis of the materials can visualize various surface properties in the form of homogeneous, heterogeneous, porosity, voids present over the surface. The undoped copper oxide and CuO-TiO₂ composite thick film sensors were examined by SEM before gas detecting tests over the films. Figure 1 a-b revealed surface morphology of the porous CuO films. SEM pictures of pure CuO and its composite with TiO₂ showed that substantial is due to variable sized particles with

interstitial spaces. This porosity helped for efficient gas adsorption and also enhanced sensitivity of gas sensors. Comparison of particles size and surface are shown in Table 2.

Table 2: Surface area and mean particle size from SEM data

Fabricated sensor	Calcination temperature (°C)	Calculated size in nm	Surface area of film sensor(m ² /g)
S ₁ (Pure TiO ₂)	800°C	140nm	2.043
S ₄ (45CuO-55TiO ₂)	800°C	254nm	3.321
S ₅ (50CuO-50TiO ₂)	800°C	201nm	2.564
S ₆ (55CuO-45TiO ₂)	800°C	208nm	2.865
S ₉ (Pure CuO)	800°C	156nm	2.136

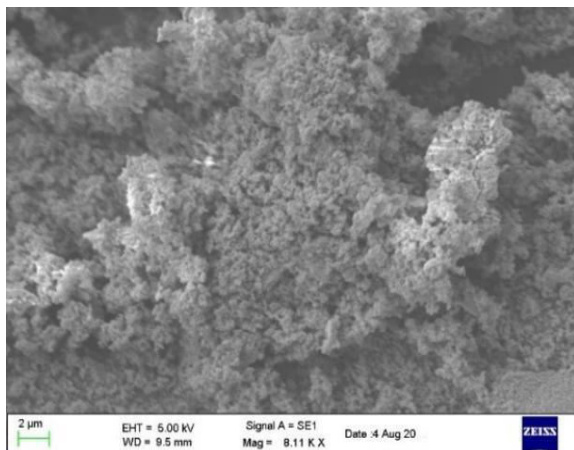


Fig.1 (a) SEM image for S₅ sample

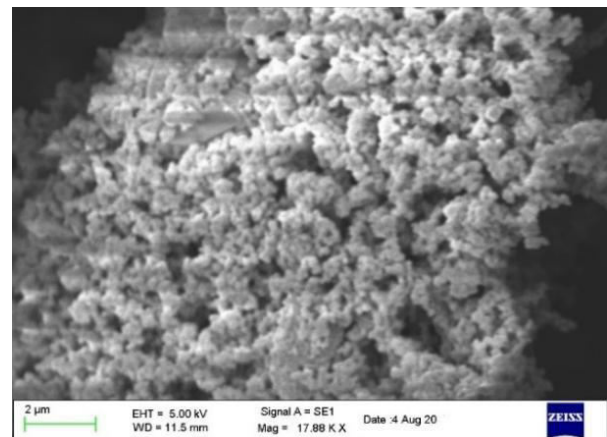


Fig.1(b)SEM image for S₄ sample

B. Electrical Characterization

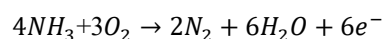
Thick film sensors of metal oxide composites were examined for electrical characterization and gas detection. Sensitivity of gas sensor in terms of resistance of sensors can be given by an equation

$$Sensitivity(S) = \frac{R_{NH_3} - R_{Air}}{R_{Air}}$$

Where R_{NH_3} is the electrical resistance of thick film in presence of Ammonia gas(NH₃) and R_{Air} is electrical resistance of thick film in ambient air.

Gas sensing characteristics of mixed oxide thick film for Gas(NH₃)

The sensing mechanism is governed by surface phenomena, where interactions occur between the gas molecules and the sensing surface. When the CuO–TiO₂ composite surface is exposed to an ammonia (NH₃) atmosphere, both NH₃ molecules and oxygen anion species are adsorbed. In ambient air, oxygen species undergo chemisorption on the material surface by capturing electrons from the sensor, forming adsorbed oxygen anions (O_{ads}⁻). This process generates a space-charge depletion region across the sensor surface, leading to a reduction in sensor resistance. The reaction between the CuO–TiO₂ composite and NH₃ can be represented as follows [10]:



It is well known fact that TiO₂ semiconductor is dominated by electrons while CuO behaves like a p-type, dominated by holes.

Higher work function of CuO and defects in the prepared composite surface leads to the formation of active sites for NH₃ adsorption. Thus, when the sensor surface is exposed to the NH₃ atmosphere, gas molecules are adsorbed on active sites of sensor and releases free electrons due to interaction between adsorbed oxygen species and NH₃. Due to this, the holes in the CuO neutralizes leading to decrease in the width of charge conduction channels, which further increases the width of the depletion layer, and hence sensor resistance increases.

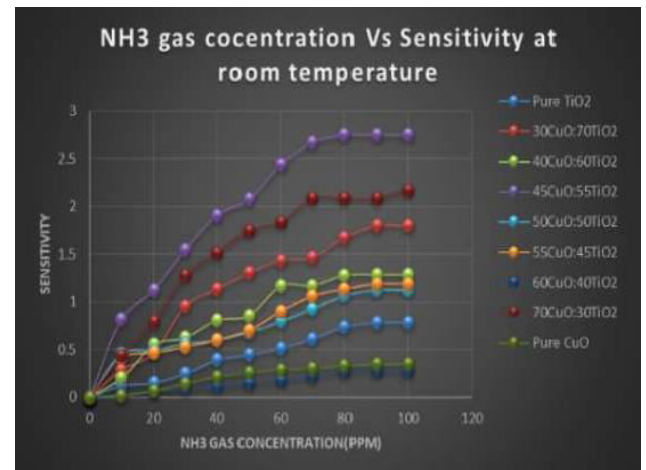
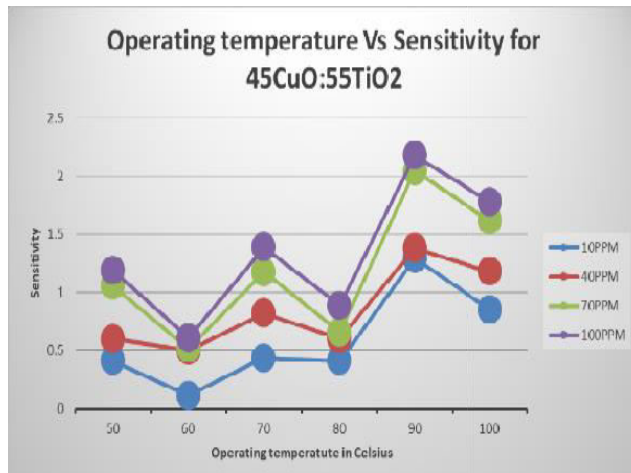
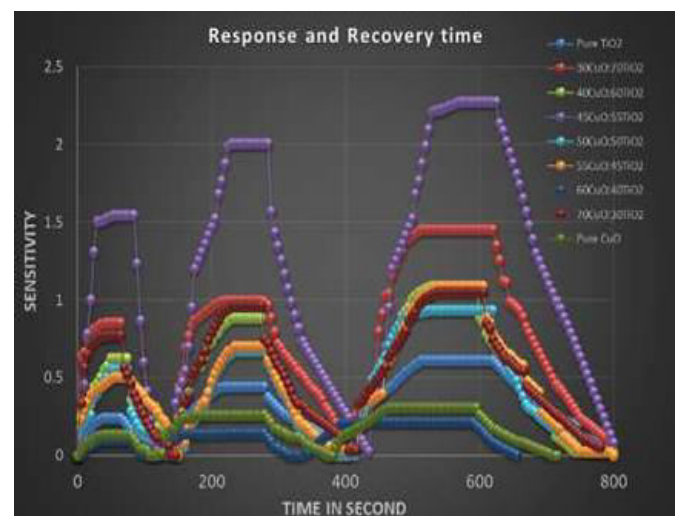
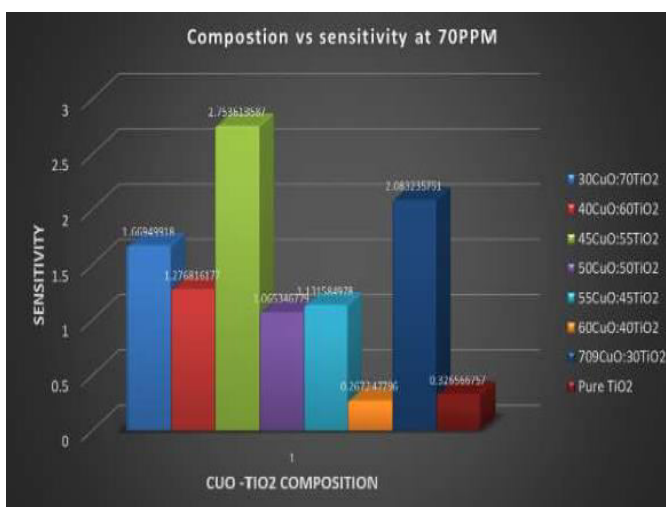


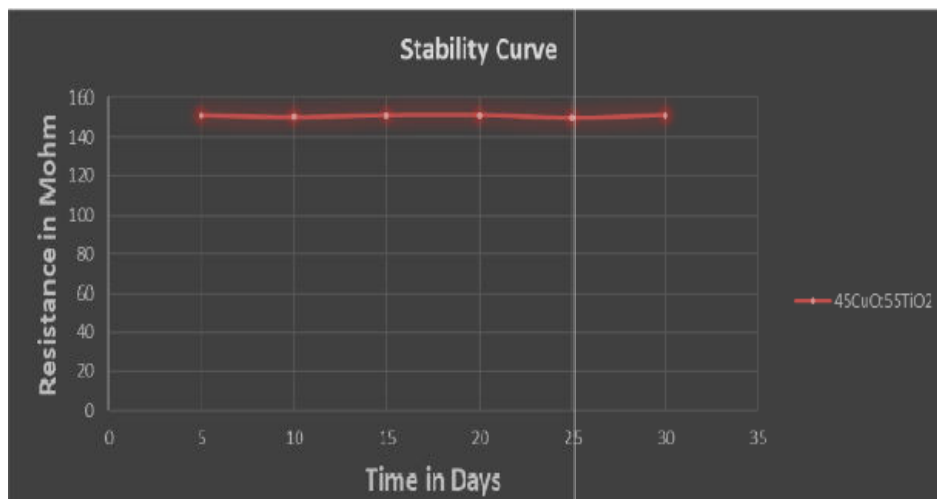
Fig. 2 shows the sensing response of the device at different operating temperatures and gas concentrations (10ppm -100ppm). From this response, it is seen that 90°C is the optimize operating temperature for optimize sensor i.e 45CuO:55TiO₂.

Fig. 3 shows the sensor responses of pure CuO, pure TiO₂, and CuO–TiO₂ composites toward NH₃ gas at varying concentrations. Incorporating CuO with TiO₂ results in a significant enhancement of the sensor response. Among the mixed oxide composites, the sample containing 45 mol.% CuO and 55 mol.% TiO₂ exhibits the highest sensitivity to NH₃, as shown in Figures 3(a) and 3(b). For evaluating response and recovery characteristics, 90% of the maximum response (i.e., a 90% drop from the equilibrium value) and 10% of the response level were selected as reference points, as presented in Fig.4. From this step-response analysis, it is evident that the 45CuO:55TiO₂ composite demonstrates shorter response and recovery times compared to other sensor compositions.



To analyze the reproducibility, we have repeated the response test 4 times for 10 NH₃ gas concentrations at 100°C temperature. The sensor responses are almost identical; which shows good repeatability as well as good reproducibility of the device. The reliability of the sensor depends on its long Therefore, the sensor response for CuO TiO₂metal oxide composite towards 10

ppm NH₃ at 90°C operating temperature has been tested for different time intervals. The response analysis up to one month shows a small deviation over time, as indicated in fig. 5.



IV. CONCLUSION

The CuO–TiO₂ metal oxide composite thick films were scrutinized as NH₃ gas sensors and characterized using SEM to examine porosity and surface morphology. Among the samples, the 45CuO–55TiO₂ composite demonstrated excellent response toward NH₃, whereas pure CuO and TiO₂ sensors exhibited comparatively poor performance. The optimized sensor achieved its highest response at an operating temperature of 90 °C for NH₃ concentrations of 70 and 100 ppm. Moreover, this sensor showed the shortest recovery time and superior stability over different time intervals. Overall, this study highlights the potential of CuO–TiO₂ composites for the development of high-performance gas-sensing devices suitable for semiconducting applications.

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