Abstract

Nowadays, semiconducting metal oxides (SMO) based nanostructures become technologically very important for environmental safety, as they are widely used as gas sensing materials towards the early detection of any toxic or dangerous materials in gas phase, as well as due to their excellent photo-catalytic properties extended to recycling/removing the environmental pollutant such as industrial dyes mixed in waste water, through a proper degradation process. In addition, they have the potential as green energy sources through water-splitting or solar cells applications.

In this thesis, p-type copper oxide (Cu_2O , CuO) and n-type zinc oxide (ZnO) based nanostructures are grown using vacuum assisted thermal evaporation of metal (Cu, Zn) films followed by controlled thermal oxidations. Additionally, mixed oxides (CuO:ZnO) are also grown using sputtering and chemical sol-gel techniques. As characterization tools, four probe measurement (surface resistivity and hall effect), X-ray diffraction (XRD), scanning electron microscopy (SEM), scanning probe microscopy (STM, AFM), Transmission electron microscopy (TEM), UV-Vis Spectroscopy, Raman spectroscopy, Energy Dispersive X-ray (EDX) analysis and X-ray photoelectron spectroscopy (XPS) have been used. Carbon monoxide (CO) sensing behaviour of CuO and ZnO based nanostructures are characterized, with a special focus on their oxidation mechanism, various analytical properties and their correlations to the gas sensing properties. In addition photo-catalytic properties of copper oxide films towards Methylene blue (MB) dye degradation are also tested.

At thermodynamic equilibrium, copper oxide phase is found to be solely determined by the oxidation temperature. Under air ambient oxidation, Cu_2O phase is formed below 320°C and afterwards CuO phase starts to appear, which is also sensitive to the oxygen partial pressure. All findings are explained in terms surface oxidation of thin Cu films, where surface kinetics and thermodynamics related to thermal diffusion as well as chemical reactivity determine the structure, morphology and chemistry of the copper oxide films. Nano-structured Cu_2O thin films with tiny faceted structures show a high photo-catalytic activity towards MB degradation under the visible light irradiation (98% within 15min). Nano-structured CuO thin films show very high sensitivity to CO gas at relatively low operating temperature (150°C, 25ppm). CO sensing results are found to be very much promising for CuO thin films grown at relatively lower oxidation temperature (350°C).

Controlled modulation in surface morphology of ZnO based nanostructures, starting from a vertical nano-wall to a laterally grown asymmetric 1D nano-rods/wires formation is observed by systematically controlling the surface kinetics and thermodynamics. Vertical growth morphology of ZnO nano-wall/sheet structures appear at relatively lower oxidation temperature (below 450^{o}C) whereas a transition to laterally grown 2D layered structures is observed above 500^{o}C. At even higher oxidation temperature of about 650^{o}C promotes an anisotropic 1D lateral growth of ZnO nano-rods. Within kinetic limitation, vertical growth is mainly controlled by the initial surface morphology of metallic Zn film whereas lateral growth of ZnO layered structures is strongly preferred by the oxide formation. Formation of ZnO nano-rods are mostly driven by the reduced surface free energy. In contrast to CuO thin films, ZnO based nanostructures grown at relatively higher oxidation temperature exhibit a superior response to CO gas as compared to that grown at lower oxidation temperature. ZnO nano-rods show a strong CO response (19%) with low operating temperature (150^{o}C, 50ppm). In addition, these nano-rods are also able to sense the ethanol vapour at room temperature.

A possible growth mechanism for doped and nano-composite has been discussed for sputtered and chemically grown mixed oxides (CuO:ZnO). All results suggest doped as well as CZO nano-composite exhibit significantly different structures and properties, which may open a new pathway for enhanced catalytic usage and selective gas sensing application of these oxides based nanostructures. Finally, all oxide materials are mainly grown through the physical route having sufficiently long duration of thermal oxidation which confirms their thermodynamic stability.

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