Cu_xO-based nanostructured thin films grown by reactive pulsed laser deposition as potential methane sensing elements.

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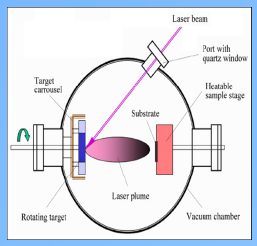
Abstract

- Undoped copper oxide (Cu_xO) thin films were grown by reactive pulsed laser deposition on glass and SiO_2 substrates.
- The surface morphology (AFM) and crystalline status (XRD) of the synthesized thin films were analyzed in correlation with their gas sensing characteristics towards two different methane concentrations (3000 and 5000 ppm) at a selected operating temperature within the (100 – 220 °C) range.
- To improve the gas sensing characteristics of the Cu_xO thin films, Au nanoparticles were deposited on the surface of the Cu_xO/SiO_2 thin film. The obtained structure was investigated by contact mode atomic force microscopy (AFM), by X-ray diffraction (XRD) and by energy dispersive X-Ray spectroscopy (EDX).
- It was also tested as a potential methane gas sensing element.

Films Preparation

- Undoped p-type Cu_xO thin films have been developed on glass and SiO_2 substrates by reactive pulsed laser deposition technique (R-PLD).
- A KrF laser (λ = 248 nm, τ_{FWHM} ~10 ns) source at 10Hz repetition rate was focused on a metallic Cu target. The laser fluence incident on the target surface was set at ~2 J/cm^2.
- The Cu_xO films were grown under a constant oxygen partial pressure of 40 Pa for 90 min and at a substrate temperature of 200 °C.
- After the film growth, the chamber was evacuated down to its nominal pressure and the Au target (99,998% purity) was ablated by the focused beam of the KrF laser for about 2 min.



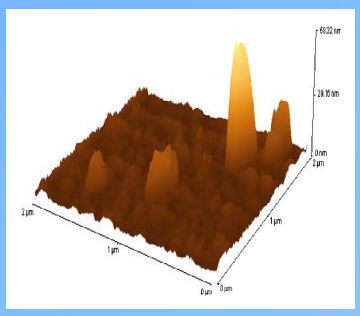
Hall-effect measurements were carried out at room temperature by using a magnetic field of 0.7 T.

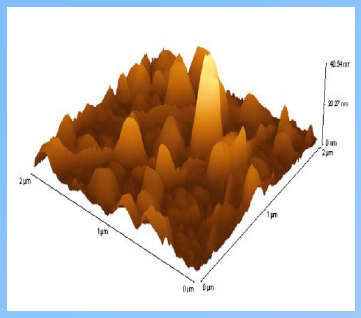
The deposited on SiO_2 substrate Cu_xO film demonstrated an increase in the resistivity and the Hall mobility while the carrier concentration decreased.

Substrate	ρ (Ω.cm)	μ_H (cm^2/V s)	p_H (cm^{-3})	Dominant Carrier Type
glass	86.3	9.8	7.4×10^{15}	p
SiO_2	166.3	132.7	2.8×10^{14}	p

$$\mu_H = \frac{R_H}{\rho} \qquad p_H = \frac{1}{e \cdot R_H}$$

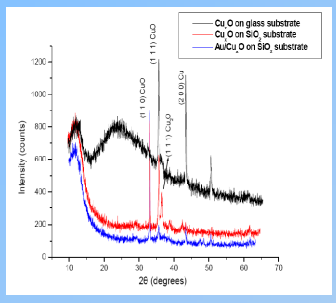
Films Characterization





The substrate type had an effect on the surface morphology of the films; the one on SiO_2 substrate was smoother than the other on glass substrate.

Substrate	Area Ra (nm)	Area RMS (nm)	Avg. Height (nm)	Max. Range (nm)
SiO_2	3.19	6.72	4.06	58.32
glass	4.10	5.96	5.58	40.54

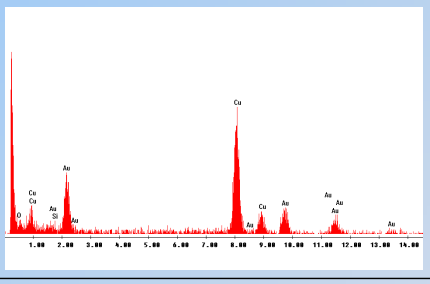


- Monoclinic crystal structure of copper oxide (CuO) revealed (peaks at **2θ = 33,1** and **35.7**)
- XRD pattern of the Cu_xO deposited on glass substrate reveals a less intense peak at **2θ = 43.5°**, which corresponds to (200) plane of Cu.
- XRD pattern of Cu_xO deposited on SiO_2 substrate reveals a second peak at **2θ = 36.4°** (Cu_2O).
- No diffraction peak of gold is observed. This is probably due to the low amount and small particle size of the gold.

$$FWHM = \frac{K \cdot \lambda}{D \cdot \cos\theta}$$

The Cu_xO film deposited on SiO_2 substrate has larger crystallites, which indicates better crystallinity.

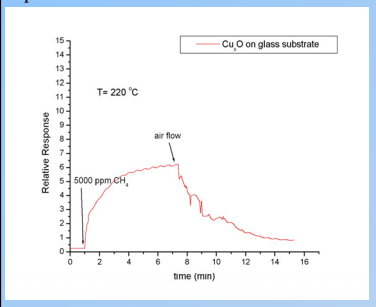
Substrate	D [nm] without Au nanoparticles	D [nm] with Au nanoparticles
glass	38.1	-
SiO_2	68.8	74.4

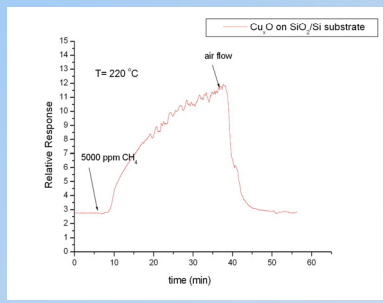


The EDX spectrum provided evidence for the presence of Au nanoparticles on the surface of the Cu_xO/SiO_2 thin film.

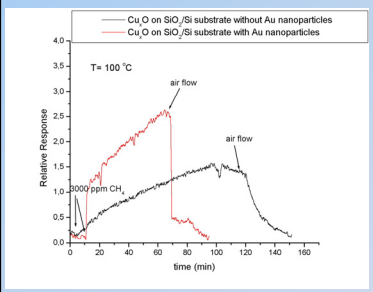
Methane Sensing Tests

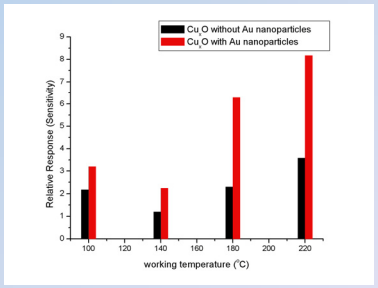
For a p-type semiconductor the resistivity decreases due to electron transfer by an oxidizing gas and increases with the presence of a reducing gas owing to electron capture into the conduction band.





- ***The Cu_xO film deposited on SiO_2 substrate exhibited higher relative response than Cu_xO film deposited on glass at working temperature of about 220°C.***
- ***The film deposited on the SiO_2 substrate exhibit high relative response even for low working temperatures such as 100°C.***





- The relative response (sensitivity) of Cu_xO film towards 5000 ppm methane in air mixture was strongly dependent on both the working temperature and surface modification.
- The film with Au nanoparticles on its surface exhibited higher relative response at working temperature of about 100°C and faster response and recovery times.

$$S = \frac{R_g - R_0}{R_0}$$

Conclusions

✓ **Undoped copper oxide (Cu_xO) thin films were grown by reactive pulsed laser deposition on glass and SiO_2 substrates.**
✓ **The influence of substrate type on the films surface morphology, crystalline status, electrical and methane sensing properties has been investigated.**
✓ **The gas sensing characteristics of these films are strongly influenced by surface morphology.**
✓ **In order to improve the gas sensing characteristics of the Cu_xO thin films, *Au nanoparticles* were deposited on the surface of the Cu_xO/SiO_2 thin film and the obtained structure increased the sensor response with respect to the unmodified one almost by 2 times.**