

Our Road Map from Ion Track Technology to Nanotechnology

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Ion Track Filters (ITFs) or Track-etched membranes (TEMs) became precursors to development of nanotechnology at GSI, Darmstadt (Germany) during 1990s. These filters were prepared by bombardment of thin polymer foils of Makrofol, Lexan, PVDF and PMMA or thin sheets of Muscovite mica using heavy ions. Author's group used heavy ion beam facility available at GSI UNILAC, Darmstadt during 1990s to prepare ITFs in our laboratory. Heavy ion tracks in dielectric films offer unique possibilities for the realization of nanometer-sized structures at low cost and high throughputs. In combination with lithography they open up new ways for biofluidic, electric, magnetic and electro-optic device fabrication. Heavy ions produce along their path a nanometer channel of modified material with track diameter between 1 and 10 nm, adjustable by the chosen ion and its kinetic energy. The latent tracks created in irradiated materials may be used directly, e.g., creating conducting and magnetic nanowires in insulating matrices or they may be selectively etched into pores and then used for nanobiofluidic applications or as templates for growing micro/nanostructures. Commercial irradiation can produce ion track filters with pore density ranging from single pore to 10^8 pores per cm^2 per second.

Several nanofabrication techniques have emerged during the last two decades for fabrication of nanodevices of wide variety. Ion track technology offers a broad variety of scientific challenges. The efficacy of the technique has been tested for growth of quantum dots, nano-crystals, nano-needles, flower patterns and nano wires with diameter in the range of 20-200nm. Porous alumina and polymer TEMs have been used as a template for fabrication of metallic and semi-conducting nanowires of uniform diameter. Nanowires have advantages over their bulk counterparts due to higher aspect ratio, diameter dependent band-gap, and increased surface scattering for electrons. Considering the present scenario in India, it is planned to fabricate semiconductor nanowires and other heterostructures for investigation of electric, magnetic, optical and structural properties for their exploitation in the area of electronics and opto-electronics in the nano-range.

1. Introduction

The field of Ion Track Technology [1, 2] was developed at GSI, Darmstadt. Ion Track Filters (ITFs) or Track-etched membranes became precursors to development of nanotechnology during 1990s. One of the first applications of ITFs was separation of cancer blood cells from normal blood by making use of Nuclepore filters [3]. These filters are prepared by bombardment of heavy ions of thin polymer foils of Makrofol, Lexan, PVDF and PMMA or thin sheets of muscovite mica. Author's group [4] used heavy ion beam facility available at GSI UNILAC, Darmstadt during 1990s to prepare ITFs in our laboratory.

Ion track technology offers a broad variety of scientific challenges. However, we have chosen this route to nanotechnology because of obvious reasons. Heavy ion tracks can be used as a tool kit for fabrication of nano devices. The scientific innovation is in the short time-scale especially on the ion track enabling of optical lithography. In the long time-scale, the use of heavy ion material modification in latent ion tracks has enormous potential in creating novel nanomaterials.

2. Experimental Technique

The methodology of the development of microstructures is based upon the work of Possin [5] and Penner and Martin [6]. Electrochemical cell used for electrodeposition of metals into etched pores was fabricated in our laboratory. The metallic ions in a supporting solution are reduced to the metallic state at the cathode which is covered by an ITF. The etched pores of ITF used would act as a template. The rate of deposition of metallic film depends upon many factors, viz. current density, interelectrode distance, cell voltage, temperature and concentration of electrolyte used in the cell.

In the present set up, anodic alumina membranes (AAM) manufactured by Whatman Company has been used to grow nanowires by electrodeposition technique. The pore size selected varies from 20 nm to 200 nm. The electrochemical cell fabricated in our laboratory was used to grow copper nanowires of 200 nm using an electrolyte with a composition of 20gm/100 ml $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 25% of dilute H_2SO_4 at room temperature. The Copper nanowires

were liberated from their host AAM matrix by dissolving it in 1M NaOH at room temperature (220C) for 1 hour. The copper nanowires grown on copper foils were dried in an oven at 50C for 30 minutes. The cleaned and dried nanowires were mounted on aluminium stubs with the help of double adhesive tape, coated with a layer of gold palladium alloy in Jeol Sputter JFC 1100 and viewed under Scanning Electron Microscope (Jeol, JSM-6100) at an accelerating voltage of 20 kV. Figure 1 shows SEM micrographs of electrodeposited copper nanowires of 200 nm diameter and length of a few microns.

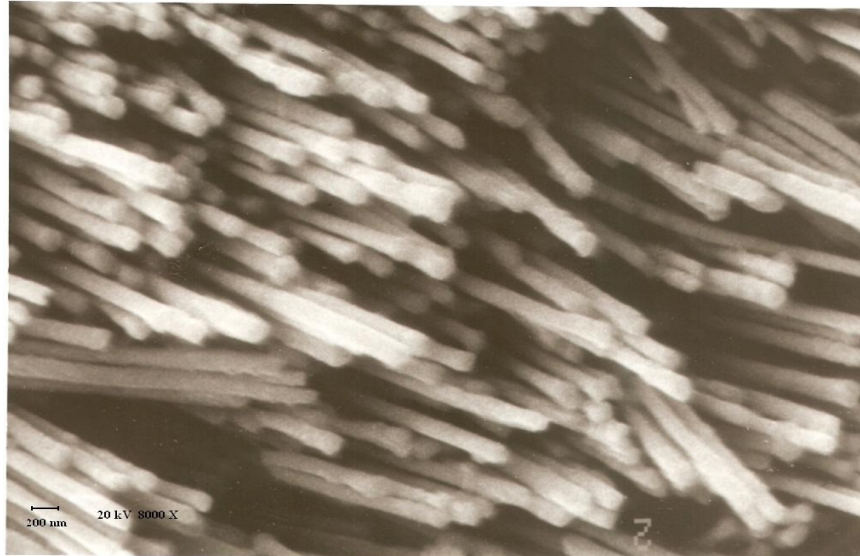


Fig.1. SEM micrograph of Copper nanowires of 200 nm diameter by electrodeposition in AAM

3. Ion Tracks Route to Nanotechnology

There are essentially two modes to use ion tracks for nanostructuring. The first is known as ITF or TEM mode described under experimental technique. The second method uses the ion tracks directly without additional etching and electrodeposition steps. This method is simpler than the template technique since no filling of the pores is required.

We have fabricated Cu nanowires both under constant and transient currents. Capping effect was observed in the second case. If over-deposition of copper is allowed for a longer duration, the capping effect results in production of exotic patterns, for example, copper flowers (Fig.3), copper buds or polycrystalline copper crystals (Fig.2). Results of our investigations have been reported [7-10].

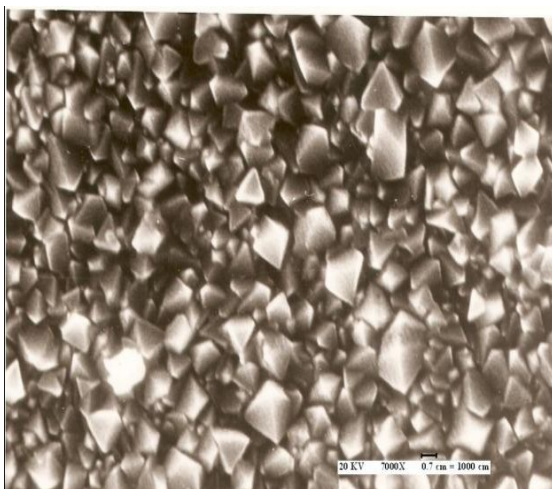


Fig.2. SEM micrograph of polycrystalline Copper crystals



Fig.3. Flower pattern due to overdeposition of copper

3.1 Fabrication of Semiconducting Nanowires

Anodic alumina membranes have been used in our laboratory for fabrication and characterization of Cu-Se and Cd-S nanowires and heterojunctions. Electrodeposition technique used in our experiment is identical in principle to that used

for the electroplating process. The experimental details are reported elsewhere [11] and identical to growth of copper nanowires in pores of AAM. When the AAM pores were approximately half-filled up with copper metal, a second electrolyte having a composition of SeO_2 (8×10^{-4} M) with 0.5 ml of 35% dilute H_2SO_4 was introduced. A potential difference of 1V was applied for 15 min. at 60°C to electro-deposit Se semiconductor over Cu metal already deposited in pores. After the electro-deposition was over, the electrolyte was drained out and the cathode was rinsed with high purity water and ethanol. The filled template with copper backing was immersed in 1N NaOH for 1h to dissolve AAM completely and to liberate the Cu-Se nanowires. Figures (4 & 5) show SEM and HRTEM images of Cu-Se nanowires.

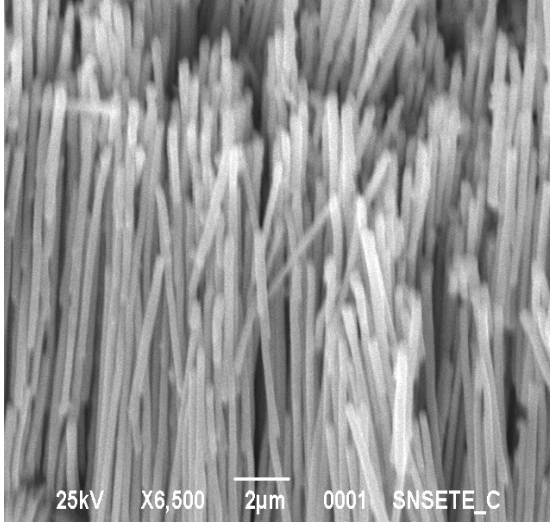


Fig.4. SEM image of Cu-Se nanowire bundles

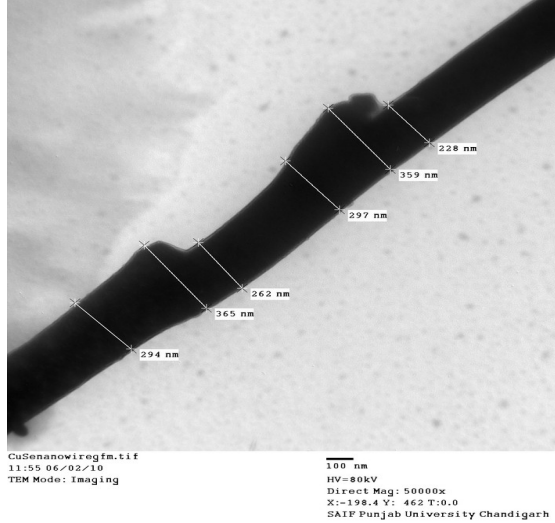


Fig.5. HRTEM image showing morphology and non-uniform diameter of Cu-Se nanowires

I-V characteristics of Cu-Se nanowires were studied using Keithley Model 4200 SCS programmable dual source meter facility of Central Scientific Instruments Organisation (CSIO), Chandigarh. I-V plot (Fig. 6) of Cu-Se nanowires was obtained using platinum probes of $0.5\mu\text{m}$ diameter tip for making contacts with copper strip and nanowire arrays. A prominent feature of I-V plot is a smooth curve showing increase of current with increase of voltage, in both forward and reverse bias modes. We may attribute this behaviour to Se semiconductor acting as a p-n junction diode but we failed to discover resonant tunneling diode (RTD) behaviour as reported by some other groups in India [12-13].

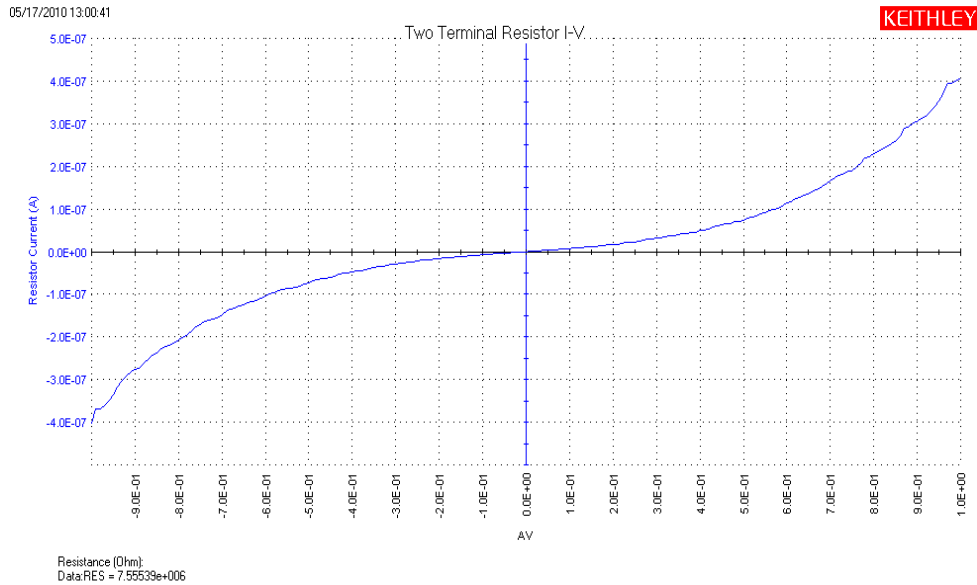


Fig.6. I-V Plot of Cu-Se nanowires demonstrating p-n junction behaviour

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