### **List of Abbreviations**

TMO Transition metal oxide

SMO Semi-conductor metal oxide

Cu Copper

 $CuO_x$  Copper oxide  $Cu_2O$  Cuprous oxide CuO Cupric oxide

Zn Zinc

ZnO Zinc oxide

*TiO*<sub>2</sub> Titanium dioxide

 $SnO_2$  Tin dioxide

 $Bi_2O_3$  Bismuth trioxide NiO Nickel (II) Oxide

Tantalum

Mo Molybdenum

W Tungsten Ag Silver Ti Titanium

CO Carbon monoxide

He Helium  $O_2$  Oxygen Ar Argen  $N_2$  Nitrogen

MB Methylene blue

*HH* Hydrogen Hydrate

*RT* Room Temperature

RF Radio Frequency

DC Direct Current

PVD Physical vapor depositionCVD Chemical vapour deposition

PLD Pulsed laser deposition

MBE Molecular beam epitaxy

XRD X-ray diffraction

SEM Scanning electron microscopy

XPS X-ray photoemission spectroscopy

UV-Vis Ultraviolet-visible

AFM Atomic force microscopy

STM Scanning tunneling microscopy

XPS X -ray photoemission spectroscopy

EDS Energy dispersive Spectroscopy

SPSTM Spin polarized scanning tunneling microscope

BEEM Ballistic electron emission microscope

SFEM Scanning field emission microscope

*PSPD* Position sensitive photo-detector

PID Proportional-integral-derivative

DMHCS Disordered mesoporous carbon spheres

LED Light emitting diodes

US-NIOSH United States National Institute of Occupational Safety and Health

*PQMS* Physical quantity measurement system

JCPDS Joint Committee on Powder Diffraction Standards

FWHM Full-width half maximum

VB Valance Band

CB Conduction Band

CZO Zn doped CuO

ZnO:Cu Cu doped ZnO

VOCs Volatile Organic Compounds

# **List of Symbols**

R Source substrate distance TSource temperature P Evaporant vapor pressure P Chamber pressure M Molecular mass of evaporant  $R_{s}$ **Sheet Resistance** Current VVoltage drop CFCorrection factor  $F_{I}$ Thickness correction factor Geometric dimension  $F_2$ Edge correction factor  $F_3$ S Probe spacing d Width of the sample l Length of the sample Thickness of the sample t Carrier concentration nCarrier mobility  $\mu$ Wavelength λ  $\theta$ Bragg angle Crystallite size DMicro strain  $\delta$ Dislocation density β Full width half maximum Electrical resistivity  $\rho$ Electrical conductivity  $\sigma$ Kubelka - Munk formula F(R)TTransmittance Ι Transmitted intensity Incident intensity of the light  $I_o$ 

Λ

Mean free path

- A Absorbance
- α Absorption coefficient
- *R* Reflectance
- v Frequency
- *h* Planck's constant
- *hv* Photon energy
- $E_b$  Binding Energy
- $E_k$  Kinetic energy
- Φ Work function
- $\Delta E$  Activation energy
- $\Delta G$  Energy change for chemical reaction
- $\Delta H$  Changes in Enthalpy
- $\Delta S$  Changes in Entropy
- D Diffusion coefficient of the oxidizing species
- $F_1$  Diffusive flux
- $C_0$  Concentration of the oxidizing species in atmosphere to film surface
- $C_{\rm s}$  Concentration of the oxidizing species at the Cu-Cu<sub>2</sub>O interface
- x Thickness of the oxide layer
- $F_2$  Reactive flux
- K Reaction rate
- S Sensitivity
- $R_a$  Sensor resistances in air ambient
- $R_g$  Sensor resistances in target gas
- C Concentration of the target gas
- *e* Electron
- $h^+$  Hole

#### List of Tables

- **Table 1.1:** Brief summary of the operating temperatures of MOs based CO sensors.
- **Table 3.1:** Average grain size for thin copper oxide films of different oxide phase.
- **Table 3.2:** Average grain size of thin CuO films after oxidation at different temperatures in air for 3 hours.
- **Table 3.3:** (a) Binding energy positions and relative peak intensities of de-convoluted O1s and  $Cu2p_{3/2}$  spectra of CuO thin films oxidized at 330°C and 600°C, respectively.(b)Relative intensity ratio of O-crst vs  $Cu2p_{3/2}$  (total),  $Cu^+$  vs  $Cu^+$  and O-crst vs O-def.
- **Table 3.4:** EDX elemental analysis of samples oxidized for 3hrs at 300°C, 350°C in air and 200°C, 300°C in oxygen ambient.
- **Table 3.5:** Hall data of CuO films, grown at different oxidation temperatures
- **Table 4.2:** Hall data of ZnO thin films grown at different oxidation temperatures for 4hrs
- **Table 4.1:** (a) Binding energy positions and relative peak intensities of deconvoluted O1s and Zn2p spectra of different ZnO thin films. (b) Relative intensity ratio of O-crst vs  $Zn2p_{3/2}$  and  $Zn2p_{3/2}$  to  $Zn2p_{1/2}$



## **List of Figures**

- **Figure 1.1:** Schematic graphical representation of CO impact on human health for different concentration and exposure.
- Figure 1.2: Schematic representation of various SMO based gas sensor research
- **Figure 1.3:** Schematic representations of gas sensing mechanism for reducing gas: (a) p-type semiconductor and (b) n-type semiconductor.
- **Figure 1.4:** Schematic representation of response curve of (a) p-type and (b) n-type material for CO gas
- **Figure 1.5:** Schematic representation of photo-catalytic dye degradation process.
- **Figure 1.6:** Schematic Representation for photo-generation of electron hole pairs for  $Cu_2O$ , (b) MB dye photo-degradation under visible light.
- **Figure 2.1:** (a) Schematic representation and (b) actual view of thermal evaporation deposition unit.
- **Figure 2.2:** (a) Schematic view of (a) plasma creation and (b) DC/RF magnetron sputtering unit, of a sputter system.
- **Figure 2.3:** (a) Schematics view of rotating crystal X-ray diffraction method with  $\theta$ -2 $\theta$  scan, (b) sample mounting state and rotating detector set up and (c) closed chamber X-ray diffractometer.
- **Figure 2.4:** Schematic drawing of (a) field emission scanning electron microscope (FESEM) and (b) interaction of focused electron beam with the matter.
- **Figure 2.5:** (a) Two basic operations (I) diffraction patterns and (II) image formation and (b) schematic view of the transmission electron microscopy.
- **Figure 2.6:** Schematic of scanning tunneling microscopy (STM).
- **Figure 2.7:** (a) Van der Waals force, (b) imaging modes dependence upon the distance between AFM probe and surface of the sample and (c) schematic diagram of atomic force microscope (AFM).
- **Figure 2.8:** Transitions of electrons from valence to conduction band in (a) direct and (b) indirect band gap.
- **Figure 2.9:** Diagram of energy levels for Rayleigh scattering and Raman scattering with Stokes and Anti Stokes line scattering.
- **Figure 2.10:** (a) Photoemission process of electrons and (b) schematic image of X-ray Photoelectron Spectroscopy (XPS).
- **Figure 2.11:** (a) A schematic diagram of (a) four point probe (b) setup image of four probe resistivity measurements.
- Figure 2.12: (a) A schematic diagram of four point of Van der Pauw method for rectangular geometric.
- **Figure 2.13:** Schematic view gas sensing measurement system and (b) digital image of measurement setup and vacuum chamber.

- **Figure 2.14:** Schematic side and top views, (b) digital image of metal oxide thin film gas sensor with top Au contacts.
- **Figure 3.1:** Optical photographs of (a) cuprous oxide and (b) cupric oxide thin films grown on glass substrates.
- **Figure 3.2:** Thin Cu films show (a) Temperature dependent sheet resistance in air, (b) R-T measurements of heating and cooling cycles of different Cu films during air annealing (c) comparison of sheet resistance during heating and cooling cycles in air as well as He ambient conditions.
- **Figure 3.3:** XRD spectra ( $\theta$   $2\theta$  scan) of thin Cu films after oxidation in air at various temperatures for (I) RT to 350°C for 3hrs durations and (II) 350°C to 600°C for different durations.
- **Figure 3.4:** Schematic representation of grain growth during the oxidation of copper thin films.
- **Figure 3.5:** Crystallite size of CuO<sub>x</sub> thin films for different oxide phase.
- **Figure 3.6:** Crystallite size of CuO thin films with oxidation temperatures.
- **Figure 3.7:** XRD spectra of thin Cu films during evolution of Cu<sub>2</sub>O oxide phases after oxidation in air at (a) 260°C and (b) 300°C, for different durations. Lorentzian peak fitting of (c-d) Cu(111) and (e-f) Cu<sub>2</sub>O (111) diffraction lines, along with their oxide growth kinetics shown within the insets.
- **Figure 3.8:** XRD spectra of thin Cu<sub>2</sub>O films transformation to CuO oxide phases during thermal oxidation in air at (a) 330°C and (b) 350°C, for different durations. Lorentzian peak fitting of (c-d) Cu<sub>2</sub>O (111) and (e-f) CuO (111) diffraction lines.
- **Figure 3.9:** XRD patterns of Cu films of different thickness (100 nm 300nm) after the oxidation at 150°C for 3hrs.
- **Figure 3.10:** XRD patterns of Cu layers oxidized at oxygen ambient at various temperatures and durations.
- **Figure 3.11:** XRD patterns of Cu layers oxidized at oxygen ambient at various temperatures and durations.
- **Figure 3.12:** Schematic representation of surface oxidation mechanism of thin copper films.
- **Figure 3.13:** SEM image of 400 nm thick Cu films on glass substrate: (a) as-grown (b) oxidized at 300°C, (c) 350°C for 3hrs annealing and (d) 350°C for 9hrs, (e) 500°C for 9hrs, (f) 600°C for 6hrs, (g) 800°C for 2 hrs and (h)1000°C for 2hrs, respectively.
- **Figure 3.14:** SEM image of 400 nm thick Cu films oxidized at 600°C for different duration of annealing (a) 3hrs, (b) 6hrs, (c) 9hrs and (e) 12hrson glass substrate.
- **Figure 3.15:** FESEM images of thermally oxygenized Cu films in oxygen ambient at (a) 200°C for 3 hours for single Cu<sub>2</sub>O phase, (b) 300°C for 3 hours for single CuO phase.
- **Figure 3.16:** AFM image of thin Cu films on glass substrate: (a) as-grown (b) oxidized at 300°C and (c) 350°C, respectively, in air ambient.

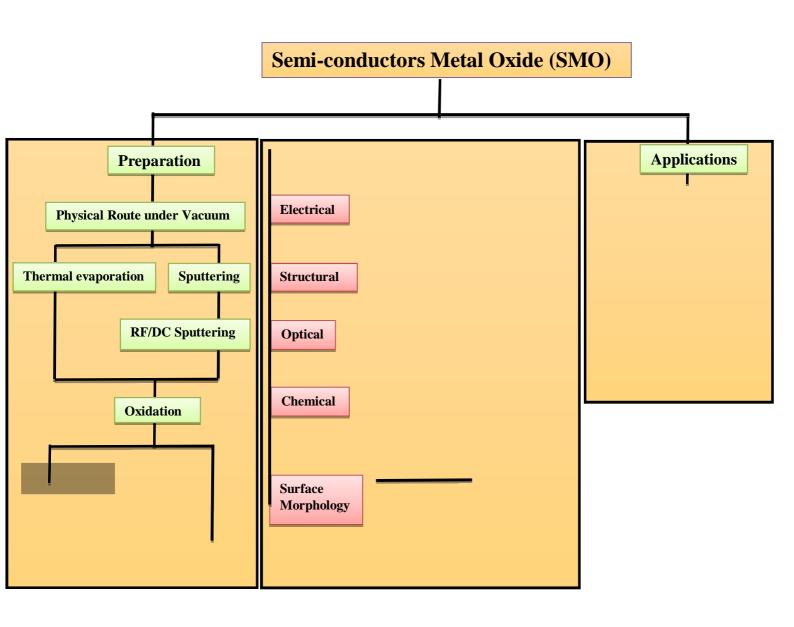
- **Figure 3.17:** STM images of thin  $Cu_2O$  films on glass substrate showing flat islands of triangular shape grown at 300°C. Scan areas (a) 500 nm  $\times$  500 nm and (b) 250 nm  $\times$  250 nm.
- **Figure 3.18:** Raster spectroscopy of thin  $Cu_2O$  films showing flat islands of triangular shape are electronically different from the other surface parts of the STM image. Scan areas (a)  $300nm \times 300$  nm.
- **Figure 3.19:** Raman spectra of various Cu oxides films grown by thermal oxidation of thin Cu films in air. Inset shows the Raman spectrum of Cu film oxidized at 220°C for 4 hours in air.
- **Figure 3.20:** UV-visible spectra of (a) Cu<sub>2</sub>O and (b) CuO thin films grown by thermal oxidation in air ambient. Inset shows the optical band gap for different CuOx thin film thicknesses.
- **Figure 3.21:** XPS spectra of different Cu oxide films: (a) Wide Scan (b) Cu2p core level and (c) LMM Auger spectra.
- **Figure 3.22**: XPS spectra of CuO films with different oxidation temperatures: (a) XPS survey Scan of 330°C, 400 and 600°C. High resolution scans for 330°C: (b) O1s and (c) Cu2p<sub>3/2</sub>. High resolution scans for 600°C: (d) O1s and (e) Cu2p<sub>3/2</sub>.
- Figure 3.23: XPS spectra of thermally oxidized thin Cu films in an oxygen ambient condition.
- **Figure 3.24:** EDX spectrum of copper oxide thin film, prepared by 3hrs of oxidation at (a) 300°C (b) 350°C in air ambient and (c) 200°C, (d) 300°C in oxygen ambient.
- **Figure 3.25:** Sheet resistance of thin Cu films (a) I-V plot at room temperature (b) R-T Plots.
- **Figure 3.26:** (a) Rectangular geometry of thin Cu film (t < s/2, a = 2.5cm and b varies from 7.5 to 2.6 cm) (b) Sheet resistance and(c) G correction factor for thin Cu films of different rectangular geometry as a function of probe spacing (s/b).
- **Figure 3.27:** Schematic representation of the surface electrical resistivity (I-V) measurement (a) top view and (b) cross-sectional view.
- **Figure 3.28:** Surface electrical resistivity (I-V) measurement of CuO films grown at different temperatures for duration of (4hr and (b) 6hr.
- **Figure 3.29:** Comparison of the surface electrical resistivity measurement of CuO thin films for different oxidation temperatures.
- **Figure 3.30:** UV-Vis absorption spectra and (b) MB dye degradations with irradiation time for nano-structured Cu<sub>2</sub>O thin film under visible light.
- **Figure 3.31:** (a) UV-Vis absorption spectra and (b) MB dye degradations with irradiation time for nano-structured CuO thin film under visible light.
- **Figure 3.32:** (a) p-type semiconducting behavior and (b) a schematic of response and recovery times of a CuO thin film based sensor in the exposure of CO gas.
- **Figure 3.33:** Variation in sensors response of (a) sample I, (b) sample II, (c) sample III for different concentration and at (d) 50ppm of CO gas as a function of operating temperature (150°C to 250°C).

- **Figure 3.34:** Change in surface electrical resistance due to exposure to various concentrations of CO gas at optimum operating temperatures(a) 230°C for sample I, (b) 250°C for sample II, (c) 280°C for sample III and (d) Sensor operating temperature increases with the oxidation temperatures.
- **Figure 3.35:** The sensors response for different operating temperatures as a function of CO concentration for (a) sample I, sample II, (c) sample III and (d) at optimum operating temperatures for all nano- structured CuO thin films based sensors.
- **Figure 3.36:** Transient behavior of the CuO sensor at optimum temperature (230°C) and 240 ppm indicating response magnitude, response time and recovery time.
- **Figure 3.37:** Surface electrical resistivity (I-V) measurement of CuO sensor samples grown at different oxidation temperatures.
- **Figure 4.1**: Temperature dependent sheet resistance of Zn thin film during annealing in air and helium (He) ambient.
- **Figure 4.2:** XRD spectra of (a, I) as grown Zn thin films and thermally oxidized at temperatures (II) 180°C, (III) 400°C and (b, I) 500°C, (II) 600°C, (III) 650°C and (IV) 700°C for 4hrs.
- **Figure 4.3:** (I) XRD spectra of (a) as-deposited Zn thin films and transformation to ZnO phases for durations of (b) 15min, (c) 30min, (d) 45min and Lorentzian fit of XRD spectra (II) Zn (101) and (III) ZnO(101) diffraction peaks as a function of oxidation time during thermal oxidation in air at 500°C temperature.
- **Figure 4.4:** Area of Zn (101) and ZnO (101) diffraction lines, along with their oxide growth kinetics.
- **Figure 4.5:** FESEM images of Zn films on glass substrate thermally oxidized at: (a & b) as-grown (c & d) 240°C, (e & f) 400°C, (g & h) 500°C and (i & j) 600°C for 4hrs. Right column shows a closer view.
- **Figure 4.6:** FESEM images of Zn Nano-rods on glass substrate. Oxidation temperature: (a & b) 600°C and (c & d) 700°C. Right column shows a closer view.
- **Figure 4.7:** FESEM results of (a) as-grown Zn film and thermally oxidized at (b) 500°C, (c) 600°C, (d) 650°C and (e) 700°C for 4hrs on SiO<sub>2</sub>/Si substrate.
- **Figure.4.8:** A schematic representation of different surface morphologies of (a) the transformation of metallic Zn to ZnO phase and (b) ZnO phases at higher temperatures.
- **Figure.4.9:** Schematic representation of different crystal planes of a ZnO nano-rod with prismatic and pyramidal facets
- **Figure 4.10:** Prismatic ZnO nano-rods: (a) SEM image, (b) TEM micrograph, (c) HRTEM image, (d) SAED pattern, and Pyramidal ZnO nano-rod: (e) SEM image (f) TEM micrograph,(g) HRTEM image, (h) SAED pattern.
- **Figure 4.11:** Raman spectra of (a) as grown Zn film and thermal oxidation of Zn films at (b) 180°C, (c) 240°C, (d) 400°C, (e) 500°C, (f) 600°C for 4 hours in air ambient.
- **Figure 4.12:** XPS (a) survey scan and high resolution spectra of (b) O1s, (c) Zn2p binding energy peaks of ZnO nano-rods formed after air oxidation of Zn films at 700°C for 4 hours.

- **Figure 4.13:** High resolution Zn2p and O1s binding energy spectra of ZnO nanostructures grown at different oxidation temperatures.
- **Figure 4.14:** Current voltage plot of ZnO thin films, prepared at different temperatures during the air annealing.
- **Figure 4.15:** Schematic of response and recovery times of a ZnO thin film based sensor in the exposure of CO gas.
- **Figure 4.16:** Responses curve of ZnO nano-rods at different operating temperature (a & d) 200°C, (b & e) 250°C and (c & f) 280°C for various concentrations of CO gas.
- **Figure 4.17:** Response curves of the ZnO nano-porous based sensor at different operating temperature (a & d) 150°C, (b & e) 200°C and (c & f) 250°C for various CO concentrations.
- **Figure 4.18:** Response curves of nano- structured ZnO thin films based sensors at operating temperature 250°C for maximum concentrations of CO gas.
- **Figure 4.19**: Ethanol vapour sensing at the concentration of (a) 2000ppm and (b) 5000ppm of ZnO nano-rods sensor at room temperature.
- **Figure 5.1**: XRD patterns of pure and doped CuO thin films with different concentration of Zn, thermally oxidized at 400°C for 4hrs in air ambient.
- **Figure 5.2**: XRD patterns of (a) pure CuO nano-particles and Zn doped (b) 0.04M, (c) 0.06M, (d) 0.08M of CuO nano-particles.
- **Figure 5.3**: Variation in Crystallite size (D) and micro-strain (ε) of CuO thin films as a function of Zn dopant concentration (power of Zn target)
- **Figure 5.4**: FESEM results of (a) pure and doped CuO<sub>x</sub> thin films with different concentration of Zn (b) Zn@50W, (c) Zn@80W, deposited using sputtering method and then thermally oxidized at 400°C for 4hrs on glass substrate.
- **Figure 5.5:** FESEM results of (a) pure CuO nano-particles (b)CuO-ZnO nano-composite with 0.08M concentration of Zn.
- **Figure 5.6:** (a) UV-visible absorption spectra, (b) Energy band gap  $[(\alpha h v)^2 \text{ vs. hv}]$  plot and (c) variation of the band gap with Zn concentration of pure and Zn doped CuO nanoparticles
- **Figure 5.7**: Raman spectra of (a) pure and doped  $CuO_x$  thin films with the power of Zn target are (b) 30W and 40W, (c) 50W and 60W, (d) 70Wand 80W.
- **Figure 5.8**: Raman spectra of (a) pure and doped  $CuO_x$  nano-particles (b) 0.04M, (c) 0.06M and (d) 0.08M)
- **Figure 5.9**: XPS survey scans sputter grown doped Zn:CuO films with various Zn concentrations (using Al- $K_{\alpha}$  line).
- **Figure 5.10**: XPS survey scans sputter grown doped Zn:CuO films with various Zn concentrations (using Mg- $K_{\alpha}$  line).
- **Figure 5.11**: A schematic of the bar graph for different phases of ZnO:CuO mixed oxides (a) Physical growth route through sputter deposition and (b) Chemical growth route through sol-gel synthesis.

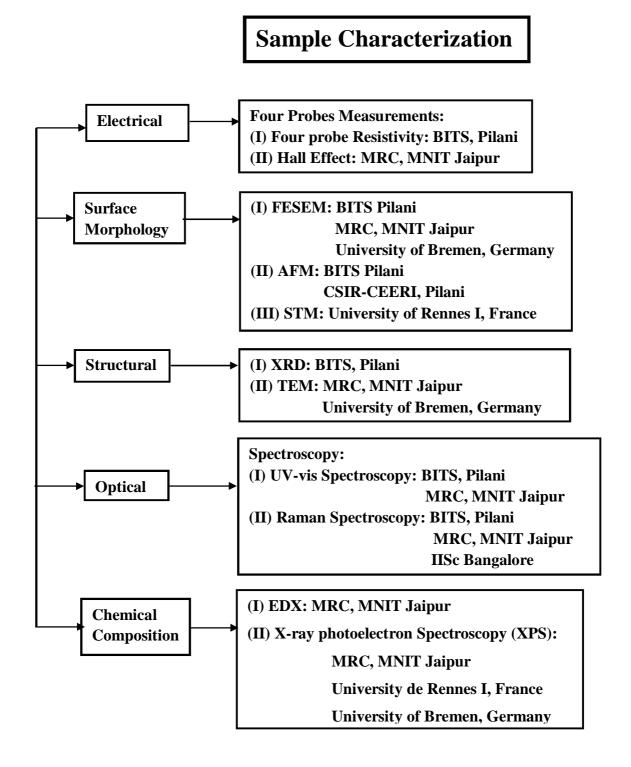


**Flow Chart I** 





### Flow Chart II



### Flow Chart III

