Research Article

Synthesis of Hierarchical Dorsal Spine Ag\(_2\)S Structures by a Solid-Vapor Reaction: The Effect of Reagent Gas Composition


Instituto de Ingeniería y Tecnología, Universidad Autónoma de Ciudad Juárez, Avenida del Charro No. 450 Norte, 32310 Ciudad Juárez, CHIH, Mexico

Correspondence should be addressed to C. A. Rodriguez González, claudia.rodriguez@uacj.mx

Received 14 February 2012; Accepted 8 April 2012

Academic Editor: Chunyi Zhi

Copyright © 2012 J. A. Muñiz-Lerma et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Silver sulfide hierarchical structures with unique dorsal spine morphology were successfully synthesized on mechanically deformed silver substrates by simple solid-vapor reactions. It has been found that it is possible to change the structures morphology by changing the reagent gas composition. The carbon monoxide (CO) presence in a reactive sulfur atmosphere was found to be the key for growing the dorsal spine structures. In all cases, the Ag\(_2\)S structures grew on the edge of the silver substrates where high plastic deformation occurred.

1. Introduction

Silver sulfide (Ag\(_2\)S) is a mixed ionic and electronic conductor above 473 K. It has three allotropic forms: \(\alpha\) (monoclinic phase stable up to 415 K), \(\beta\) (bcc phase stable from 415 K to 873 K), and \(\gamma\) (fcc phase stable above 873 K) [1–3]. The \(\alpha\)-Ag\(_2\)S is the focused of this research and it is considered an important semiconductor with a bandgap of 1 eV at room temperature and high absorption coefficient (approximately 104 cm\(^{-1}\)) [4].

Semiconductor nanostructures have important applications in many fields such as solar energy conversion devices, switches in optical computers, and infrared detectors [5]. The morphology of these semiconductor nanostructures has a great impact on their properties. Therefore, great research efforts are concentrated on the morphology control during the semiconductor synthesis [6].

Many methods to synthesize silver sulfide nanostructures with different morphologies have been reported. These routes include hydrothermal routes, sonochemical reactions, and solid-gas reactions among others and produce silver sulfide nanostructures in bulk, in a template, or over a metallic substrate [7–10]. It is well known that there is a potential to grow silver sulfide nanostructures on substrates for further applications [11, 12].

An important synthesis mechanism of nanostructured semiconductors is the solid-vapor mechanism. Some of the advantages reported for this route have been simplicity, mild reactions conditions, and the possibility to grow nanostructures on a metallic substrate [13]. Reagent gas composition on the synthesis of silver sulfide nanostructures by a solid-vapor reaction has been reported for various authors [12, 14–17]. However, to the best of our knowledge, the effect of carbon monoxide (CO) gas on the morphology of silver sulfide hierarchical structures obtained by solid-gas reactions has not been reported yet. In this work the CO effect is reported. It has been found that it is possible to change the Ag\(_2\)S structures morphology on silver substrates by manipulating the reagent gas composition. The obtained structures vary from a leaf like structure to hierarchical dorsal spine structure with high surface area. Additionally, the effect of mechanical deformation of the silver substrate on the preferential growth of the structures is reported.
2. Experimental Procedure

Silver foils (99.99% Ted Pella, P/N 91118) with a thickness of 0.1 mm were cut into substrates of $(3 \times 4 \times 0.1 \text{mm})$ and cleaned during 5 minutes in absolute ethanol by ultrasonic bath. For the solid-vapor reaction, a quartz tubular furnace of $2'' \times 24'' \text{L}$ with inlet and outlet valves was used as reactor. The silver substrate along with $20 \text{mL}$ of deionized water and $3 \text{g}$ of sublimed sulfur (99.97%, Fermont PQ9122) was placed in the reactor. These reactants were used to generate a reactive sulfur atmosphere on the basis of the international standard ASTM B809 [18]. The temperature was set at $110^\circ \text{C}$, the pressure was 1 atm, and time was varied from 6 to 40 h. To study the effect of CO in the reagent gas composition, a mixture of 100 ppm CO/N$_2$ gas (BW Tech., P/N BW CG2 M100-103) was flowed at 1 sccm. The outgases were passed through a sodium hypochlorite solution (CAS: 7681-52-9) to diminish the risk of gas emissions to the environment. After each test, the samples were analyzed using a Field Emission Gun Scanning Electron Microscopy (Jeol JSM-7000F) coupled with an Energy Dispersive X-Ray Spectroscopy (EDS) and by X-ray powder diffraction using Cu K $\alpha$ radiation (XRD, X’Pert Pro de PANalytical, $\lambda = 0.1542 \text{nm}$). High-Resolution Transmission Electron Microscopy (HRTEM, Jeol JEM-2200FS) was used on selected samples to confirm the phase presence by the measurement of interplanar distances.

3. Results and Discussion

The resulting silver sulfide structures with and without CO presence at 12 h are shown in Figure 1. The structures synthesized in presence of CO exhibit a unique hierarchical dorsal spine morphology while the structures obtained without CO showed larger structures with a leaf-like morphology similar to the nanostructures reported by Chen and Gao that were obtained using a hydrothermal method with AgNO$_3$, H$_2$O, NH$_3$, alcohol, and CS$_2$ as precursors [8]. In both cases, EDS analyses (Figure 2) showed that these samples are formed by silver (Ag) and sulfur (S).

The silver sulfide structures were identified by XRD as $\alpha$-Ag$_2$S (acanthite phase) using the PDF card 01-089-3840 calculated from ICSD using POWD-12++ of the PANanalytical X’pert high-Score plus PDF2 2003 database. The XRD patterns (Figure 3) showed that the most intense peaks were the ones corresponding to the $(-101)$, $(-212)$, and $(013)$ planes for the leaf-like structures and the $(023)$ and $(013)$ planes for the hierarchical dorsal spine structures. All peaks in these two XRD pattern appear at the correct $2\theta$ value.
Figure 3: XRD of silver sulfide structures synthesized with CO gas (a) and without CO (b). In both cases, silver phase which comes from the silver substrate is also observed.

Figure 4: FE-SEM of the hierarchical dorsal spine structures.

but the most intense peaks are not the ones reported for the acanthite phase on the card 01-089-3840. These intensity differences could be explained by the preferential orientation that these structures showed during the growing process. Morales-Masis et al. [9] also reported this effect for Ag$_2$S thin films.

High-magnification FE-SEM images (Figure 4) showed that the dorsal spine is formed by 2D nanostructures arranged by layers in the range of approximately 65 to 89 nm. HR-TEM images (Figure 5) showed interplanar distances of 2.45 Å ± 0.05 and 3.11 Å ± 0.05. The interplanar distance of 2.45 Å ± 0.05 could correspond to the planes (013) or (121) of the acanthite phase since the reported values for them (card 01-089-3840 of the PDF2 2003 PANanalytical X’pert high-Score plus database) are very similar (2.42 Å and 2.43 Å, resp.). The interplanar distance of 3.11 Å ± 0.05 corresponds to the plane (021) of the acanthite phase.

The silver sulfide structure formation is related to a solid-vapor growth mechanism where the silver sulfide layers could be formed according to reactions 1 to 3, in a similar manner to the sulfidation of resistors reported by the electronic industry [19]. The reaction is nondependant of water presence but it is known that water increases the speed of reaction [20, 21]:

\[
\begin{align*}
2Ag + S^{2-} &= Ag_2S + 2e^- , \\
Ag_2S + S^{2-} &= Ag_2S_2 + 2e^- , \\
2Ag + Ag_2S_2 + 2e^- &= 2Ag_2S .
\end{align*}
\]

If there is an excess of sulfur in the atmosphere, an unstable compound Ag$_2$S$_2$ can be formed. Then, new silver ions diffuse through the silver sulfide to react with the unstable compound and sulfur in the atmosphere. The silver diffusion and the supply of S$^{2-}$ ions to the surface have an effect on the structure growth. In the case where there is CO presence, it is possible that carbonyl sulfide gas (COS) is formed. According Graedel et al. [20] COS and silver react in a similar manner to H$_2$S and silver to form Ag$_2$S. Once again, the nanostructure formation is due to a solid-vapor reaction where there are an adsorption and desorption of the growing elements that come from the vapor phase causing the growth of the expected compound. The open spaces in the obtained nanostructures could be explained by
a momentary reaction between the COS and the silver that could generate a trunked path and a preferential growth. This is in agreement with the effect of subproducts or unstable compounds in the crystal growing theory of nanostructures of solid-vapor reactions explained by Gouzhong and Wang [22].

Figure 6 shows the effect of the time on the structure growth and shows how this hierarchical dorsal spine morphology is due to an incomplete dendritic growth. After 6 h, structures with dorsal spine morphology appear at the silver substrate edge. After 12 h exposure, these structures grow mainly longitudinally, and after 40 h, the dorsal spine structure acts as central trunk for secondary and tertiary branches. Each branch is formed by ordered layers in the nanometric scale. Han et al. [23] reported similar time effect in the growth of copper sulfide dendrites due to the reaction between solid sulfur and carbon coated-copper grids at room temperature.

In all cases, the structures grew on the edge of the silver substrates where high plastic deformation occurred. This
could be explained with the dislocations effect in the reaction kinetics of a metallic substrate. The reaction kinetics can be increased by the creation and movement of dislocations. According to Chupakhin et al., crossed dislocations have a great influence since they create high-energy points which increase atomic mobility [24].

4. Conclusions

Silver sulfide morphology is highly affected by the atmosphere. Leaf like structures are obtained by a solid-vapor reaction between silver and an atmospheres containing sulfur and deionized water. If CO (100 ppm) is added to the atmosphere, a hierarchical dorsal spine morphology or a dendritic morphology is obtained depending of the exposure time. The use of mechanically deformed silver substrates allows to grow the structures at the substrates edges. The dislocations occurring due to the mechanical deformation promote the structure growth. The high surface area of these hierarchical dorsal spine structures and the possibility to create templates to grow them by mechanical deformation could open new application possibilities for the electronic and energy industry.

Acknowledgments

Authors thank FOMIX-CONACYT for the financial support (Grant no. 127614), Universidad Autónoma de Ciudad Juarez and Instituto de Ingeniería y Tecnología for the usage of research facilities, and M.C. Carlos Ornelas of CIMAV-Mexico for his assistance with HRTEM.

References

Submit your manuscripts at http://www.hindawi.com