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Cu_2O/CuO thin film p-p nano-heterostructures for gas sensing

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Abstract:

Thin films of Cu_2O/CuO deposited by reactive magnetron sputtering followed by controlled annealing in air are proposed as new p – p type nano-heterostructures for gas sensing. Homogenous Cu_2O thin films are obtained up to 20% O_2 in Ar+O_2 sputtering atmosphere. Annealing for 1h at 400°C results in bilayer structure of Cu_2O/CuO sensitive to 8 ppm NO_2 at 155°C.

Key words: gas sensors, nanomaterials, heterostructures, thin films, CuO, Cu_2O

Introduction

In comparison to single metal oxides, the nano-heterostructures appear as very attractive alternative solutions especially in photocatalysis [1] and gas sensing [2]. The most frequently studied combinations are n-n type (e.g. TiO_2-SnO_2 [3]) and n-p type (e.g. ZnO-CuO [4]). While the application of n-type metal oxides is widespread in gas sensing, much smaller number of papers concentrates on those of p-type. However, thin/thick films and nanowires of p-type semiconducting CuO and Cu_2O have been recently given a particular attention [5-7] due to their good electrical conductivity, direct band gap and availability.

From all different classes of nano-heterostructures, we concentrate on bi-layer and multilayer thin films with well-defined interfaces. To the best of our knowledge, this is the first report on NO_2 gas sensing by thin films of Cu_2O/CuO prepared by magnetron sputtering followed by controlled annealing in air.

Experimental

Thin films were deposited onto silicon, amorphous silica and alumina substrates by reactive magnetron sputtering from Cu (99,999%). The influence of oxygen content in Ar+O_2 gas mixture (15-35%) on the growth mechanism and the resulting properties was studied. Film thickness was measured with a Talysurf CCI Taylor Hobson optical profilometer. Crystallographic structure was determined by X-ray diffraction at glancing incidence with a Philips X'Pert Pro diffractometer. Film morphology was studied with a FEI Helios NanoLab 600i scanning electron microscope. Film transformation to Cu_2O/CuO nanostructure was performed by annealing in air at 400°C for a controlled amount of time. Gas sensing measurements were carried out in a custom-made system capable of detecting resistance changes under stabilized temperature chosen within the range from 20°C to 400°C, humidity concentration of 50% Rh and modulated gas flow up to 20 ppm NO_2.

Results

Thin films deposited by the reactive magnetron sputtering from the Cu target up to 20%O_2 crystallize mostly in Cu_2O cubic structure. Low oxygen concentrations of 15% and 17.5% O_2 in the reactive mixture indicate a tendency towards amorphisation while the presence of metallic Cu cannot be excluded (Fig.1a). Crystallization in CuO monoclinic structure takes place as a result of annealing in air at 400°C (Fig.1b). Oxygen diffusion towards the substrate can be controlled by annealing time and after 1h it was possible to obtain a Cu_2O-CuO bilayer heterostructure shown in Fig.2. The electrical resistance R of the films depends on the oxygen content in the Ar+O_2 sputtering mixture and at 15-17.5% O_2 can be optimized for gas sensor measurements by a suitable choice of film thickness (Fig.3).

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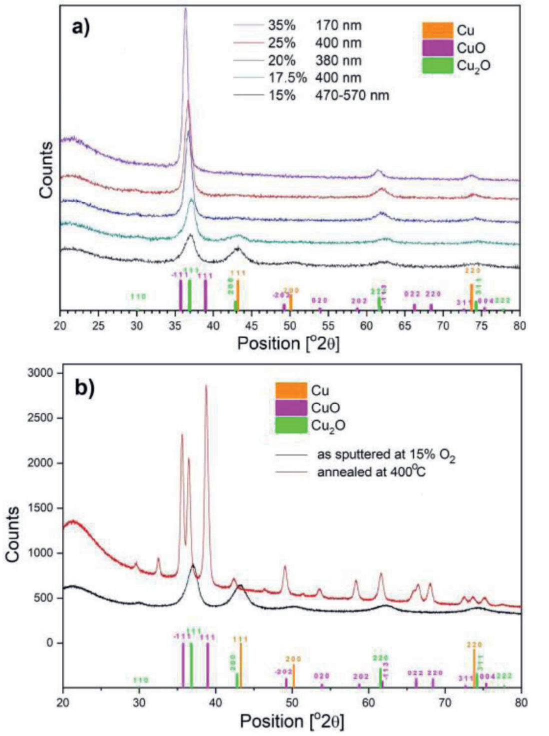

Fig. 1. XRD GID patterns for (a) as-sputtered thin films deposited from Cu target in the reactive magnetron sputtering in the Ar+O_2 gas mixture, (b) annealed thin film

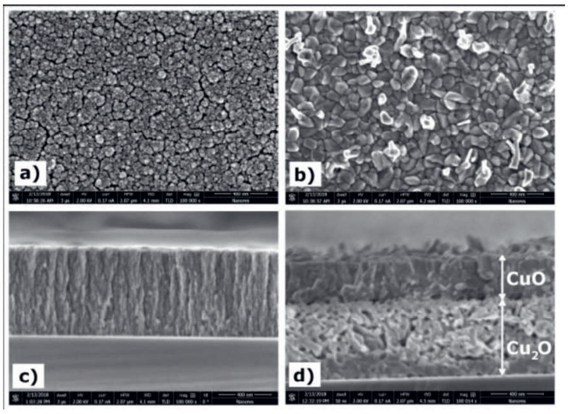

Fig.2.SEM images of: (a) the surface of as-sputtered thin film obtained at 15% O_2, (b) the surface of the same film after annealing in air at 400°C, (c) cross-section of the film presented in (a), (d) cross-section of the film presented in (b).

Dynamic changes in R upon NO_2 on/off profile presented in Fig.3 at a constant but relatively low temperature of 155°C are reproducible for the consecutive cycles. However, a drift in the baseline signal can be clearly seen. Stabilization of the baseline is expected in Cu_2O-CuO bilayer structures.

Conclusions

Several factors affecting the growth, fundamental properties and gas sensing behavior have been identified in the case of Cu_2O-CuO thin films deposited by reactive magnetron sputtering from Cu target in the Ar+O_2 atmosphere. Bi-layered structure was obtained for samples grown at low oxygen concentrations (less than 20% O_2) by annealing in air at 400°C for a controllable amount of time. The films respond to the changing NO_2 concentration by a resistance decrease typical for p-type gas sensors.

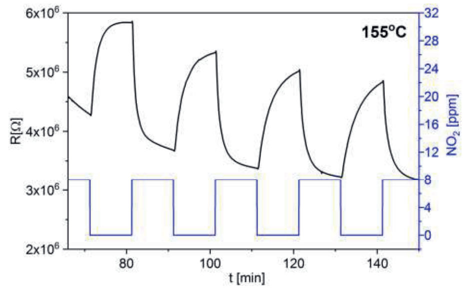

Fig. 3. Dynamic changes in the electrical resistance R of Cu_2O thin film obtained by magnetron sputtering at 17.5% O_2 upon 8 ppm NO_2 at 155°C

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