

Larissa Dloczik · Rolf Koenenkamp

Nanostructured metal sulfide surfaces by ion exchange processes

Received: 27 November 2002 / Published online: 3 December 2003
© Springer-Verlag 2003

Abstract A scalable preparation procedure for structured semiconducting sulfide films from zinc oxide by means of subsequent anion and cation exchange processes is described, which is low in cost and waste production. The starting material was columnar ZnO films, which were grown in electrodeposition by O₂ reduction. Here, their detailed morphology depends on the substrate and the process parameters. These films were converted to ZnS by reaction with H₂S gas or sulfur vapour at temperatures around 450 °C. In this process the columnar morphology of the ZnO is preserved. A partial conversion is also possible and leads to tubular ZnS films. Then the ZnS films were reacted in metal salt solutions to convert them further to Ag₂S, Cu₂S, Bi₂S₃ and Sb₂S₃ films. Here the columnar or tubular morphology was, in general, also reproduced, but its outer quality depends on the interaction of the involved processes, namely dissolution, precipitation and exchange inside the solid. This was further examined by a series of Ag₂S films from modified solutions.

Keywords Ion exchange · Metal sulfides · Microstructuring · Thin films · Zinc sulfide

Introduction

The performance of catalytic and microchemical reaction systems, sensors, solar cells and opto-electronic devices depends on the material and the structure of its

Presented at the 3rd International Symposium on Electrochemical Processing of Tailored Materials held at the 53rd Annual Meeting of the International Society of Electrochemistry, 15–20 September 2002, Düsseldorf, Germany

L. Dloczik (✉) · R. Koenenkamp
Hahn-Meitner-Institut Berlin,
Glienicke Strasse 100,
14109 Berlin, Germany
E-mail: dloczik@hmi.de
Tel.: +49-30-80622610
Fax: +49-30-80623199

surface. Most of the existing procedures for tailoring such a surface on the nano-scale are specific to one material, or require expensive equipment. Moreover, for the production of thin-film photovoltaic cells, cost-efficient large-area processing and avoidance of toxic ingredients would be desirable. Thin films of the transparent conductive oxide ZnO have found wide application here. They can be deposited, e.g. by sputtering, spray pyrolysis or sintering. As a starting material for our study we preferred electrodeposited ZnO, since this can be obtained in especially deep and well-crystallized columnar structures [1]. However, for chemical and wet applications, ZnO has the disadvantage of being attacked by wet environments outside the pH window of 8–12.

Experimental

Electrodeposition of columnar ZnO

ZnO was electrodeposited with a Bank PSG 95 potentiostat in a three-electrode cell (Metrohm) with a custom-built sample holder electrode on various metal- or SnO₂:F-coated glass samples. The aqueous deposition solution contained bubbling O₂, 5×10⁻⁴ M ZnCl₂, 1×10⁻⁶ M AlCl₃ and 0.1 M KCl (99.999%) supporting electrolyte [1]. Cleaning and galvanostatic pre-conditioning of the SnO₂:F-coated glass samples, typically with 4 mA/cm² for 15 s, is described in more detail elsewhere [2]. A further increase of seed coverage on this kind of substrate can be obtained by previous electro-etching in 0.5 M H₂SO₄ at -800 mV vs. NHE for 15 s, followed by rinsing with 1 M HNO₃ and water.

Deposition was carried out at 80 °C for typically 3 h in the range of -450 to -750 mV vs. NHE, depending on the conductivity of the substrate. The cell was equipped with a custom-built flow shaper to generate a more laminar flow along sample areas up to 5 cm×5 cm.

Conversion to ZnS

The morphology-transferring conversion of the structured ZnO samples to the chemically more stable ZnS [2] was carried out in an evacuable quartz-tube oven with a 5% H₂S-in-argon mixture at 350–450 °C. Alternatively, the sample was heated with calculated

amounts of elementary sulfur in fused quartz tubes at 500–550 °C, to obtain pressures in the range 100–4700 hPa (calculated as S₂ gas).

Electroless metal ion exchange

Since a further conversion of the structured ZnS to better semi-conducting or better light-absorbing materials was desired, the columnar or tubular ZnS substrates were reacted at elevated temperatures with aqueous solutions containing Cu⁺, Ag⁺, Sb³⁺ or Bi³⁺ salts and complexing acids. Special details for Bi³⁺ are given elsewhere [2]. The reaction parameters are given in Table 1, together with the solubility product constants of the sulfides and their respective metal ion concentrations in water. Most samples were subsequently annealed for a short time, to obtain better crystallinity for characterization.

The conversion of smooth, chemical-bath-deposited ZnS films to other metal sulfide films by ion exchange processes has been described [3]. It depends on the solubility of the respective sulfide. Solubility product constants and maximum sulfide and metal ion concentrations calculated from these can in principle be used to predict if this conversion will proceed without loss of material, or if it will be accompanied by dissolution of ZnS. The former is probable if the maximum metal ion concentration of the product, which is permitted by its solubility product constant and counterion concentration, is much lower than the respective maximum concentration of Zn²⁺. On the other hand, if this maximum permitted metal ion concentration is higher for the product sulfide than for ZnS, concomitant dissolution has to be expected. However, the question of the solubility of a metal sulfide in water is sometimes not answered easily. Differing values can be found in the literature, since dissolution is coupled with pH-dependent protonation to HS⁻ and dissolved H₂S. Moreover, some of the higher charged cations are involved in further pH-dependent equilibria with hydroxo and oxo ligands.

Thin film characterization

The prepared samples were examined by grazing incidence X-ray diffraction (XRD) with a Bruker Axs D8 Advance diffractometer with Cu K α radiation and by scanning electron microscopy with a LEO 1530 Gemini electron microscope.

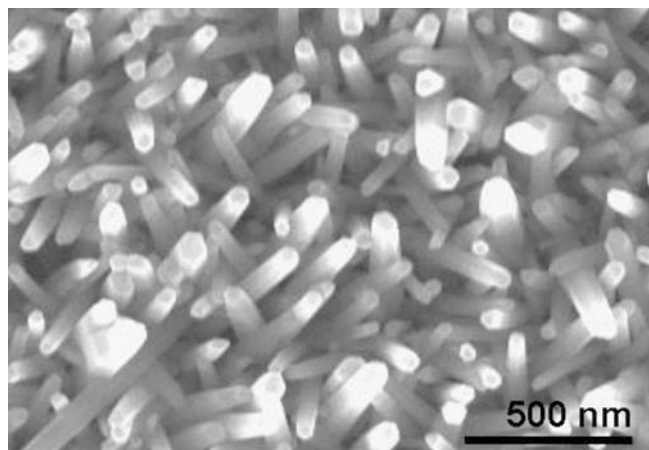


Fig. 1 Columnar ZnO electrodeposited on a substrate of gold evaporated on Cr on glass

Results and discussion

Figure 1 shows columnar ZnO grown on a gold film evaporated on Cr on glass. This substrate displays an atomic-flat (1,1,1) surface, on which the columns grow more parallel than on polycrystalline, rough SnO₂:F glass [2]. In some places they grow so well aligned that they fuse into blocks. A strictly hetero-epitaxial ZnO electrodeposition has been reported on GaN basal-plane surfaces [4]. Furthermore, on this gold substrate the columns grow much denser and smaller, and reach only half the diameter as on SnO₂:F glass. We attribute this to an easier seed generation and therefore denser seed coverage.

In Fig. 2a a recognizable landmark has been selected on a sample of columnar ZnO grown on SnO₂:F glass, and Fig. 2b shows the same after thorough sulfurization in sulfur vapour. By this, the columns have become

Table 1 Survey of materials, solubility products, concentrations and preparation conditions for metal ion exchange with ZnS

Sulfide	ZnS	Cu ₂ S	Ag ₂ S	Sb ₂ S ₃	Bi ₂ S ₃
Sulfide solubility product constant [7] ^a	2×10 ⁻²² M ²	1×10 ⁻⁴⁹ M ³	6×10 ⁻⁵³ M ³	3×10 ⁻⁵⁹ M ⁵	2×10 ⁻⁷² M ⁵
Metal ion conc. from sulfide solubility product constant (M) ^b	1×10 ⁻¹¹	6×10 ⁻¹⁷	5×10 ⁻¹⁸	2×10 ⁻¹²	4×10 ⁻¹⁵
Salt concentration in conversion solution (aqueous)	–	50 mM CuCl	50 mM AgNO ₃	150 mM K-Sb-tartrate	100 mM Bi(NO ₃) ₃ as triethanolamine complex
Additives in conversion solution	–	10 mM tartaric acid	3 mM acetic acid	70 mM tartaric acid	650 mM tartaric acid
Time and temperature for cation exchange	–	10–35 min, 100 °C	7–17 h, 70 °C	2 h, 100 °C	24 h, 100 °C
Subsequent annealing	–	5 min, 250 °C, air	none	20 min, 300 °C, N ₂	30 min, 250 °C, N ₂

^aThe solubility product constant L of an ionic compound A_xB_y in a solvent (generally water) is defined as the product $L = [A]^x[B]^y$ of the ion concentrations [A] and [B] at saturation. So its dimension is M^(x+y). The use of this concept is that L remains constant even if [A] or [B] is increased from another source. This precipitates some amount of [A]_x[B]_y, which can in principle be quantified by this concept

^bIf n moles/L (M) of the ionic compound A_xB_y are dissolved, this gives ion concentrations of [A] = xn and [B] = yn . With n at saturation, the solubility product constant is $L = (xn)^x(yn)^y$. Then the concentration [A] = xn in this row is obtained as $xn = x(L/(x^x y^y))^{1/(x+y)}$

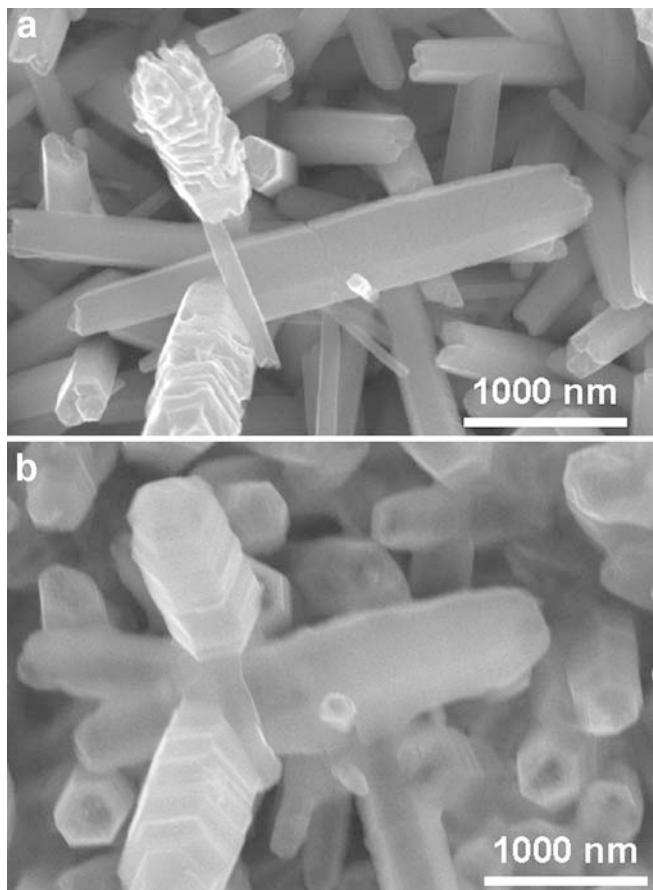


Fig. 2 (a) Selected landmark on a ZnO sample electrodeposited on SnO₂:F glass; (b) the same sample after 3 h of sulfurization at 550 °C in 2400 hPa S vapour (calculated as S₂)

thicker, and a narrow void has formed inside, which is better seen in the further converted sample in Fig. 3a. This change in shape confirms earlier results, where crystallization of small ZnS platelets perpendicular to the main axis was observed on partially converted ZnO columns [2], suggesting that material transport during conversion takes place mainly in the radial direction. For this process, the out-diffusion of Zn ions is likely to be faster than the in-diffusion of S. This would bring the ZnS growth front to the outer periphery of the columns.

On the other hand, the conversion with H₂S limits itself to wall thicknesses of about 50 nm, so that only samples with sufficiently thin ZnO columns could be fully converted by this method. This sulfur source gives H₂O as a by-product and appears to produce denser tube walls. A full conversion of thinner ZnO films by H₂S is described elsewhere [5].

Figure 3a shows excellent morphology reproduction of a sample of thick-walled ZnS tubes after short reaction with a Cu⁺-containing solution. The XRD of this sample (Fig. 3b) indicates partial conversion to Cu₂S, with some ZnS remaining. Thinner-walled ZnS tubes have been completely converted under the same conditions, also with good morphology reproduction. Their characterization by XRD is, however, complicated by

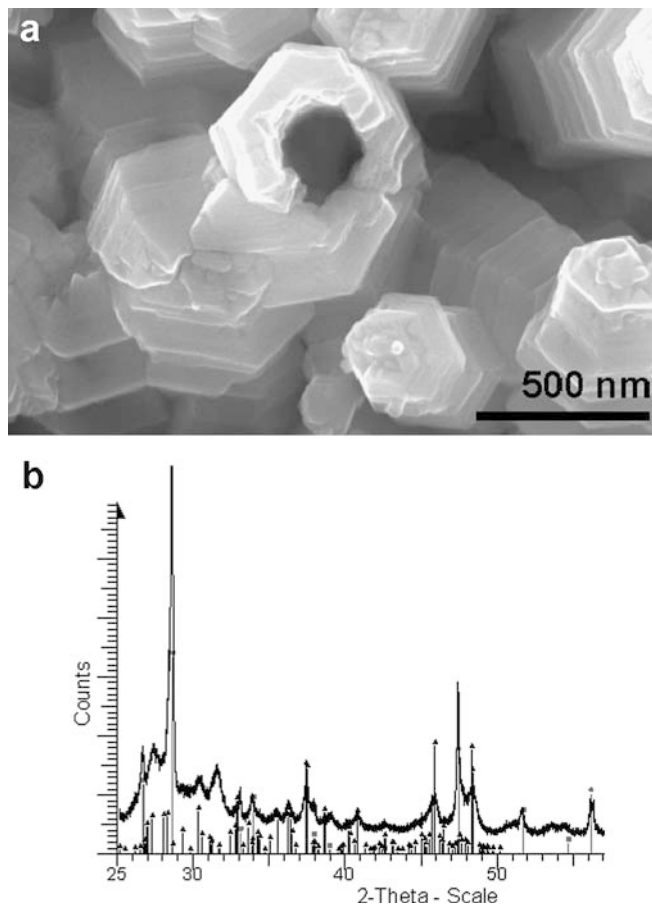


Fig. 3 (a) A thick-walled sample of ZnS after reaction with Cu⁺-containing solution; (b) XRD of this sample, showing remaining sphalerite ZnS (strongest two reflections, *grey pattern*), cassiterite SnO₂ substrate (*grey pattern*) and the pattern of the “chalcosine low” type Cu₂S (*black*)

the existing variety of similar Cu₂S and mixed-valence Cu_xS species, in which the mean oxidation state of Cu can range from 1+ to 2+. Conversion to Cu₂S without ZnS dissolution could be expected from its much lower solubility (Table 1). However, for conversion of ZnS to Ag₂S, in spite of its even lower solubility, a poor morphology reproduction was obtained with the given Ag⁺ concentration (Fig. 4a). Nevertheless, its crystalline phase can be clearly identified from the XRD as acanthite, and no more ZnS phase is detected (Fig. 4d). For a first explanation of this, we consider the sulfide conversion stepwise: it always starts from a metal sulfide precipitate which forms in a first step directly at the surface, near the surface or in a less close distance, depending on the solubility difference of the starting and final sulfides. A comparatively high solubility of the product leads to a loss of material during conversion and was observed as markedly thinned tube walls in the conversion of ZnS to Sb₂S₃, as a sulfide with similar solubility. The second step is the interstitial transport of product cations into the ZnS lattice. The sulfide anions are not supposed to diffuse at these temperatures. The third step is the exchange against Zn²⁺ at its lattice

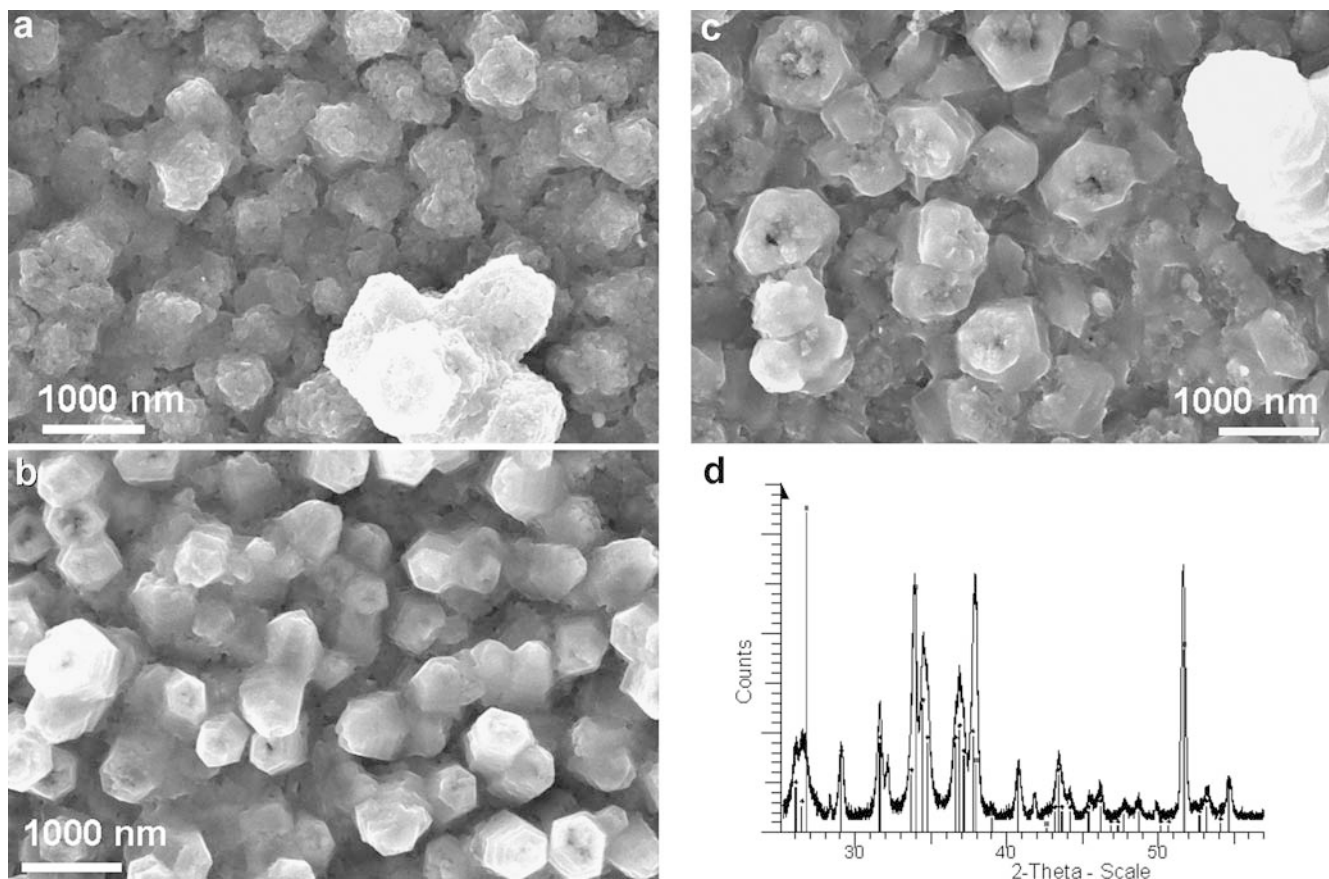


Fig. 4 Ag_2S samples obtained from reaction of structured ZnS for 7 h at 70°C with a solution of (a) 50 mM AgNO_3 , (b) 0.05 mM AgNO_3 , (c) 50 mM complexed $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$. (d) XRD of a typical sample, indicating full conversion to acanthite phase Ag_2S (black pattern) on SnO_2 substrate (grey pattern)

place, and a greater or smaller lattice rearrangement in type, volume and stoichiometry. The influence of this on the visual quality of the morphology reproduction is not obvious. Then, as a fourth step, the transport of Zn^{2+} to the surface follows [6].

To maintain electroneutrality, the last three steps should take place simultaneously, where one of them can be rate determining. They can be regarded as a whole process here, which for Cu^+ , as an especially fast migrating ion, keeps pace with the initial deposition at the surface, but not for Ag^+ , since this ion is bigger and therefore slower diffusing inside solids. This is confirmed by the better reproduced morphology of the sample in Fig. 4b, for which the initial Ag_2S deposition was slowed down by using a 1000-fold lower Ag^+ concentration. Figure 4c represents an intermediate case, where the concentration of free Ag^+ was largely reduced by the complexing agent thiosulfate, but consumed free Ag^+ could be replaced quickly by dissociation of the complex.

Similarly, for the conversion of ZnS to Bi_2S_3 , a strong complexing agent is required to bring the Bi^{3+} into solution at all. This makes the initial deposition slow, and therefore a fair morphology reproduction was

obtained [2], in spite of the slow diffusion of Bi^{3+} in solids due to its high charge.

Conclusions

Nanostructured ZnO films can be converted to a choice of metal sulfide films with the same or a similar nanostructure. By two subsequent ion exchange processes, complete material exchange is achieved. The quality of the morphology reproduction is governed by the exchange kinetics. To mobilize also the anions in the first step, a higher temperature is required than for mobilizing only the cations in the second step. The differences in the quality of the morphology reproduction can mostly be explained by the competition of the initial precipitation rate at the column surface, which is very fast for Cu^+ and Ag^+ , with the subsequent overall conversion rate inside the solid, which is especially fast for Cu^+ . The former can be slowed down by reduced concentration of free reactant cations to improve the morphology reproduction. The latter can proceed under real conditions also along surfaces and grain boundaries, and also in the liquid or gas phase, which means its rate is empirical for the specific type of sample, rather than predictable from tabulated values of the material. On the other hand, the change in the lattice dimensions was not found to correlate with the quality of the morphology reproduction here.

References

1. Peulon S, Lincot D (1998) *J Electrochem Soc* 145:864
2. Dloczik L, Engelhardt R, Ernst K, Lux-Steiner MC, Koenen-amp R (2002) *Sens Actuators B* 84:33
3. Engelken RD, Ali S, Chang LN, Brinkley C, Turner K, Hester C (1990) *Mater Lett* 10:264
4. Pauporté T, Lincot D (1999) *Appl Phys Lett* 75:3817
5. Gao YM, Wu P, Baglio J, Dwight K, Wold A (1989) *Mater Res Bull* 24:215
6. Ristova M, Ristov M (2001) *Appl Surf Sci* 181:68
7. Weast RC, Astle MJ, Beyer WH (1985) *Handbook of chemistry and physics*, 66th edn. CRC Press, Boca Raton, p B222