Track-etch membranes as tools for synthesizing nano-/micro-structures and devices

Abstract: *This review article addresses the art and science of specific technique- the "Template Synthesis"(TS) used as a route in the development of nano-/micro materials and structures involving metals, non-metals, semiconductors, magnetic multilayered nano wires, conducting polymers, glasses, nano tubules, wires and whiskers etc .The recent past has witnessed keen interest being generated on the use of innovative technologies like TS in the production of nano materials' fabrication reported from various authors and from our lab. The strategy for embedding matter of interest within the etched pores or channels in the track-etch membranes as template is the material's placement through some suitable mechanism at the desired places viz., pores.*

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1. INTRODUCTION

In the fast developing technologies era, nanotechnology is the one significant technology that has already taken a lead and a big leap. Indeed, it is now realized that the small matter does not matter small! It appears to be all set for bringing in revolution in the development and advancement of techniques involved in the synthesis and fabrication of sensors and devices with great potential. The conventional techniques for fabrication of very low dimensional wires- say quantum wires include wet chemistry, electron beam lithography, focused ion beam techniques and atomic-beam lithography (see refs in Huixin and Tao, 2004) .That has shown the ways for adopting newer alternative approaches which are relatively inexpensive, easier to handle and synergistically adorned with high efficacy. Nanotechnology is one of the fastest growing new areas in science and engineering and deals with science and technology associated with dimensions in the range of 0.1 to 100 nm. The ability to fabricate structures with nanometric precision is of fundamental importance to any exploitation of nanotechnology.

It is now well known that size of the devices and components dictate many unusual traits and characteristics where quantum effects become more predominant. In the recent years, there has been a tremendous spurt in the potential applications of metallic as well as non-metallic nano/micro structures and materials. Quasi-one-dimensional nanostructures and materials like nano wires, fibres, tubules etc. having high aspect ratio, would provide unusual and uncommon properties like strength and hardness enhancement, dramatic changes in electrical conduction, field-ion-emission through tunneling phenomenon, optical, magnetic, and chemical and other important functional attributes etc are found to be enhanced when the size reduction comes into play. Materials with nano-scopic dimensions may exhibit quantized conductance (Landauer,1989) which not only has potential technological applications in various areas but also is of fundamental interest.

It has been approximately five decades since researchers first began exposing materials like polymers to ionizing radiation, and reporting the occurrence of cross-linking and other useful effects. Today, a substantial commercial industry is in place based on processing of polymers with radiation. Innovation in this field has by no means ended; important new products made possible through radiation technology continue to enter the marketplace, and exciting new innovations in the application of radiation to macromolecular materials are under exploration at research institutions around the world.

This article reviews the technique- the "Template Synthesis" (TS), involving the porous membranes (specific reference is made to track-etch membranes) which are spin-off from the radiation-matter interaction and are used as tools in the development of nano-/micro materials, structures and devices. The recent past has witnessed keen interest being generated on the use of innovative technologies like TS in the production of nano-materials' fabrication involving materials like metals, non-metals like semiconductors, magnetic multilayered nano wires, conducting polymers, glasses, nanotubules, wires and whiskers etc reported from various authors and from our lab (Chakarvarti and Vetter, 1998; Martin, 1996; Brumlik et al, 1994; Chakarvarti and Vetter, 1993; Kumar et al, 2004a,b,c,d,e,f; Sekhon et al. 2004; Kumar et al., 2005; Chakarvarti et al., 2005; Kumar and Chakarvarti, 2006; Chaudhri *et al.* 2005 and refs there in).

1.1. Nano Synthesis Approaches

All the conventional and available nano-synthesis techniques can be categorized into two complementary approaches:

- The Top-Down approach - starting with the bulk material and carving the way down to the nano-scale, and
- The Bottom-Up approach- starting at the molecular level and fabricating up the material through the small cluster level to the nano particle and the assembly of nano particles.

The potential of combining radiation effects with nano materials has been recognized from the very early stages of nano-science research. In the many uses of nano structures, and nano particles in particular, from catalysis, bio sensing, nano-electronics, magnetic applications including separations, mechano-chemical conversion, and to molecular computing, radiation can play a significant role.

Many nano structured systems, like metal sulphide semiconductors of nanometric matrices, PC-controlled biochips for programmed release systems, nano-ordered hydrogels based on natural polymers, development of. Poly-saccharides (Andrzej et al., 2005; Chmielewski et al., 2007) emerge out from the use of radiation (UV beam, electron-beam, or focused ion-beam) techniques which offer unmatched reproducibility and very narrow size distribution.

2. TRACK-ETCH MEMBRANES ENABLED NANO-/MICROTECHNOLOGY

2.1 Track- Etch Membranes (TEMs)

Insulating solids when exposed to heavily ionizing particles can store damaged trails, known as latent ion tracks, which are the zones of radiation damage brought about by electronic energy transfer mechanisms along the trajectories of highly energetic heavy ions impinging upon an insulating solid. In polymers, this radiation damage often leads to chain scissioning along the ion tracks that promotes an enhanced chemical etchability. As a consequence of such track etching, narrow and long parallel pores emerge-the so-called etched tracks. The formation of micro porous and nano porous membranes having highly uniform geometry and precisely determined structures is an exciting example of industrial application of ionizing radiation. Track - etch membranes (TEMs) were first made by irradiation of polymeric sheets, micas, and glasses with fragments from the fission of heavy nuclei such as californium or uranium (nuclear track etch method). The second method makes use of heavy ion beams, usually of energy on the order of several MeV, from accelerators and presents quite a few advantages over the former one which are: (a) no induced radioactivity in the irradiated material when ion energy is below the Coulomb barrier; (b) all tracks show the same etching properties; (c) deeper penetration in the material owing to higher energy of particles; (d) higher density (even >10^9/cm^{-2} for smaller pores) track arrays; (e) easier control of the impact angle and production of arrays of parallel tracks. The mechanisms involved and proposed for the formation of the latent tracks are well documented (Fleischer et al., 1975). Some of the widely used polymers for ion track membranes are polyethylene terephthalate (PET) and polycarbonate (PC).

According to sensitization and etching with an alkali solution (NaOH, KOH for instance), uniform cylindrical, conical, tunnel-like, or cigar- like pores have been obtained. Pore sizes or ~~dimensions depend upon various~~ factors, viz. the nature and energy of incident particles, the target material, etch conditions, e.g. temperature, nature of etchant, pre-etch storage conditions, etc. and are controllable. Thin film polymer membranes having highly uniform pore size and a wide variety of porosities in well-distributed areas of the template (patterning) are already commercially available.

TEMs, are also known as Nuclear Track Filters (NTFs). The etched pores can have diameter ranging from few nm to mm with aspect ratio as high as 10-1000. There exists a wealth of literature on SSNTDs and related topics. The particle track-etch technique, therefore, enables the generation of definite shaped pores which can either be used individually in the form of single particle track or collectively in the form of pore arrays constituting many pores-distributed either stochastically (pore density as high as 10^{10}/cm^2), or in a well defined spatially geometry through the control of the drilling particle beam used in "write mode". Areal dispersion usually lies between 2 to 20% and a 10MeV/nucleon heavy ion (Fischer and Spohr, 1983). The crafting of TEMs templates through ions have been discussed in details (see for example, Fleischer et al., 1975; Spohr, 1990 : Fischer and Spohr, 1983; Ferain and Legras, 2003and refs therein). The pores can be "drilled" with alignment in any direction depending upon the angle of incidence of the beam with the target. Fig.1 (a,b) shows SEM photographs of a processed polycarbonate (Makrofol) NTF with monodispersed pores

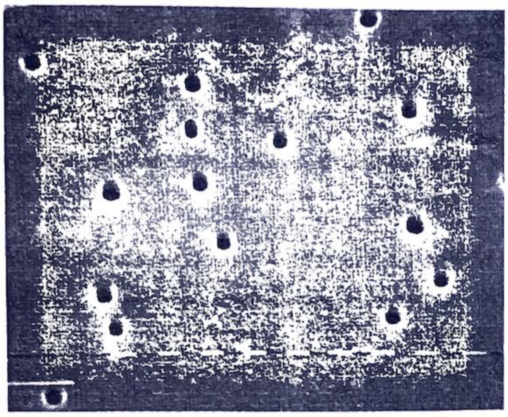

Fig. a

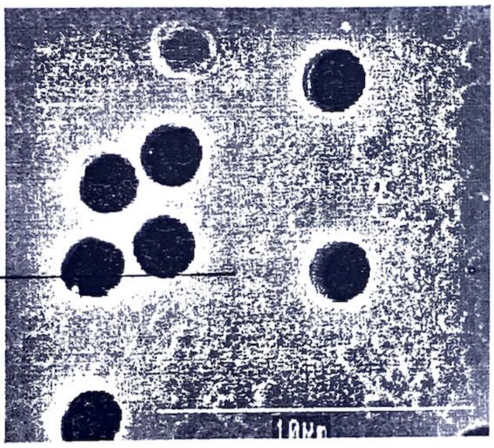

Fig. b

A processed TEM template with mono dispersed pores of dia ca.1 um

2.2. Template Synthesis-A technique

A template, in a general sense, may be defined as a pre-designed structure within which a network exists which can be utilized for further use. Thus, for example, a membrane with pre-fabricated cavities or pores of known morphology, number, distribution and configuration may also act as a template the pores of which can facilitate replication by any suitable means. The strategy for embedding matter of interest within the etched pores or channels in the template is the material's placement through some suitable mechanism at the desired places viz., pores. This can be accomplished in four ways.(1) using the capillary action of the pores/channels and enabling the solution of the dissolved material entering into the pores, followed by slow evaporation of the solvent. This will lead to growth of supersaturated structural elements. (2) electrodeposition, where one side of the template, coated with a metallic layer, or the template support itself, is used as a cathode for electroplating; (3) chemical polymerization where a solution of the desired monomer and initiator, in which the template membrane is dipped, is left to diffuse through the pores of the templates leading to a polymerization reaction in these pores; and (4) electroless plating where a catalyst to the pore walls is applied which facilitates the deposition of metal on the activated pores of the template. The micro- or nanomaterials, which are produced in this way, take the form of wires or tubules. Magnetic, conducting and superconducting nanowires and nanotubules in array or isolated mode possessing special properties have been manufactured in this way. The template approach has been extensively investigated in the synthesis of various nanostructures and this strategy is most commonly and widely used to prepare free standing, non-oriented and oriented nanowires or nanorods or nanotubes; the latter is also referred to as nanorod or nanowire or nanotube arrays. The generated structures can be monodisperse homogeneous or heterogeneous, multi-layered, short, squat fibrils, long needles, hollow tubules, tapered conical (single or double cones) elements etc depending upon the template-factors. Bio-templates are also explored for the growth of nanowires and nanotubes such as Cu, Ni ,Co and Au nanowires. An electrical insulator is required for a template to be used in electrochemical deposition. Template materials should be chemically and thermally inert during the synthesis and following processing steps. Also, depositing materials or solution must wet the internal pore walls and for the synthesis of nano rods or nanowires, the deposition should start from the bottom or one end of the template channels and proceed from one side to another. However, for the growth of notubules, the deposition should start from the pore wall and proceed inwardly. Inward growth may result in the pore blockage, so that should be avoided in the growth of "solid" nanorods or nanowires. Kinetically, enough surface relaxation permits maximal packing density, so a diffusion-limited process is preferred.

The technique of TS (Ozin,1992) may be classified into three categories depending upon the mode of use of templates(1)- the negative template method, positive template method and surface step-edge template method. The negative template methods, the most popular and widely used techniques of TS allow the use of prefabricated nanopores in solid templates and the material is deposited into these pores using normally electrochemical techniques. The basic and underlying principle of negative TS is similar to that of producing materials through the use of replication e.g., die-casting or moulding like making ice-candies. After removing (say by way of dissolving) the host template, free standing elements as wires, cylinders or conical structures can be obtained. The method has been regarded as "brute-force" method as the synthesized ensemble structure depicts the true replication of the morphology of the pores (Foss 2002). The positive template methods use wire-like substrates like DNA (size ca.2 nm), carbon nanotubes (Sima et al., 2004) etc. on the outer surface of which the material is deposited to the desired dimensions. The removal of templates can produce wire-like or tube-like structures. Other positive templates have been discussed by Huixin and Tao (2004).The surface Step-Edge templates, also known as "step-edges decoration" uses the fact that there is preferential or selective deposition of many materials initiating on the defect sites. Zach et al (2000), and Bera et al. (2004) used this technique for generating conductive metal oxide (MoOx) at the step edges of HOPG, which after reduction in appropriate environment could yield metallic Mo nano wires.

When elctrodeposition is carried out, the nucleation of nanostructures on the electrode substrate via template pores during electrodeposition is influenced by the crystal structure of the substrate, specific free energy and other factors like adhesion energy, orientation of the lattice of the substrate etc and the final size distribution of electrodeposits is strongly dependent upon the growth and nucleation kinetics (Bera et al., 2004). Template assisted electrodeposition process can be divided into two categories: active template assisted process which results from growth of nuclei that essentially nucleate at the pores and defects of the substrate, while the other is known as restrictive template-based electrodeposition used mostly in the synthesis of metallic nano wires, involves deposition of metal into the prefabricated and designed pores within an inert, insulator membrane or template. TEMs, porous alumina, conductive polymers, carbon etc have been used as templates which fall under this category (Bera et al., 2004).

The technique is blessed with simplicity and nano/microstructures with extraordinary low dimensions have been reported to be produced (see refs in Ozin,1992; Foss, 2002; Braun et al.,1998) which are otherwise difficult to manufacture using lithographic methods. Here in the present review, detailed discussion has further been carried only on negative template synthesis using TEMs as templates for synthesis of nano-/micromaterials.

2.2.1 History and development of negative template Synthesis

The first demonstration of the art of filling the pores of a membrane with silver was given by Bean (1969) followed by Possin (1970) who utilized electrodeposition technique in the fabrication of thin wires as small as 400 Å using mica with etched pores as templates for synthesis of such elements of the nanostructures. Williams and Giordano (1984) claimed to have reduced the size down to 80 Å after effecting some refinements to the technique. Penner and Martin(1987) reported on the generation and characterization of ultra-microelectrodes with radii as small as 1000 Å. Klien et al.(1993) reported on the fabrication of graded CdSe/CdTe hetero-structures and development of chemistry for fabricating II-VI chalcogenide semiconductors CdSe and CdTe within the template membranes producing micro-diode arrays consisting of micro-cylinders retinal rod cells- the photoreceptors in the human eye and having ca. five times smaller diameter than that of photoreceptors. Team led by Prof. Charles Martin at Colorado State University, USA, has been actively engaged in exploring exploiting the TS for its full potential and a large number of reports are available (see refs Huczko, 2000). Researchers at GSI at Darmstadt, Germany (where this author has had also his first hand-on experience with the technique of TS for a short duration during early nineties), have also many reports to their credit for developing the technique further and generating nano/microstructures (see, for example, ref. Spohr,1990).A large bulk of literature since then has been published on the negative TS and its applications (see refs in Chakarvarti and Vetter, 1998; Huczko, 2000; Martin, 1994). This lab has also been reporting from time to time on the synthesis of nano-/microstructures, devices and tubules using TEMs as templates (Chakarvarti and Vetter, 1998; Martin, 1996; Brumlik et al., 1994; Chakarvarti and Vetter, 1993; Kumar et al., 2004a,b,c,d,e.f; Sekhon et al., 2004; Kumar et al, 2005; Chakarvarti et al, 2005; Kumar and Chakarvarti, 2005; Chaudhri et al., 2005).

2.2.2 Template Materials

While sieving properties of porous membranes have been used from as early as some thousand of years but it is relatively only recently that a technological application like TS of nano/microstructures has been brought to this process- almost a bi-product having no relation with sieving properties. Until recently where the use of positive template synthesis has started, most of the work had been carried out using negative template synthesis involving mainly two types of membranes-TEMs and porous alumina(Al_2O_3).Others include nanochannel array glasses, xeolite, proteins etc. A wide variety of other nanoporous solids that can be used as templates are cited elsewhere (see, for example, Martin,1994)

2.3 Electrochemical Cells and electrodeposition

A scientific treatment of galvanic process is in fact complicated and development of optimum plating conditions may be obtained through one's personal experience obtained through repeated \ trials under the given inputs. The age and condition of electrolyte viz.; temperature, pH, concentration, agitation rate, purity of solvent as well as electrolyte solute, additives and their amount, uneven current distribution, increase of specific resistivity of electrolyte, formation of gas bubbles and gas blankets at electrodes excessive inter electrode distance etc affect the quality of deposition. Plating in small crevices or pores is very difficult. The solutions should have good micro-throwing powers-the ability of a solution to plate into fine cavities or defects on the surface such as pores, pits, polishing lines and scratches, besides the good covering power- the ability of an electrolyte to deposit metals into pores where current density is low. Copper, for example, has poor macro-throwing power but can possess excellent micro-throwing power. Electrodeposition of metals such as those which are more electronegative (eg., aluminum, molybdenum, tungsten, titanium, tantalum, zirconium and niobium etc) is not always possible from aqueous solutions. Electrodeposition on metals in corrosive electrolytes or galvanic deposition of noble metals such as gold and silver on base metals like copper needs much care as the adhesion of the plated mass is found to be poor. With micro porous membranes, rinsing off the membranes with 3% H_2SO_4 followed by distilled water and absolute ethyl alcohol would facilitate the galvanic process in the case of metals like zinc, indium etc(Possin,1970). Pre-soaking of the cleaned and washed template with the given electrolyte is also helpful (Chakarvarti and Vetter, 1991). Many detailed studies of the electrochemical fabrication process for nanostructures has been reported by different workers (Schonenberger et al.,1997; Whitney et al.,1993; Ensinger, 2007).

For electrodeposition of metals, some special types of electro-plating cells are used (Penner and Martin,1987; Chakarvarti and Vetter,1991; Dobrev et al.,1995) which offer a low ohmic voltage drop across the electrodes even when the cell is filled with a poorly conducting electrolyte. There are various cell designs available- two electrodes and three electrode cells. The cell designed by Dobrev et al. (1995) has the provision for mechanical stirring besides a thermostat or maintaining the desired temperature of the water contained in a jacket surrounding the cell as constant. We used a very simple cell as shown in Fig. 2.

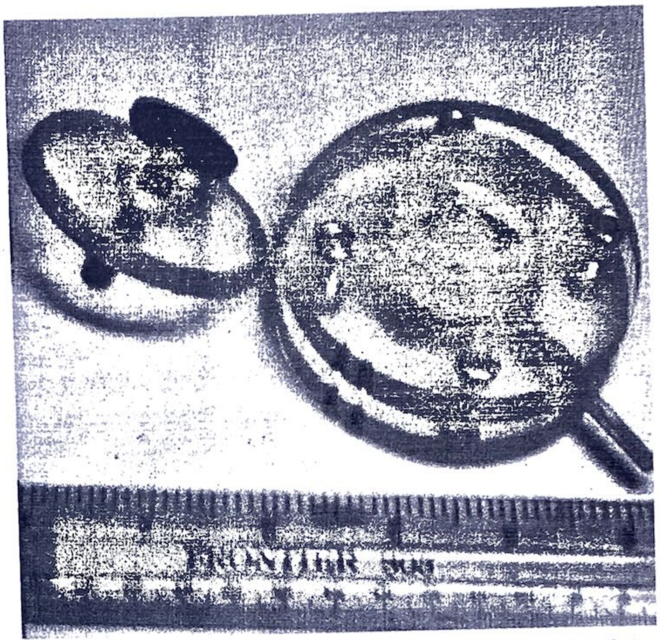

Fig. 2. Two-electrode electrodeposition cell used in template synthesis of nano-/micro structures

Electrodeposition is accomplished by simply coating one face of the overlaid template with a metal film (preferably gold) to serve as a working electrode on which electrodeposition takes place. The thickness of the film is appreciably large if the pores in the templates have also larger size. Alternatively, a metallic tape with conducting adhesive on the surface may also be used for fixing up the template membrane while the pores on the other face act as channel templates with one end sealed (Chakarvarti and Vetter, 1991). In order to make the pore walls conducting so as to be conducive in convenient electrodeposition by way of providing molecular anchors, the template may be moistened with solution like chloroplatinic acid (Penner and Martin,1987) before electrodeposition is carried out. The use of electroless plating on the pore walls of polymeric templates might also be useful before galvanic process is started. This needs etching of polymer surfaces with chromic-sulphuric acid solutions followed by activation by immersion in tin and palladium solutions, or a colloidal solution containing these ions. This process is called "conditioning" which is required to improve the wettability of the polymer surface which further facilitates adhesion of the plated metal. During electrodeposition of the metal at the cathode, the depletion of the metal ions increases the absolute value of the deposition potential and if this exceeds the hydrogen over-voltage for the given process, hydrogen also deposits resulting into a loss of plating efficiency and increase in pH of the elctrodeposited metal, ultimately causing "burning" of the thin deposition. In order to avoid the development of over-potential, factors like increase in bath temperature and the agitation or the electrolyte are helpful for applying deposition potential and monitoring the current and potential drop across the cell, a good constant voltage (potentiostat) power supply is needed. It is found that while DC electrodeposition can produce good quality nano wires but the filling of the pores is partial ca.10-20% (Prieto et al., 2001). A high filling ratio as well as generation of uniform array of structures can be achieved by using AC electrodeposition. Various AC pulse shapes like saw-tooth waves, triangular, sine waves, but not square wave (square- wave potential pulses may be used for obtaining multilayered nano wires, see ref. Piraux et al., 1994) with varying frequencies have been used for better results, increased crystallinity and homogeneity (Yin et al., 2001). Nielsch et al. (2000) used pulsed electrodeposition method and demonstrated that it suits for uniform deposition of porous alumina with almost 100%. From our experience, we have found that initial high voltage for short duration followed by low values (the process is called "striking") produces good results. Chakarvarti and Vetter (1998) have suggested a formula in order calculate an approximate optimum current for satisfactory results. It is of interest to note that the template synthesized materials (metals as well as semiconductors in the form of solid cylinders, wires or whiskers can be crystalline (Dobrev et al., 1995; Chakarvarti et al.,1996).

2.4 Synthesized nano-/microstructures and devices: some results

Some of the metallic, non-metallic homogeneous and heterogeneous structures and devices (RTDs) synthesized in this lab are shown in the Figs. 3 to 15.The templates used in all cases were TEMs of Makrofol polycarbonate having pores with different shapes (some cylindrical and others conical). The Makrofol foils were got irradiated at UNILAC at Gesellschaft fur Schwerionenforschung (GSI), Darmstadt, Germany. Also some polycarbonate foils were obtained from Whatman. More details and descriptions can be found from the references quoted.

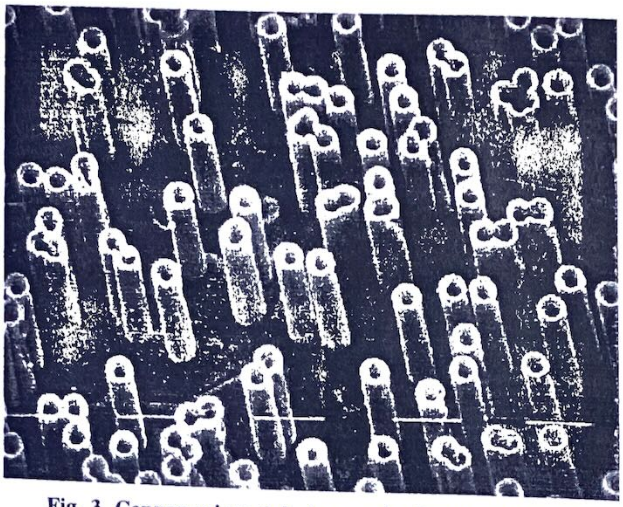

Fig. 3. Copper micro-tubules synthesized in PC TEM

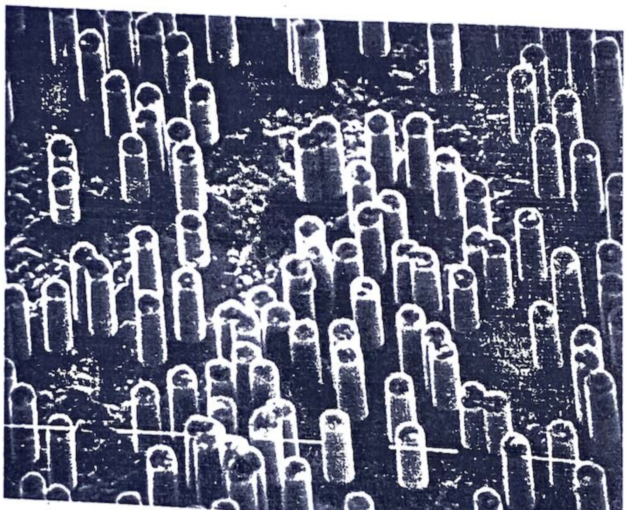

Fig. 4. Copper cylindrical microstructures

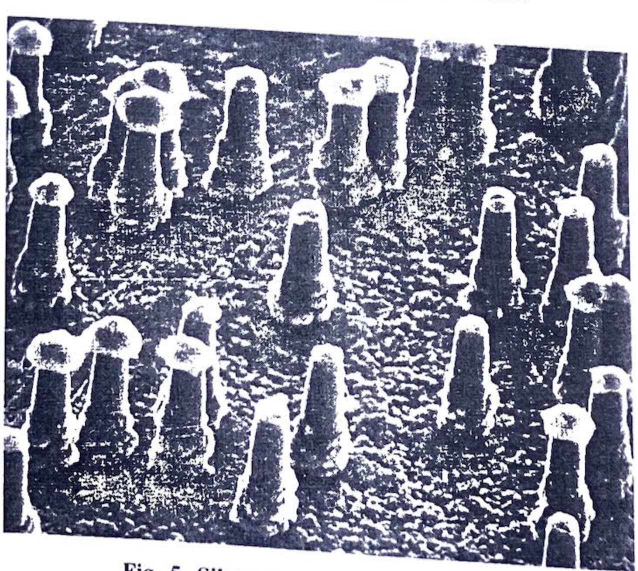

Fig. 5. Silver tapered microstructures

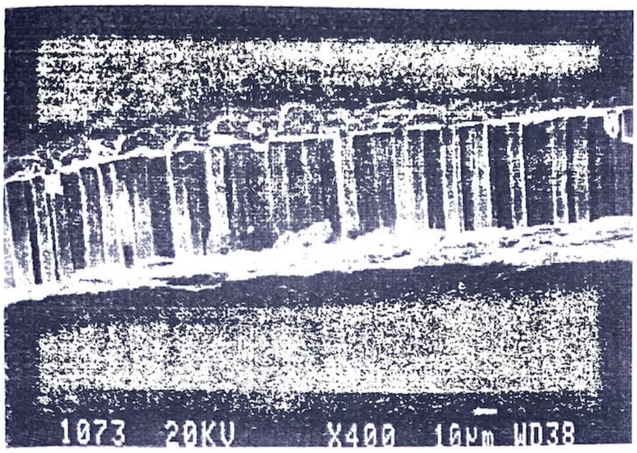

Fig. 6. Polypyrrole (PPy) micro-tubules

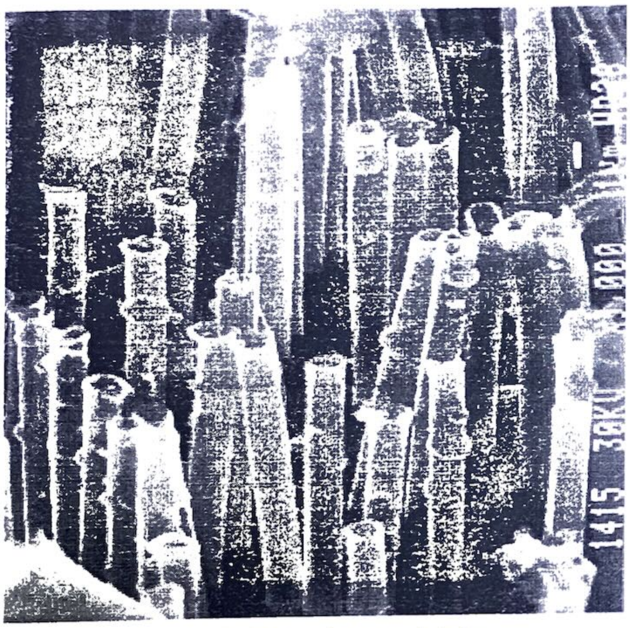

Fig. 7. Polypyrrole nano- tubules

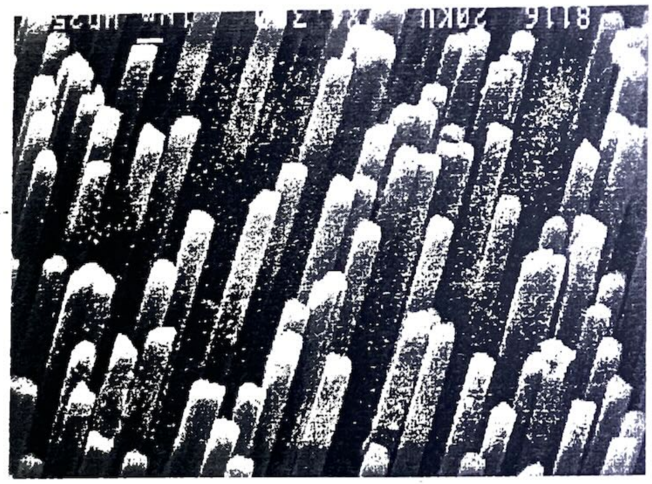

Fig. 8. Silver free-standing structures

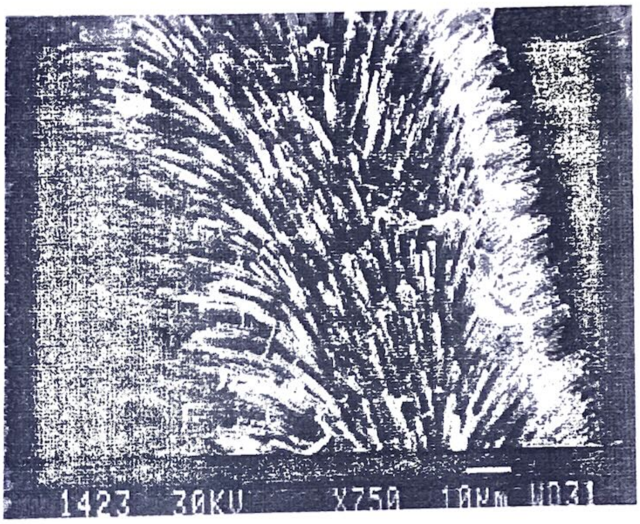

Fig. 9. PPy nano-tubules observed by folding the edge of the sample template

Fig. 10. Silver-selenide microstructures

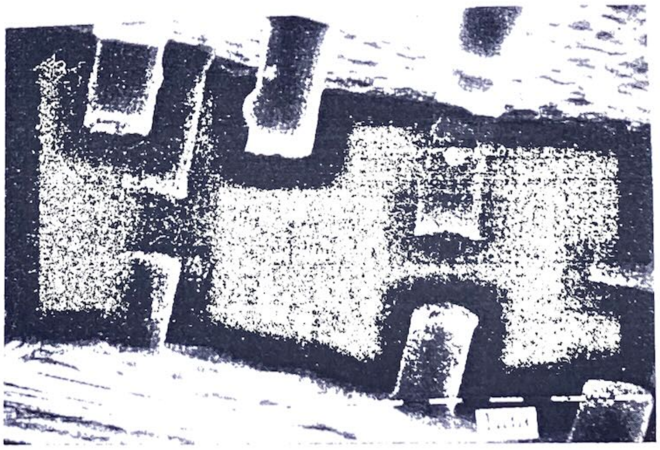

Fig. 11. Copper-selenium heterostructures-Unzipped structures

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