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Heavy Ion Tracks Route to Nanotechnology

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Abstract

Heavy ion tracks recorded in dielectric materials were found to have a width of 5-10 nm using SEM. Heavy ion beams were used for irradiation of Polymers and Muscovite mica to create Ion Track Filters (ITFs) using UNILAC facility at Darmstadt, Germany. The electrochemically etched pores of ITFs used would act as a template. The simple principle of electroplating is used to create heterostructures. The rate of deposition of metallic film depends upon current density, inter-electrode distance, cell voltage, electrolyte concentration and temperature etc. The use of ITFs looks quite promising in the fabrication of micro and nanostructures. The morphology of such structures produced through electrochemical methods and replicas of etched tracks in ITFs have been investigated in detail. The efficacy of the technique was tested for growth of quantum dots, fibers, cones, whiskers, micro and nano wires. A 3-dimensional ensemble of Cu-Se was grown electrochemically using ITF of Makrofol-KG. Replication of etched pores in ITFs has been used to develop microtubules. Presently, we are engaged to develop quantum dots, nanorods and nanowires of copper, iron and bismuth using Anodic Alumina Membranes (AAM), Polycarbonate ITFs and Reverse Micelle technique. The preliminary results of our investigations will be presented at NADPA-2008.

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 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 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.

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.

Experimental Techniques

The Makrofol-KG samples were irradiated at GSI heavy ion linear accelerator, UNILAC using ^{132}Xe (14.0 MeV/u) ion beams. All the irradiations were made at an angle of 90^0 w.r.t. surface of the detector. The irradiated samples were cut into small pieces and etched in 6N NaOH solution at various temperatures, viz. 40, 50, 60 and 70^0C. The etched and dried samples were scanned under a Carl Zeiss optical microscope and the pore diameters were measured using a calibrated Filler eyepiece. The variation of pore diameter with temperature was investigated. It was realized that chemical etching was not helpful in creating sub-micron size pores [4], for which we need electrolytically controlled etching.

Heavy ion track-etched filters (ITFs) thus prepared were used as templates for fabrication of microstructures, namely copper pins, buds, fibrils, microtubules etc. 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, inter-electrode distance was kept 0.5 cm and an electrolyte with a composition of 20gm/100 ml $CuSO_4.5H_2O$ + 25% of dilute H_2SO_4 at room temperature was used. A current of 0.025 A/cm^2 was applied for 50 min. for Makrofol – KG filters. The developed microstructures were coated with gold using sputtering technique and then scanned under SEM (Jeol, JSM-6100) for morphological and structural studies.

For template synthesis of metal-semiconductor heterostructures [4,7], the synthesis is accomplished by filling desired metal from one side until the growth has taken place half-way through the pores. The process is interrupted, followed by deposition of required semi-conductor from electrolyte though the other side of the ITF. This process was used for fabrication of micro-diode arrays. The 3-dimensional heterostructure of Cu-Se was grown using electrolytes of $CuSO_4.5H_2O$ + 25% of dilute H_2SO_4 and $Na_2SeO_3.5H_2O$ by template synthesis technique. Fig.1 shows the morphology of Cu-Se ensemble grown recorded by AFM. The X-ray diffraction pattern (Fig. 2) clearly shows the peaks due to Cu-Se heterostructure and metallic Cu.

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 $CuSO_4.5H_2O$ + 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 (22^0C) for 1 hour. The copper nanowires grown on copper foils were dried in an oven at 50^0C 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. The images of Copper nanowires were recorded on the photographic film in the form of negatives at various magnifications. Fig. 3(a, b) shows SEM micrographs of electrodeposited copper nanowires of 200 nm diameter and length of a few microns.

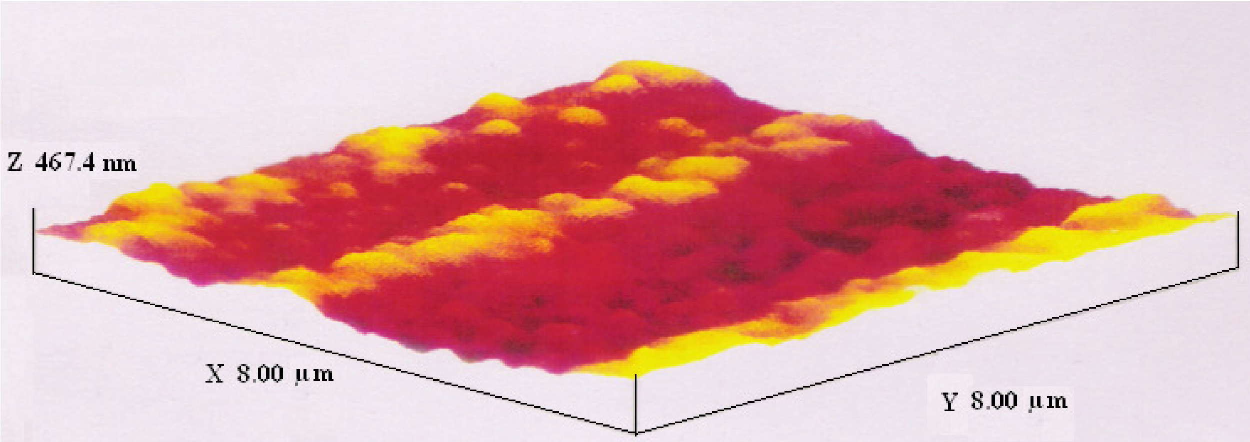


Fig. 1 AFM image of 3-dimensional ensemble of Cu-Se grown electrochemically using ITFs of Makrofol-KG

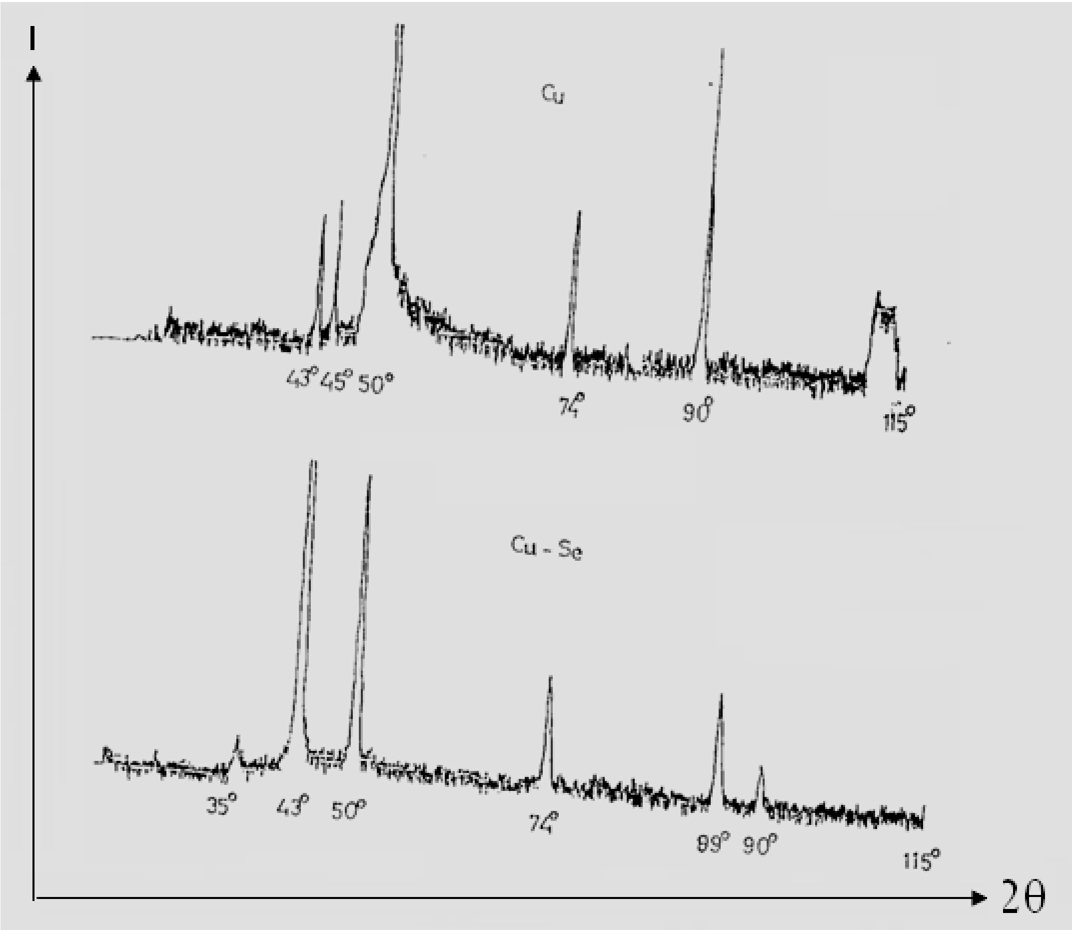
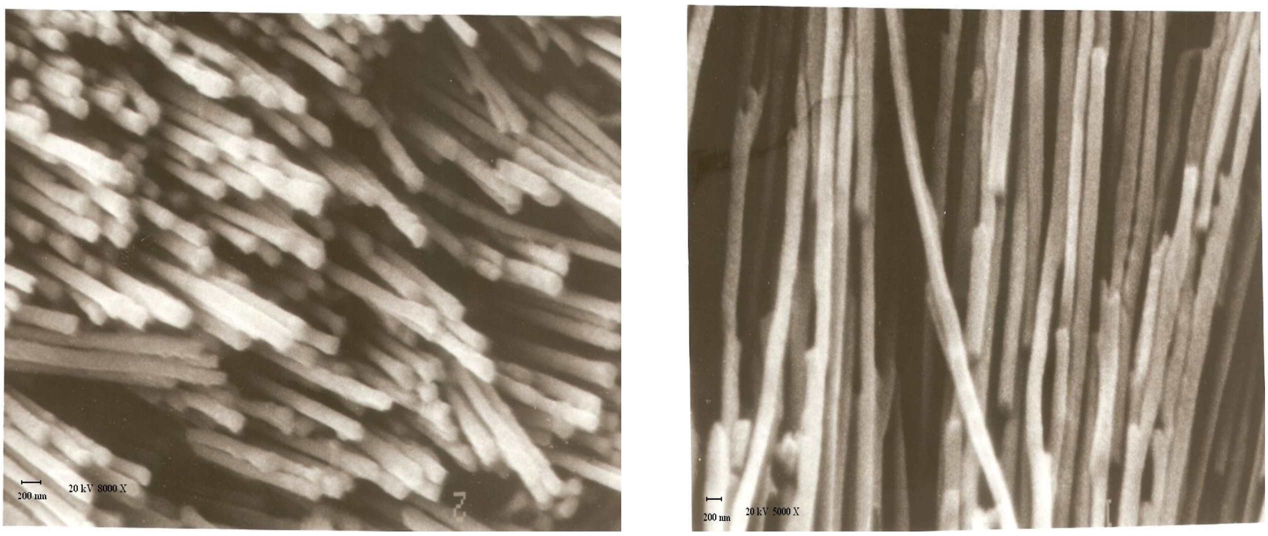


Fig.2 X Ray diffractogram of Cu and Cu-Se hetrostructure showing different peaks



(a) (b)

Fig .3 SEM micrographs of Copper nanowires of 200 nm dia. grown by electrodeposition in AAM

Ion Tracks Route to Nanotechnology

It has become evident that heavy ion beams can also be used in nanotechnology [8-10], since ion tracks have just the right size for nanostructuring (1-10 nm) and the track length can be varied upto several μm by choosing the appropriate sample thickness. In this way, quasi zero-dimensional quantum dots or quasi one-dimensional nanowires can be created.

There are essentially two modes to use ion tracks for nanostructuring. The first is known as ITF or track-etched membrane (TEM) mode described under experimental techniques. 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. Author's group has utilized both these modes.

Recent experiments [10] have confirmed a dramatic increase in the electrical conductivity of ion irradiated diamond-like carbon (DLC), the material changing from insulating (diamond-like) to conducting (graphite-like) carbon in the ion track. This led to creation of thin conducting wires in an insulating matrix. Another material of interest is zinc-ferrite ($ZnFe_2O_4$) which is paramagnetic in its original state. It gets converted to ferromagnetic state by ion beam irradiation [11]. A similar conversion can be induced in YCo_2 [12]. Fig. 4(a, b) shows the topography and enhanced conductivity recorded in 1-GeV Uranium ion irradiated DLC film using Scanning Probe Microscope (SPM) in the contact mode. Each ion track is characterized by a small hillock at the impact site of a single ion and by a huge increase of current through the film [10].

Our Future Outlook

After installation of universal NT-MDT M4 SPM in our laboratory, our thrust area program is focused on fabrication of quantum dots and nanowires using the heavy ion track route [13-15]. Since the dimensions of the dot are in the order of 10 nm or less, one is in a regime where quantum effects become dominant. We propose to investigate single electron effects, as evidenced by Coulomb blockade, observable at even room temperature [16]. Our second line of attack is going to be chemical route of Reverse Micelle technique (17-18). Transmission Electron Microscope (TEM, 200 kV FEI) micrographs of nanorods of Barium carbonate and naocrystals of Iron oxalate prepared in our laboratory are shown in Fig. 5(a, b).

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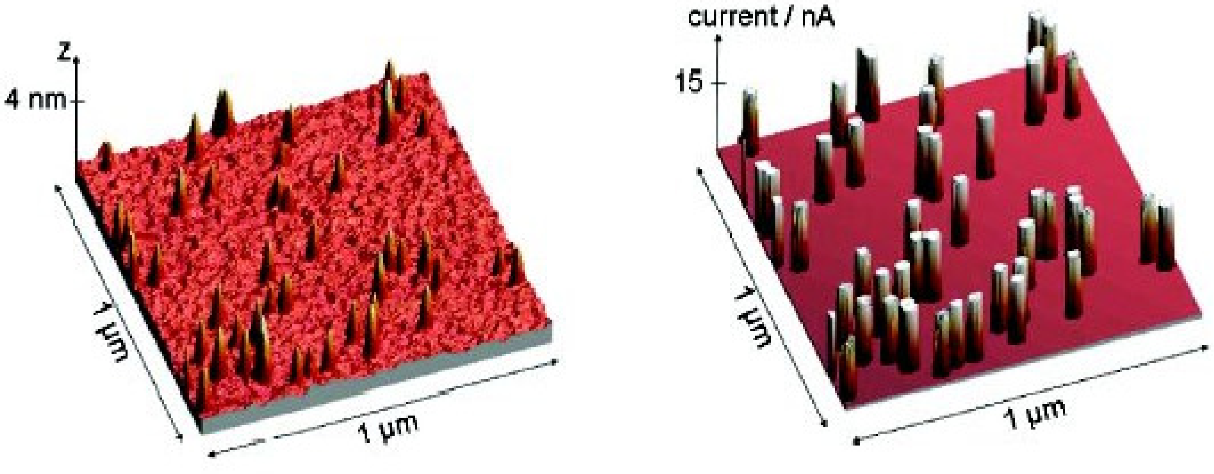
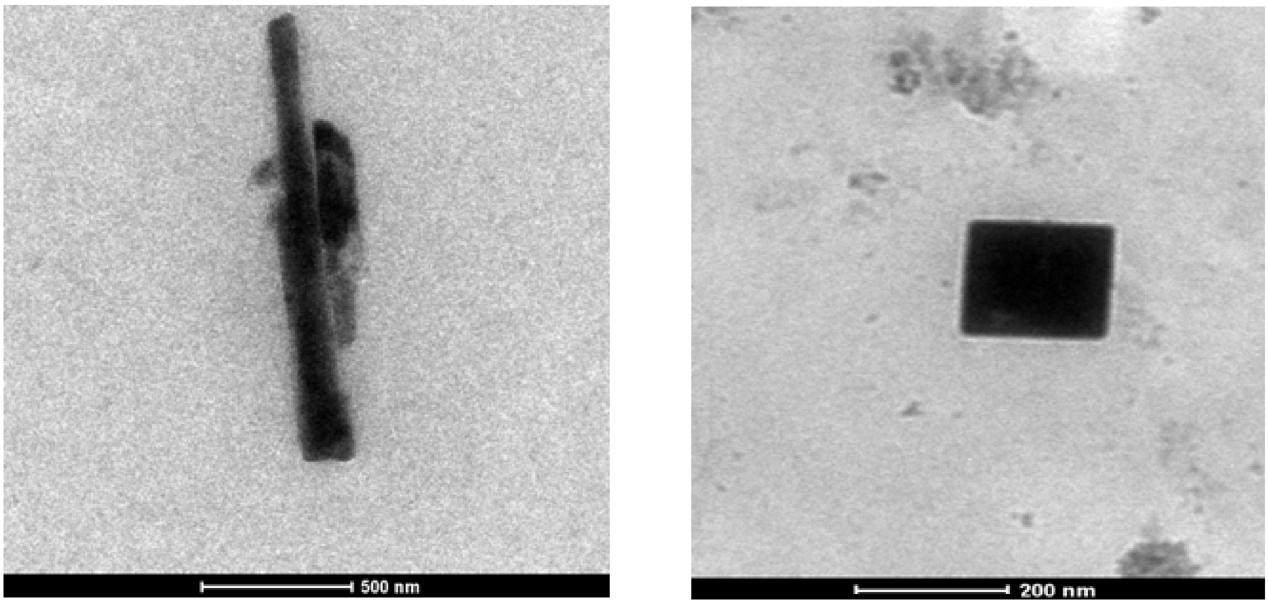


(a) (b)

Fig. 4 SPM images of 1 GeV Uranium ions irradiated dimond like carbon (DLC) film : (a) Topography and (b) Current in contact mode



(a) (b)

Fig. 5 TEM micrographs: (a) Nanorod of Barium Oxalate, and (b) Nanocrystal of Iron Oxalate

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