# Electrochemical synthesis of conical $Ag_2S$ nanostructures and their optical properties

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In the recent years a great deal of attention has been paid to the fabrication of II–VI group semiconductor compounds such as CdS, CdTe and $Ag_2Se$ because of their fundamental importance and potential applications such as electronic devices [1–3], field emitters for plane displaying [4] and in solar cell panels. The electrodeposition has been widely used to fabricate nanostructures in the nanochannels of templates [3]. The ion track etched membranes are ideal templates to prepare nanostructures of desired shapes because of defined pore shapes and size under different etching conditions. The silver sulfide ($Ag_2S$), an important II–VI binary semiconductors with a band gap $E_g \sim 1$ eV has relatively high absorption coefficient [5]. The compounds of this group have a wide variety of potential applications such as infrared detectors and photosensitive films in optoelectronic devices [6], principal elements in thermo power cells and solar selective coatings. The conical nano structures of $Ag_2S$ have been fabricated by electrodeposition. Electrodeposition is a versatile, cost effective technique combining low processing cost with ambient conditions that can be used to prepare metallic, polymeric and semiconducting nanostructures [7]. Using template synthesis [8, 9], we have successfully fabricated the conical $Ag_2S$ nanostructures by direct current electrodeposition into the nanochannels of ion track etched membranes from 50% DMSO solution containing $AgNO_3$ and elemental S. These conical $Ag_2S$ nanostructures may be used as nano-infrared detectors.

10 micron thick polycarbonate film was irradiated with 13.6 MeV/n $U^{238}$ ions having flux $10^6/cm^2$ at GSI, Darmstadt, Germany. Conical pores in the irradiated polycarbonate samples were generated utilizing the asymmetric track-etch technique [9]. The irradiated sample was fitted in an electrochemical cell in such a way that the sample separated the cell into two chambers. One chamber was filled with 9 M NaOH solution and other was filled with neutralizing solution (NaCl + formic acid). The two electrodes (platinum) of the electrochemical cell were connected to a power supply [10–12]. The etchant starts etching the sample from one side and as soon as it reaches the backside of the sample, the current in ammeter increases rapidly resulting in the formation of conical tracks. For observing the break-through time and interrupting the etching process at a precise time, we measured the electric resistance of the polymeric foil. The break-through time was observed after 50 min (Fig. 1). By observing the current we could determine when the cones had reached the back side and pores had been created followed by interruption of etching process. This is a rough estimation to guarantee that the pores have just reached the back side. The longer etching time produces larger holes and shorter times are not sufficient to produce observable holes on the back side of the foil [13].

The nuclear track filter having average pore diameter from one side of ca. 5 micron and other side as 200 nm tip was produced by the method discussed above. Since the membrane used contained conical

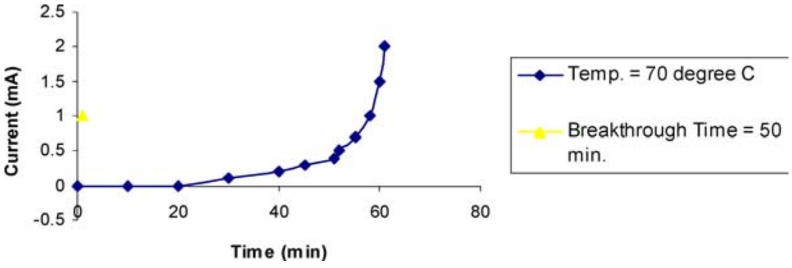

*Figure 1* Current vs. etching time for polycarbonate NTF membrane. The break-through was observed after 50 min.

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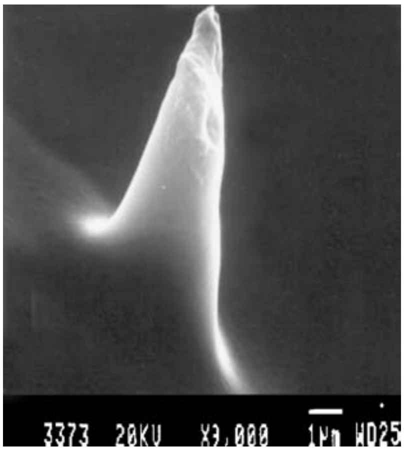


*Figure 2* SEM photograph of an isolated $Ag_2S$ nanostructure (with tip diameter 200 nm).

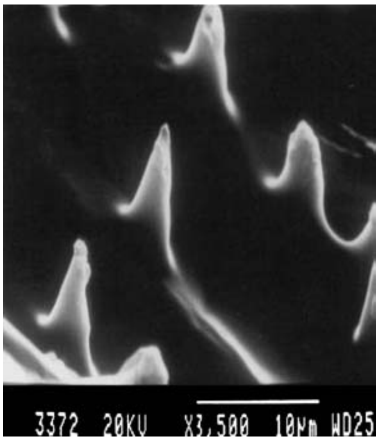
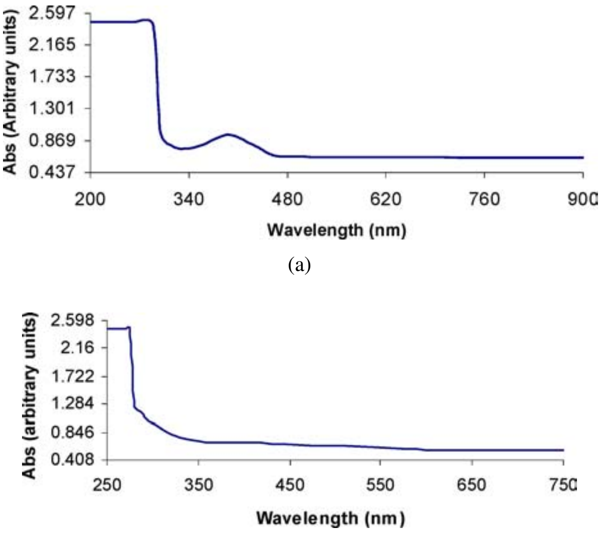


*Figure 3* SEM photograph of $Ag_2S$ conical tipped nanostructures.



(a)

(b)

*Figure 5* (a) UV-visible absorption spectrum of silver sulfide nanostructure embedded in polycarbonate NTF membrane. (b) UV-visible spectrum of polycarbonate NTF membrane (without silver sulfide structure).

pores, nanostructures of the desired material ware obtained by replication via pores. The electrodeposition of $Ag_2S$ would take place through pores whose dimensions and geometry, therefore, would dictate the morphology and geometry of the nascent nanostructure produced [8, 14]. Electrodeposition of $Ag_2S$ conical nanostructures was carried out using an electrolyte containing 0.055 M/l $AgNO_3$ and 0.19 M/l elemental S dissolved in 50% DMSO solution [15]. The pH of the solution used was adjusted to 2. The electro deposition was carried out for 35 min at 8 V (current 0.06137–0.09160 A) at the temperature of $100 \pm 2$ °C with the anode as pure silver sheet. After the electrodeposition was over, the electrolyte was drained out and the cathode was rinsed with Milli Q water followed by air-drying. The makrofol NTF was dissolved in $CH_2Cl_2$ solvent followed by rinsing with water and ethanol for further analysis [8, 9, 16]. The electrodeposited semiconductor nanostructures were characterized by UV-visible spectroscopy (Systronics UV-VIS Spectrophotometer: 119) and scanning electron microscopy (SEM, JEOL JSM 6100 instrument). The cleaned and dried samples were mounted on specially designed aluminium stub with the help of double adhesive tape, coated with a layer of gold palladium alloy in “JEOL, FINE SPUTTER

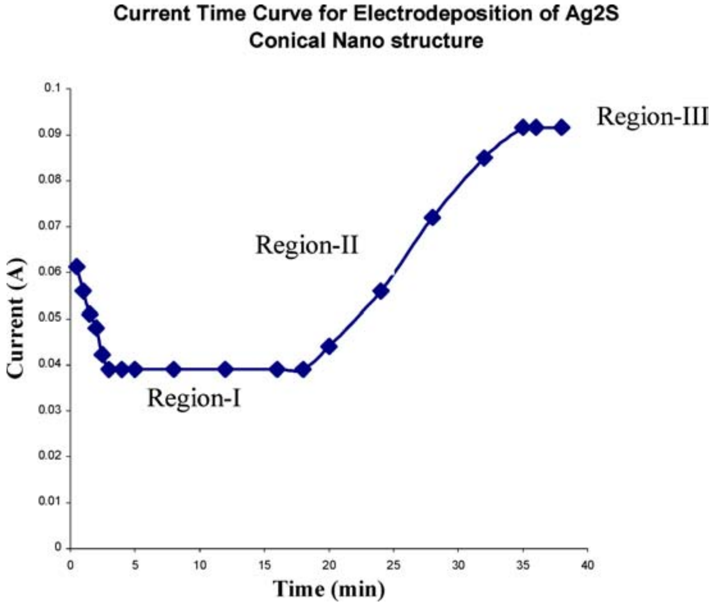


*Figure 4* Current–time curve for electrodeposition of $Ag_2S$ in polycarbonate NTF membrane. Region-I: Corresponds to growth of $Ag_2S$ structures in to the pores. Region-II: Pores are completely filled and upon them hemispherical caps are formed. Region-III: Corresponds to the overdeposition.

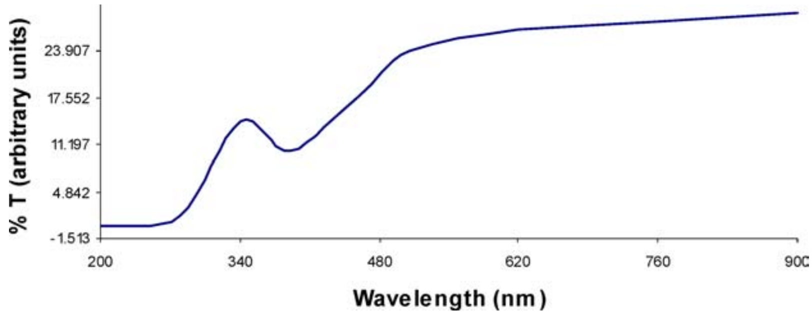


*Figure 6* UV-visible transmission of silver sulfide nanostructure embedded in polycarbonate NTF membrane.

JFC 1100" sputter coater and viewed under the SEM at an accelerating voltage of 20 KV. The $Ag_2S$ conical nanostructures with stochastically distributed elements revealing the finer details of the constituents and of the etched pores of the host NTF are shown in Figs 2 and 3.

From Figs 2 and 3, it can be seen that the $Ag_2S$ nanostructures are conical with tip diameter 200 nm and length of about 10 micron corresponding closely to the pore size and shape of ion tracks in etched membrane. Furthermore, it can be seen that the nanostructures can be filled continuously in to the conical pores of the ion track etched membrane by direct current electrdeposition. To study the morphological and optical properties as a function of the length of the nanostructures the electrodeposition process was stopped before the structure emerged from the membrane surface as indicated by an increase of the current (see Fig. 4). Fig. 4 shows the three regions of structure growth which correspond to the deposition of the materials in to the pores until they are filled up to the top surface of the membrane followed by continued growth and finally forming of hemispherical caps over the ends of the wires (see Fig. 4 region-II). The third region corresponds to the formation of material layer on the top surface of the membrane It is difficult to determine the end of the synthesis, because no constant current is observed. For this reason it is preferable to use smaller deposition current in order to decrease the deposition rate.

The UV-visible absorption and transmission spectra of the $Ag_2S$ nanostructures obtained are shown in Figs 5a, b and 6, where the onset of the absorption appears at 390.4 nm, corresponding to the characteristics absorption band of bulk $Ag_2S$. This peak is absent in polymer foil (Fig. 5b), which confirms the absorption shown by $Ag_2S$ structures. Similar explanation can be given to transmission spectra (Fig. 6).

The possible mechanism of the electrodeposition of $Ag_2S$ nanostructures from the equeous DMSO solution containing $AgNO_3$ may be represented as

$$[Ag^+ + e^- \rightarrow Ag] \times 2$$

$$2Ag + S \rightarrow Ag_2S$$

$$\overline{\underline{2Ag^+ + 2e^- + S \rightarrow Ag_2S}}$$

It is assumed that the electrochemical reduction of the absorbed sulphur atoms around the electrode surface gets converted in to sulphur ions ($S^{2-}$) which are consumed by $Ag^+$ to form $Ag_2S$ [14]. The reduction of $Ag^+$ on the surface ofelectrode is more favorable than the reduction of S to $S^{2-}$.

We have successfully fabricated the conical $Ag_2S$ nanostructures in ion track membrane. The shape and size of the structures can be controlled by the pore size and shape of the template. Furthermore, the SEM and UV-visible spectroscopy confirm the formation of the nano-tipped $Ag_2S$ structures.

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