Optical properties of bio-inspired silver sulfide structures

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Abstract

Bio-inspired silver sulfide structures with leaf like morphology were successfully synthesized over mechanically deformed silver substrates by simple solid–vapor reactions. The effect of time and voltage in the synthesis and control of these silver sulfide structures was studied as well as their influence in the optical properties. Structures synthesized at 1 V, 10 h, 75 °C and 1 atm showed a bandgap of 1.15 eV, according calculations using the Kubelka–Munk function, which is very similar to the reported optimal value for solar cells applications.

Keywords: Silver sulfide, solar cells, bandgap, absorption.

Introduction

Bio-inspired materials are those novel functional materials inspired from nature [1]. Bio-mimic has attracted great interest since natural biomaterials exhibit outstanding integrated properties [2]. Green plant's leaves photosynthesis is reported as the most efficient process for solar energy conversion and storage being the leaves surface the gate for light harvesting through their hierarchical structures [3]. One of the major challenges regarding solar cell technology is to improve optical absorption to increase efficiency. Therefore, large efforts are dedicated to the fabrication and improvement of light trapping structures. Bio-inspired structures are considered good candidates for this purpose considering the relation between surface structure and photovoltaic effect.

Moreover, it has been proposed that multi-scale structures with leaf-like morphology could enhance the optical paths of light and the efficiency in solar cells [4].

Metal sulfide structures are of great importance for energy conversion and storage applications [5]. Among these materials, silver sulfide in the acanthite phase presents a narrow and direct bandgap of approximately 1 eV in bulk and a high absorption coefficient (104 cm^{-1}) [6,7]. Important research efforts have been dedicated to the synthesis of this material and its morphological control. The reported synthesis methods for silver sulfide structures include several routes such as hydrothermal, sonochemical and solid–vapor reactions. The silver sulfide obtained by these routes results on a variety of different morphologies produced as isolated structures or over templates or metallic substrates [6–9]. There exists scientific interest to grow silver sulfide structures over substrates for further applications [10,11]. Solid–vapor reaction is an important synthesis method for semiconductors manufacturing. Some of its advantages are simplicity, mild reactions conditions and the possibility to grow structures on substrates [8]. Reagent gas composition during the synthesis of silver sulfide micro/nanostructures by a solid–vapor reaction has been reported by several authors including our research team which recently reported the effect of carbon monoxide gas on the morphology of silver sulfide hierarchical structures obtained by solid–gas reactions [12–15]. It was found that it is possible to change the structures morphology from a leaf like to a hierarchical dorsal spine by varying the reacting atmosphere. This work is aimed to understand the effect of time and voltage on the morphological control of silver sulfide structures during their synthesis as well as to

determine how these parameters influence their optical properties. Currently, the results indicate that voltage and time stimulate the structure growth and at certain synthesis conditions (1V, 10h, 75°C and 1 atm) the structures exhibit promissory optical properties for solar cells applications.

Experimental procedure

Silver substrates of 10 x 10 x 0.1 mm were obtained from a 99.99% silver foil from Ted Pella (P/N 91118) and cleaned in an ultrasonic bath during 5 min using absolute ethanol. The substrates were clamped to a DC power supply on their counter corners and then placed into a reactor chamber with 20 mL of deionized water and 3 g of sublimed sulfur (99.97%, Fermont PQ09122). All connections inside the reactor chamber were wrapped with aluminum foil to avoid outgassed contaminants in the atmosphere. The reactants were used to generate a reactive sulfur atmosphere according to the international standard ASTM B809. The temperature was set at 75 °C, the pressure was 1 atm, reaction times were 10 and 40 h and the voltage was varied from 0 to 3 V.

The resulting specimens were analyzed with a Field Emission Gun Scanning Electron Microscopy (Jeol JSM-7000F) coupled with an Energy Dispersive X-ray Spectroscopy (EDS) and High Resolution Transmission Electron Microscopy (HRTEM, Jeol JEM-2200FS). Image Analysis using the Clemex Vision PE Software was used to measure structures length, width and seeds size. The results are the average values of more than 150 structures or seeds. Reported Feret's diameter corresponds to the longest distance between two points along the selected structure.

The optical bandgap and the electronic transition types were determined by means of the optical absorption spectrum [9] from 0.5 to 5.0 eV, using the Kubelka–Munk function $F(R)$ [10].

$$F(R) = \frac{(1-R)^2}{2R} = \frac{\alpha}{S} \tag{1}$$

where, R is the reflectance, α is the absorption coefficient, and S is the scattering coefficient. The reflectance measurements were obtained in a UV–Vis CARY 5000 spectrometer. The absorption coefficient α is related to the incidental photon energy by means of the following equation:

$$\alpha = A(h\nu - E_g)^n \tag{2}$$

where A is a constant that depends on the properties of the material, hv is the energy of the incident photons (h is Planck's constant and v is the frequency of the photon), E_g is the optical bandgap, and n is a constant value that depends on the transition type: n = 2 for direct transition and n = 1/2 for indirect transition.

Results and discussion

FE-SEM images of the bio-inspired structures with a leaf like morphology are shown in Fig. 1. The images clearly show that the increase of time and voltage during the reaction stimulate the structure growth. The structures grow as a result of the solid–vapor reactions between the silver substrate and the reactive sulfur atmosphere. The proposed growth mechanism for these structures is similar to the sulfidation of resistors for the electronic industry [12]. Initially, S^{-2} ions react with silver (Ag) and forms silver sulfide (Ag_2S). Then the remaining sulfur ions in the atmosphere react with the recently

formed silver sulfide producing an unstable compound (Ag_2S_2). The reaction continues since the unstable Ag_2S_2 promotes the diffusion of silver ions through the silver sulfide to start over with the initial Ag_2S formation. These reactions are not water dependent but it is reported that its presence increase the speed of reaction [13]. The proposed reactions are shown in our previous work [11]. Fig. 2 shows examples of the structure growth differences between the substrates center and edges. Leaf-like structures grow preferentially on the substrate edges where the plastic deformation is higher due to the creation and movement of dislocations. Chupakhin et al. have reported that crossed dislocations increase atomic mobility by the creation of high energy points [14]. At the center of the substrates, fewer and smaller leaf-like structures are found as well as some seed crystals that correspond to the initial structures growth stages. Optical properties presented in this work were measured over the entire substrates.
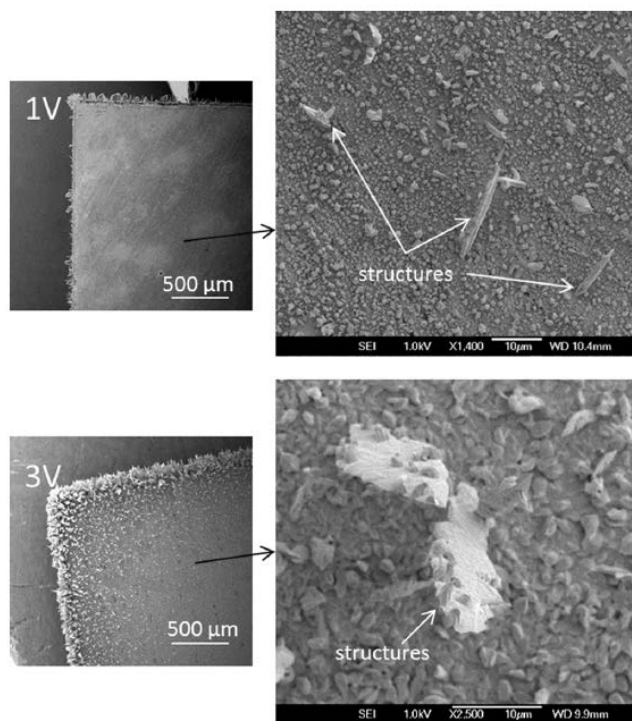
Fig. 2. Examples of substrates top view and substrates center morphology at 75 °C and 1 atm.
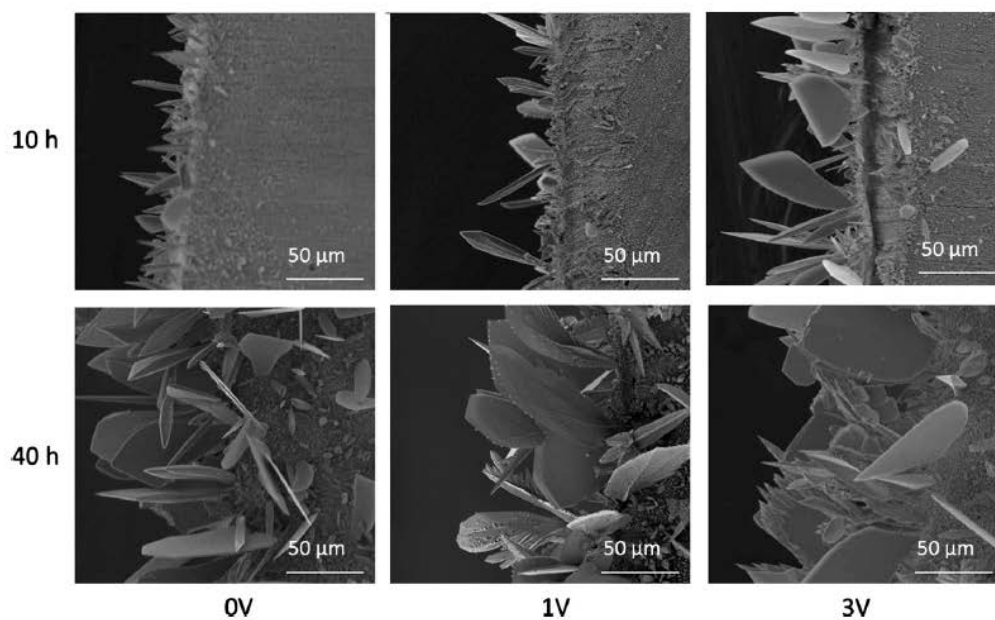

Fig. 1. FE-SEM images of bio-inspired structures with leaf like morphology synthesized at 75 °C and 1 atm. The effect of time and voltage can be observed.

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Fig. 3(a) and (b) shows the increment on length and width of structures with time and voltage. It can be observed, that the structures average length varies from 27 to 70 lm and width from 7 to 50 lm. At 10 h of reaction, the voltage mainly influences the structure's length. On the contrary, at 40 h of reaction, its main effect is on the width and quantity of structures. Also, it is observed that the structures reach a critical length (approximately 60 µm) when the silver diffusion reaction path changes its preferential direction thus increasing the structure width. Seeds average sizes at the center of the substrates also increase with voltage and time (Fig. 3(c)).
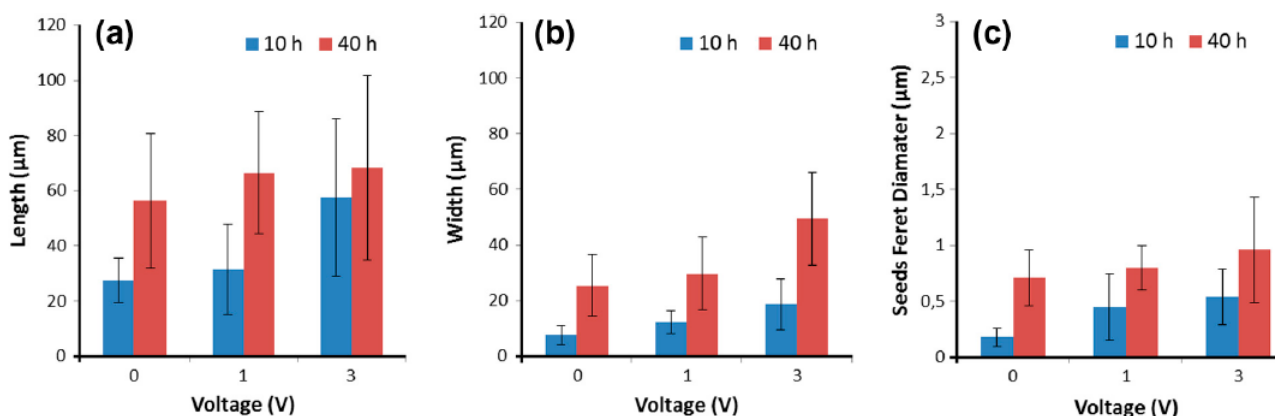

Fig. 3. Effect of time and voltage in the structures length (a), structures width (b) and seeds (c) at 75 °C and 1 atm.
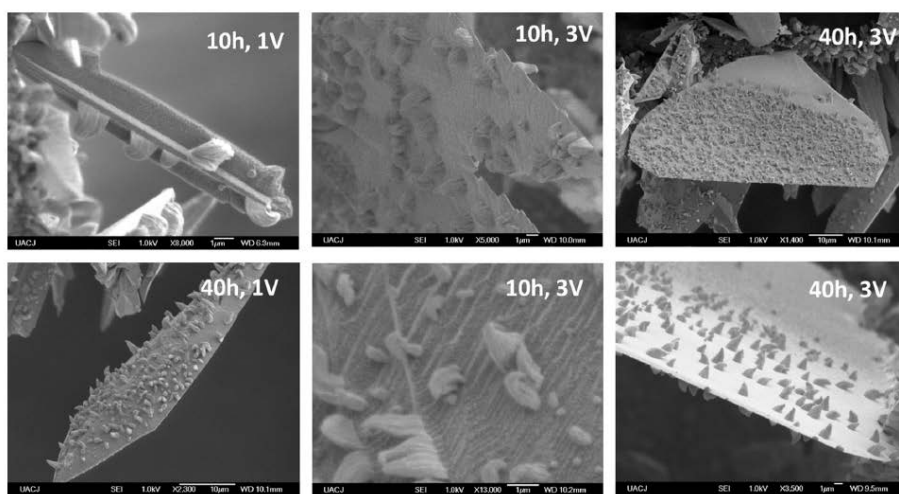

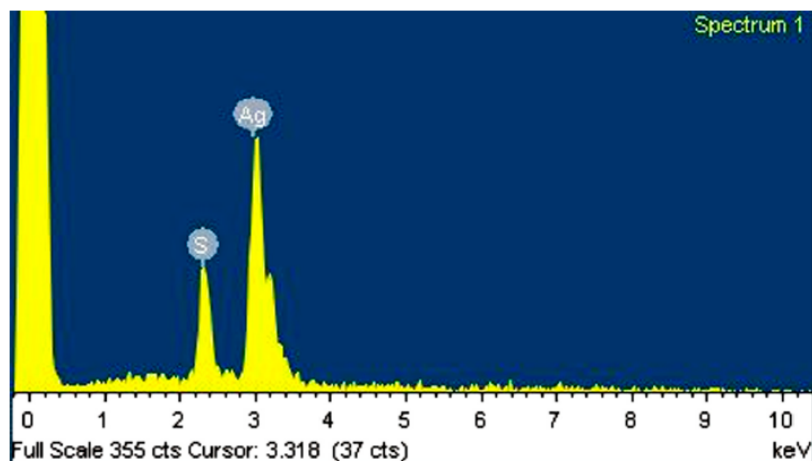**Fig. 4.** FE-SEM images showing examples of leaf like structures with secondary prickles growth (75 °C and 1 atm).

Fig. 5. Example of EDS spectrum of leaf like structure and their prickles. Sample synthesized at 1 V, 10 h, 75 °C and 1 atm.
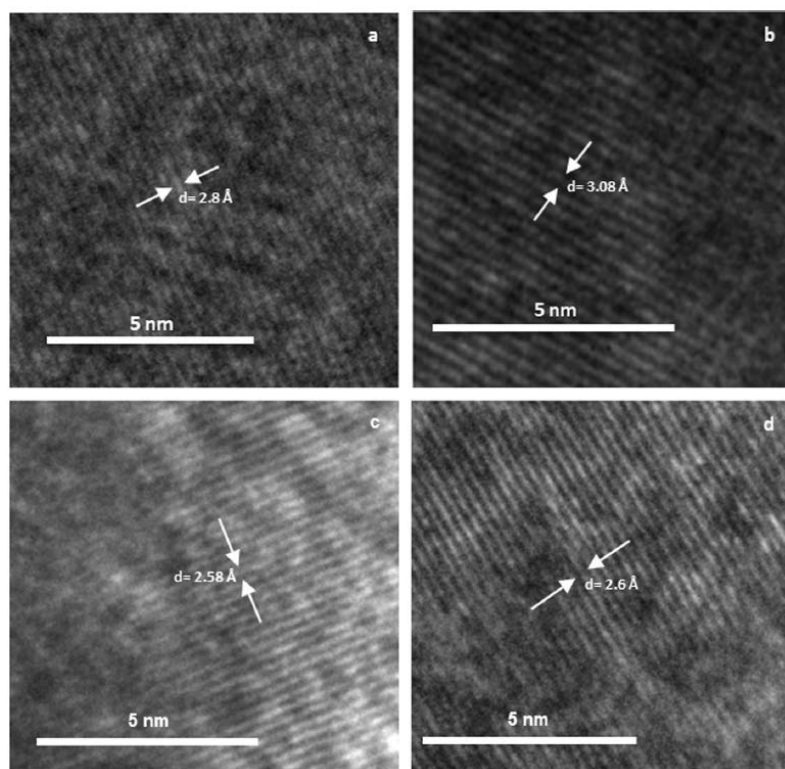

Fig. 6. HRTEM images showing lattice spacing of samples synthesized at 1 V, 10 h (a and b) and 3 V, 10 h (c and d).

Higher magnification FE-SEM images of the leaf-like structures are shown in Fig. 4. In the images, the growth of secondary structures with a prickle like shape in the range of 100 nm–1.5 lm is observed. The presence of these structures increases the

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surface area which could enhance the light harvesting process. All samples showed these secondary structures and the number of them increases with the reaction time and applied voltage. However, large variations in the amount of prickles were found between structures of the same substrate.

An example of the EDS analysis of the leaf like structures and their prickles is seen in Fig. 5. The spectrum shows the presence of silver (Ag) and sulfur (S). No other elements were detected. Moreover no significant differences were found between samples spectrum. Peaks relative intensity was similar.

Fig. 6 shows HRTEM images of the sample obtained at 1 V, 10 h, 75 °C and 1 atm, and 3 V, 10 h, 75 °C and 1 atm. The measurements of the lattice spacing of 1 V and 10 h sample exhibit values of ~2.80 Å and ~3.08 Å which are in agreement with the values reported for the (-112) and (-111) diffraction planes of the monoclinic silver sulfide acanthite phase according the PDF card reference code 01-089-3840. Sample synthesized at 3 V and 10 h shows lattice spacing of ~2.60 Å and ~2.58 Å which correspond to the planes (-121) and (022) of the same phase. The planes (-112), (111), (-121) and (022) are among the strongest diffracting planes for the monoclinic silver sulfide acanthite phase.
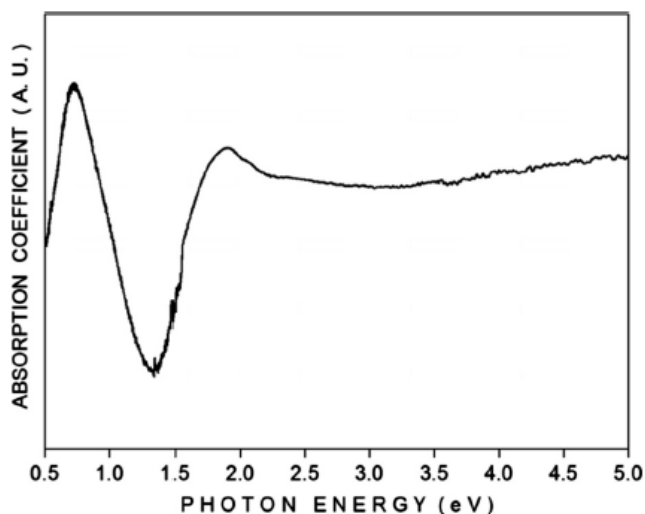
Fig. 7. Absorption coefficient of leaf like structures (sample 10 h, 1 V, 75 °C and 1 atm).

The absorption coefficient spectrum of sample obtained at 1 V, 10 h, 75 °C and 1 atm, is shown in Fig. 7. Two main centered absorption bands are observed at ~0.75 eV and ~1.85 eV which indicates the existence of electronic transitions around these energy levels. Fig. 8(a) and (b) shows the bandgap energy needed to produce direct and indirect transitions. They were calculated using Eq. (2) with data from Fig. 7. The direct and indirect transition occurs at 1.15 and 0.91 eV respectively. The bandgap value of semiconductor is an important requirement for solar cells. There is a trade-off between large and small bandgap values where optimal bandgap is about 1.1 eV [15]. The direct and indirect transitions of samples synthesized at 0 and 3 V were also calculated but these samples did not show a measurable optical response. The Kubelka–Munk function was nil. It is considered that the sample synthesized at 0 V does not have enough structures to produce a semiconductor behavior then the response of the conductor (silver substrate) predominates. Regarding the samples

produced at 3 V, their optical response could not be quantified by this technique due to the differences in size and orientation of the structures. Future work includes photo luminescence studies.
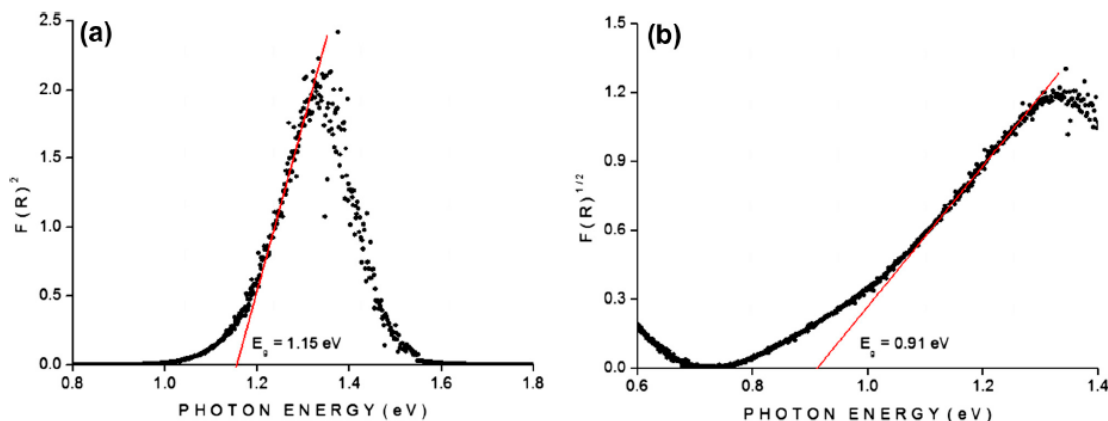

Fig. 8. Bandgap energy for (a) direct transition and (b) indirect transition. Sample synthesized at 10 h, 1 V, 75 °C and 1 atm.

Conclusions

Silver sulfide bio-inspired structures were successfully synthesized by a simple solid–vapor reaction. They show a leaf-like morphology with the presence of secondary prickle like structures. It was found that the structures growth can be controlled by varying time and applied voltage during the synthesis. The bandgap value of the structures synthesized at 1 V, 10 h, 75 °C and 1 atm, was calculated to be 1.15 eV which is very close to the optimal value for solar cells applications.

Acknowledgments

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