

NON-GALVANIC SYNTHESIS OF Ag₂Se NANOWIRES USING ANODIC ALUMINA MEMBRANE AS TEMPLATE AND THEIR CHARACTERIZATION

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Highly ordered crystalline Ag₂Se nanowires of diameter 200 nm have been successfully prepared through simple non-galvanic (chemical) route in paired cell using Anodic Alumina Membrane (AAM) as a template; AgNO₃ as cation precursor agent and Na₂SeSO₃ as Se precursor, respectively at room temperature. The qualitative analysis of the EDAX spectrum of nanowires shows that the atomic composition of Ag and Se in synthesized nanowires is close to 2:1 stoichiometry. UV-VIS absorption spectrum is used to estimate the optical band gap of nanowires that is found to be 1.85 eV.

Keywords: Ag₂Se nanowires, Chemical synthesis, Anodic Alumina Membrane

1. Introduction

In the past few years, low dimensional structures such as wires, fibers and tubules, have attracted much attention because of their fundamental importance and potential myriad applications in the field of science and technology [1-2]. Many efforts have been made to produce one dimensional nanostructure keeping in mind the fact that electrical and optical properties can be varied via chemical control over the size and diameter of the structures [3-5]. Semiconductor compound materials in general play important role in band gap engineering mainly due to their special tenability in electronic and optical properties by the three dimensional confinement of carriers [6-7]. When nano-scale semiconductor materials are fabricated, their density of electronic states will change in systematic manner, which strongly influences the electronic and optical properties of the materials [8-9]. Furthermore, nano- sized semiconductor material particles exhibit some unique properties such as quantum confinement size effect [10], nonlinear optical properties [11] and some other physical and chemical properties [12] besides their potential applications in research and development of nano-devices.

Among I-IV ($A_2^I B^{IV}$) group of compound semiconductors, Ag₂Se is important compound because it shows two distinct crystallographic phases [13]. The high temperature phase (α -Ag₂Se) shows the properties of super ionic conductor and is used as the solid electrolyte in photochargeable secondary batteries [14], while its low temperature phase (β -Ag₂Se) is a narrow band gap

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semiconductor and has wide applications in the field of thermoelectronics and photosensitizer in photographic films or thermochromic materials [15-16].

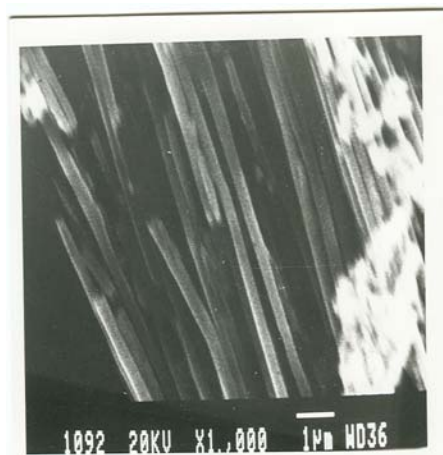


Fig. 1 SEM image of aligned and ordered Ag₂Se nanowires

There are various techniques used in the fabrication of nanostructures but the template synthesis is a versatile and economic for synthesizing the variety of nanomaterials including metals, semiconductors, heterojunctions, conducting polymers, CNTs etc [17-18]. The structures generated by this technique may be homogeneous or heterogeneous (including long needles, tubules, tapered and conical etc.) depending on the pore size, shape and geometry of the template used with complete control over aspect ratio [19-20].

Recently, Glanville et al. [21] have produced the Ag₂Se nanowires by template directed synthesis in which silver was deposited first in to the pores of the template followed by electrodeposition of selenium. Further, Ag₂Se nanowires have been also produced by Chen et al. [13] through the pores of AAM from alkaline solution containing AgNO₃ and SeCl₄ by electrodeposition at 65°C. Highly precise conditions and as pre-requisites like concentration, pH and cathodic potential are required to have good stoichiometry ratio for Ag and Se.

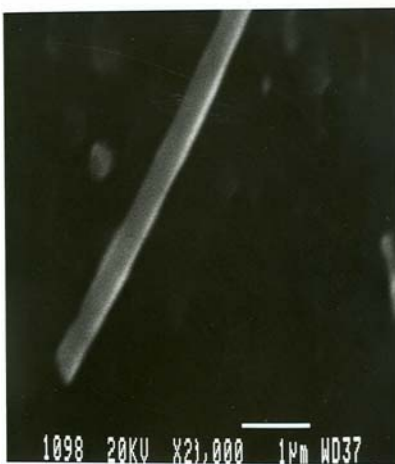


Fig. 2 SEM image of an isolated Ag₂Se nanowire

The aim of this paper is to establish the non-galvanic method (chemical method) for synthesis of ordered Ag_2Se nanowires using AAM as template. The nanowires of Ag_2Se have been synthesized by putting the AAM template in between two chambers of a paired cell and AgNO_3 solution is employed as Ag^{2+} source and Na_2SeSO_3 in the presence of OH^- ions employed as Se^{2-} source. The atomic ratio of Ag/Se can be controlled to 2:1 by tuning the deposition parameters. Electron microscopy, EDAX and UV-VIS characterization were performed for morphological, quantitative composition and optical band gap analysis, respectively.

2. Experimental

The AAM anodisc-21 (Whatman, UK) with pore diameter 200 nm was used as template for the fabrication of ordered Ag_2Se nanowires. All the chemical reagents used were RA grade and without further purification. AgNO_3 , Na_2SO_3 and Se powder were from s.d.fine-Chem Ltd. Mumbai, India, and all solutions were prepared in de-ionized water. The AAM template was fitted in a paired cell in such a way that it separated the cell in two chambers. For the deposition of Ag_2Se nanowires, one chamber was filled with 100 mM solution of AgNO_3 (pH = 4) and other one was filled with 50 mM solution of Na_2SeSO_3 with a pH value 12, adjusted by KOH. Na_2SeSO_3 aqueous solution (0.5M) was prepared by refluxing 0.05 M Se powder in 100 ml Na_2SO_3 aqueous solution (1M) for 3 hours [22]. After filling, the cell was left for 12 hours at room temperature so that Ag_2Se nanowires are formed inside the pores of AAM.

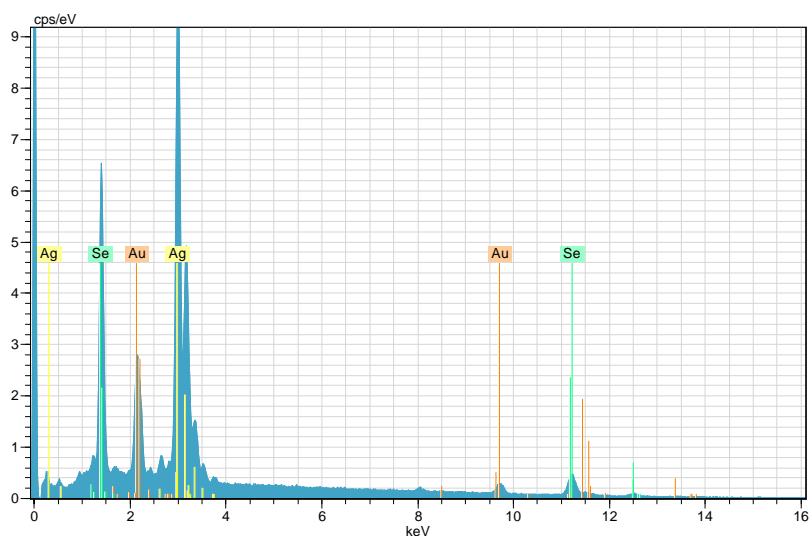
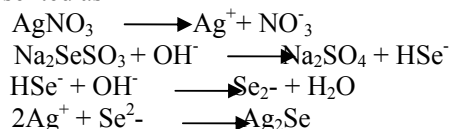


Fig. 3 EDAX Spectrum of crystalline Ag_2Se nanowires

The morphological characterization of Ag_2Se nanowires was examined by SEM by first liberating them from the matrix by dissolving AAO template in 1M NaOH solution at 25°C for 1h followed by subsequent washing. The cleaned and dried samples were mounted on special designed aluminum stubs with the help of the two way adhesive tape, coated with a layer of gold using JEOL, FINE SPUTTER JFC-1100 sputter coater and viewed under JEOL, JSM 6100 SEM. EDAX analysis of gold coated nanowires was carried out by RENTEC: Model QX-1 instrument. The optical absorption spectra were recorded with in the range 300-900 nm using Syntronics UV-VIS spectrophotometer: 119.

3. Results and discussions

The possible mechanism of formation of Ag_2Se nanowires from aqueous solution in two chambers of a cell may be represented as



In one of the chambers of cell, the cationic precursor solution AgNO_3 produces Ag^{2+} ions while in the other chamber of cell, the anionic precursor solution Na_2SeSO_3 hydrolyses in the presence of OH^- ions to give Se^{2-} . In the pores of AAM, Ag^{2+} combine with Se^{2-} to give Ag_2Se precipitate. When the cell is left for adequate time (here 12 hours), the above process continues till the pores are completely filled with the Ag_2Se . This results into the formation of Ag_2Se nanowires.

Figs.1, 2 show SEM images of Ag_2Se nanowires. It can be seen that diameter of nanowires is about 200 nm that closely corresponds to the diameter of pores of AAM template used and also all the Ag_2Se nanowires are oriented and the length, diameter and direction of growth of Ag_2Se are quite uniform which is due to the confined growth of nanowires in the ordered pores of AAM template. For the quantitative compositional analysis, the chemical composition of nanowires was determined using EDAX technique. The EDAX spectrum shown in Fig.3 clearly reveals that nanowires are composed of Ag and Se and quantitative analysis from data table 1 indicates that the atomic ratio of Ag and Se is nearly 2:1. The Gold (Au) peak is due to the coating of Au thin layer on Ag_2Se nanowires prepared for taking EDAX spectrum.

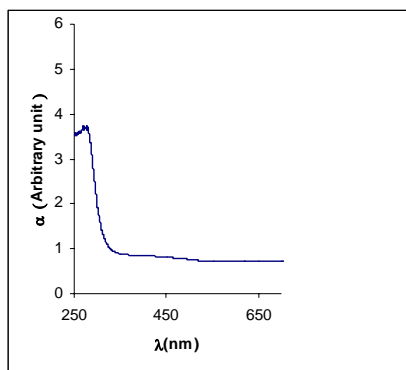


Fig. 4 (a). Plot of absorption coefficient (α) versus wavelength (λ)

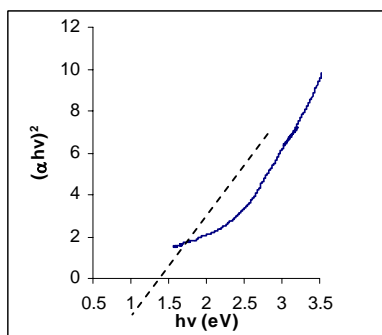


Fig. 4 (b). Tauc plot (Dotted line is a theoretical fit) for Ag_2Se nanowires.

Table 1: EDAX results of the sample showing element (El), atomic number (AN), series, weight % and atomic % of the elements.

El	AN	Series	Weight %	Atomic %	Error %
Ag	47	L-series	66.96	58.11	2.1
Se	34	K-series	25.68	30.45	2.9
Au	79	L-series	4.07	11.44	1.1

Fig. 4 (a) shows the UV-VIS absorption spectrum of nanowires. The optical band gap of Ag_2Se nanowires is estimated from UV-VIS absorption spectrum and the Tauc plot [23] in Fig 4(b). The optical band gap obtained from this fit is 1.85 eV, which is greater than the bulk value of Ag_2Se thin-films reported in the literature [24]. This increase in optical band gap is due quantum confinement effect [25].

4. Conclusions

Crystalline Ag_2Se nanowires are template synthesized in the pores of AAM using non-galvanic (chemical) method at room temperature. The SEM analysis shows that nanowires are crystalline, highly ordered and uniform in diameter. EDAX analysis indicate good stoichiometry ratio of Ag and Se. From the optical absorption spectrum and Tauc plot, the calculated value of band gap of Ag_2Se is 1.85 eV. The mechanism of growth of the nanowires is also demonstrated. This method is suggested to be used, too, in the synthesis of other chalcogenides.

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