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New polymorph γ-$CuWO_4$ inspired by γ-$CuMoO_4$: Experimental identification and theoretical verification

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A B S T R A C T

In the context of our efforts to develop hydrogen gas sensors, two samples of ternary $CuWO_4$ with the same crystalline structure have been prepared by two different non-equilibrium techniques. We show that the materials' structure is significantly different from the known stable one, and we identify that it is very similar to that of previously reported γ-$CuMoO_4$. We use ab-initio calculations to confirm that the newly identified phase, γ-$CuWO_4$, represents a local energy minimum. We present very similar calculated and measured lattice constants and X-ray diffractograms. We make a case that the low-temperature formation of the metastable γ-$CuWO_4$ phase is facilitated by easier kinetics and/or by Cu-rich composition of our samples, and we show that it converts to the stable phase after annealing to 600 °C.

There are worldwide efforts [1,2] to continuously improve the performance of semiconductor metal oxide-based gas sensors, for various applications in the field of hydrogen economy, environmental monitoring, breath monitoring or food analysis. The sensors are of particular interest at the nanometer scale, where the large surface-to-volume ratio significantly improves their sensitivity. Further progress has been achieved by moving from homogeneous metal oxides to nanocomposites, nanostructures, heterojunctions and core-shell nanoparticles (NPs), which combine two semiconductors such as n-type WO_3 and p-type CuO [3–12]. Sensing of a wide range of gases has been reported using this pair of materials, ranging from hydrogen [12] and hydrogen sulfide [10] through ammonia [6] or acetone [5] to xylene [3] or sarin [9].

In this context, we are making efforts to prepare WO_3+CuO based sensors by two different deposition techniques which realize two different designs: (i) film of WO_3 on nanoparticles of CuO and (ii) alternating monolayers of nanoparticles of WO_3 and nanoparticles of CuO. In both cases, the research includes annealing of the as-deposited sensors to various temperatures in synthetic air. While the sensing performance of the materials and devices obtained will be published separately, the present paper deals with one of these materials itself. We have found that at a temperature of at most 400 °C, a new polymorph, referred to as γ-$CuWO_4$ throughout this paper, formed at the interface of WO_3 and CuO. The structure of this polymorph is significantly different from that of the known stable phase which is usually given without any Greek letter and which we refer to as α-$CuWO_4$ for distinguishing purposes. However, the structure of the newly identified polymorph is very similar to the known γ-$CuMoO_4$ phase.

The aim of this paper is to examine the existence of the newly identified polymorph γ-$CuWO_4$, to specify under which conditions did it form, to confirm that it constitutes a local energy minimum according to ab-initio calculations, and to check whether it converts to stable α-$CuWO_4$ after annealing to a sufficiently high temperature. In addition to a possible usefulness of γ-$CuWO_4$ itself, the presented information is expected to be useful for the correct interpretation of results obtained by the numerous practitioners dealing with the aforementioned devices based on WO_3+CuO.

The sample based on a combination of a thin film of WO_3 on CuO NPs was prepared in two steps. First, the NPs were prepared utilizing a magnetron-based gas aggregation source (MGAS). The MGAS (HVM Plasma) was attached to a main deposition chamber, where a silicon substrate was mounted to a rotating substrate holder kept at a room temperature. The MGAS featured of a cylindrical magnetron equipped with a 50 mm diameter Cu target placed inside a cylindrical aggregation chamber measuring 100 mm in diameter, terminated by a conical ending with a 4 mm diameter orifice. The NPs were prepared in Ar atmosphere at an Ar flow rate of 100 sccm and a pressure of 80 Pa. The magnetron was driven in DC mode and operated at a constant discharge power of 100 W. Second, 40 nm thin film of WO_3 was deposited on top of

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