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D. Fink
HMI
Berlin, Germany

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D.Fink[1], A. Chandra[1,2], P.Alegaonkar[3,4], A.Berdinsky[5], A.Petrov[6], D.Sinha[7]

[1]HMI Berlin, Glienicker Str. 100, D-14109 Berlin, Germany
[2]Department of Physics and Astrophysics, University of Delhi, Delhi-110 007, India
[3]Sungkyunkwan Univ., Dept.of Advanced Materials Engineering, Nano Materials and Devices Laboratory, Suwon, KyungGi-Do, 440-746, Korea
[4] Department of Physics, University of Pune, Pune – 411 007, India
[5] Novosibirsk State Tech. Univ., Karl-Marx Av. 20, 630092, Novosibirsk, Russian Federation
[6] Inst. of Solid State and Semiconductor Physics NAS Belarus, 20072 Minsk, Belarus
[7] Department of Chemistry, Nagaland University, Lumami Campus, Nagaland, India

Abstract

With interest rising recently in nanostructures of all kinds, attention was also given to etched ion tracks in insulators. The emerging nanopores with a very high aspect ratio enable one to create new functionalities especially in thin polymeric foils and oxide-on-silicon structures, when combined with electronic, optical, catalytic or sensing materials.

These materials are often inserted into the nanopores in the form of nanoparticles, for several reasons. On the one hand, quantum effects can easily be exploited in this way, and on the other hand, tailoring of size and distance of (semi)conducting nanoclusters enables one to obtain any desired conductivity value between insulating and metallic of the nanocluster/nanopore devices. Also, the very large surface areas of nanoclustered materials may be useful for initiating chemical reactions e.g. for sensing, catalytic, or medical purpose. Nanotubes may be grown within the nanopores, which enhances the range of possibilities greatly. Potential applications of these strategies are outlined.

Keywords: etched ion tracks, nanopores, nanoparticles, nanotubes, nanoelectronics

E-mail.fink@hmi.de

1. Introduction: The tools for swift heavy ion-based nanoarchitecture

1.1 Nanopores

There are several possibilities to produce nanopores. On the one hand, there are quite a number of self-orienting nanoporous materials available, such as porous alumina or zeolites. Also, biological membranes are known to be rich in nanopores that enable the cell metabolism (e.g. nutrient and waste exchange). Finally, the pores between sintered nanoclusters are of nanometric dimensions.

Here, we concentrate, however, on pores produced by etching of swift heavy ion-irradiated materials. A number of insulators, such as mica, silicon dioxide, silicon oxynitride, and some polymers such as polyethylene terephthalate (PET, mylar), polycarbonate (PC, makrofol), polyimide (PI, kapton), polyallyl diglycoll (PADC, CR39), cellulose nitrate (CN), and others have the property of becoming quite sensitive to the attack of strong etchants such as acids (e.g. HF for the silicon-based materials) or KOH (e.g. for PC or PET and mica) after swift heavy ion irradiation [1]. In suitable cases, the etching rate increases by up to three orders of magnitude along the ion tracks as compared with the unirradiated bulk material. As a consequence, long nanopores emerge with aspect ratios (length to diameter ratios) of up to 1000.

Hitherto, polymer foils with such parallel nanopores have found applications especially in filtering technology for special purpose in medicine and semiconductor industry. Recently, ideas have emerged to use such microporous foils also in the areas of medicine and food packing industry as sterilized foils [1,2], as sensors [1,3], or for various nanodevices in electronics and electrical engineering [1,4].

For the above purpose, usually some suitable materials are inserted into the etched tracks, to give them a new functionality. Up to now, most of the derived nanostructures are quite simple, comprising of just one type of material inserted. Only in very few cases, axially or radially structured track multi-fillings were reported, e.g. for applications as giant magnetoresistance (GMR) elements, condensors or batteries [1].

Also nanoparticles and nanotubes belong to the arsenal of materials which can, in principle, be inserted into nanopores for the above described purposes. This has already been done successfully [2,5,6], but to our knowledge there does not yet exist any systematic overview about the possibilities of nanoparticle and nanotube architecture in nanopores. This is attempted in the present paper.

1.2 Nanoclusters

Nanoclusters can be produced by precipitation from a corresponding supersaturated solution (e.g. a concentrated salt solution) or via some chemical reaction (e.g. a reduction reaction of an amonia silver complex salt solution by a weak reducing agent such as glucose [7,8]), and subsequent rapid interruption of the deposition process. Meanwhile, a number of nanoclusters are also commercially available, either as powder (e.g. anatase, TiO_2) or as colloidal solution (e.g. Au). It is convenient to put nanoclusters into solution by surrounding them with suitable ligands, and to sonicate for a prolonged time.

Nanoclusters have a number of peculiarities which make them interesting for applications, such as their chemical, electronic, optical and mechanical properties.

Chemical properties: Nanoclusters are soluble in liquids, either after bonding with suitable ligands (e. g. amyl acetate as in the case of $LiNbO_3$ nanocrystals (own results, unpublished) which prevent their self-clustering and enable their stability in the liquids, or after having been diluted to a very high degree (e.g. less than $2x10^{-4}$ weight % as in the cases of expanded graphite (EG) or carbon nanotubes (CNTs) in methanol or isopropanol) (own results, unpublished). Also, nanoclusters often show catalytic properties (e.g. anatase, TiO_2 [2]).

Electronic properties: First, the variation of nanoclusters in size makes their band structures tunable from conducting via semiconducting to insulating which means that their electronic properties can be readily tailored. Also, by variation of the distance of nanoclusters, the macroscopic resistivity of a nanocluster distribution can be tailored from conducting via semiconducting to insulating. Further, the different conduction mechanisms operating at different cluster-to-cluster distances give rise to different current/voltage correlations and different temperature dependences [9].

Nanoclusters can store discrete amounts of charge which makes them susceptible for quantum effects, such as the construction of single electron transistors with their step-like current/voltage characteristics [10,11]. The possibility of charge storage by nanoclusters enables one to construct nanocapacitors, but it also leads to the frequent occurrence of hysteresis curves in current/voltage diagrams of nanocluster-containing electronic devices. Longitudinally expanded nanoclusters such as CNTs have pronouncedly anisotropic electronic properties, i.e., different conductivities in different directions. Finally, one should mention magnetic nanoclusters which are polarizable.

1.3 Nanotubes

Whenever a small amount of material is deposited within a nanopore (e.g. by precipitation from liquid phase), it will preferentially be deposited on the pore walls. If the amount of deposited material is large enough to form a continuous film, one calls the resulting structure a nanotube or nanotubule. Such nanotubes have been successfully produced with C_{60}, Ag, Cu, Au, conducting polymers, and many other materials [1,3,7,8,12,13]. They can be isolated by dissolution of the host matrix. Ofcourse, the length of these nanotubes never exceeds the thickness of the nanopore-bearing foil. The electronic properties of such tubes are primarily determined by the tube material, and can be scaled down to the tube size. However, for tubes of conducting polymers, the axial tube conductivity increases with decreasing tube diameter, due to the increasing alignment of the polymer molecules along the tube axis. Quantum effects of such nanotubes should exist, but to our knowledge have not been examined.

Recently, the growth of carbon nanotubes (CNTs) within etched tracks in SiO_2 layers on Si has been attempted successfully [14]. Very long CNTs emerge, their shapes sensitively depending on the production technique.

2. Nanoclusters and –tubes on planar surfaces

2.1 Nanoclusters on planar surfaces:

When an atom gets adsorbed at a planar surface, it may undergo some surface diffusion until it becomes immobile. Immobilisation is usually the consequence of trapping at some surface defect, which can be either an intrinsic one (e.g. a structural defect or a suitable impurity), or an intentionally introduced one. The latter one can be of physical or chemical origin. The physical ones are structural defects that can be created by mechanical damage, laser or energetic particle irradiation [1,15,16]. In chemical deposition technology, the formation of trapping centers for mobile atoms/clusters is known as "activation". Here, atoms of metals such as Sn or Pd are chemically bonded to the insulator surface to initiate the condensation of other atoms (preferentially metals) or nanoclusters on them [1,17]. Therefore, such trapping centers are also called "*nucleation centers*".

In case of tailoring the emerging 2D *nanocluster distribution* by ion irradiation, this is determined by the distribution of nucleation centers which initiate the deposition of the nanocluster material, hence by the points of impact of the ion beam. This has a great application potential as it allows very precise structuring of the nanocluster distribution, (e.g. by using ion microbeams or masks [18]).

The *nanocluster density* (hence also the average cluster-to-cluster distance) depends on the magnitude of the surface damage by the ion beams, hence on the magnitude of transferred (nuclear and electronic) energy by the projectile ions. The latter is a consequence of the choice of projectile specie and energy, and of the ion fluence. There is always a minimum density of deposited nanoclusters on a surface, which is determined by the intrinsic defects of the material. Therefore, one should strive for as pure materials as possible.

The *nanocluster size* depends on the duration of precipitation. If the deposition is not interrupted, the nanoclusters will merge with each other to form continuous layers. Alternatively, if the overall amount of material available in the corresponding solution is not sufficient, the deposit will of course remain nanocrystalline.

2.2 Nanotubes on planar surfaces

Nanotubes of *non-carbonaceous materials* on planar surfaces can be produced by the following steps: first a polymer foil is ion-irradiated and subsequently etched to form nanotubes, and thereafter the desired material is deposited into the nanotubes. This can be done by either chemical deposition or electrodeposition [1]. Thereafter, the tube-containing polymer foil is dissolved.

The growth of *carbon nanotubes* (CNTs) on planar surfaces is readily accomplished by chemical vapour deposition onto Fe or Ni catalyst particles which were deposited on the surface beforehead. The catalyst distribution determines the final CNT distribution.

3. Nanoarchitecture within Nanopores

3.1 Nanoclusters in Nanopores:

Nanoclusters can be inserted into nanopores from solution if their dimensions differ sufficiently, e.g. if nanoclusters of a few nm to ~20 nm size or so are embedded in etched ion tracks with ~50 nm to a few µm diameter. Nanoclusters in colloidal solution can easily be transported into the tracks, and be deposited there e.g. by evaporation of the solvent. (Example: deposition of ~ 5 nm large Au nanoclusters within nanoporous insulating layers on silicon from a commercial colloidal Au solution, for electronic purpose [6]).

As on planar surfaces, nanoclusters can be immobilized also on the inner ion track walls by corresponding nucleation centers. However, the narrow pore topology imposes some problem to tailor the nanocluster distribution. Here, the long range of energetic ion beams can be exploited quite usefully, as a precise structuring can be achieved in-depth within the nanopores by varying the projectile energy [1].

3.2 Nanotubes in Nanopores

Nanotubes can be produced of every material which is capable to enter nanopores in the liquid phase, by letting the liquid subsequently solidify (e.g. in the case of liquid metals or polymerizing monomers), or by letting dissolved matter precipitate (e.g. C_{60} in toluene solution), or by letting suitable materials react chemically (e.g. $Ag^+ + Br^+ \rightarrow AgBr\downarrow$) on the nanopore walls. The deposition time determines the thickness of the nanotube walls. Ofcourse, the nanotube length cannot exceed the nanopore length in this case.

Carbon nanotube (CNT) growth was successfully accomplished within etched tracks in SiO_2 layers on Si [14]. For this, first Ni nanocrystals were inserted preferentially into the etched tracks, and thereafter the CNT growth was initiated by chemical vapour deposition (CVD). The CNTs grow wherever there are catalyst nanocrystals available. Interestingly, both the plasma enhanced and the thermal CVD give rise to completely different CNT structures. While TCVD leads to spaghetti-like bundles of CNTs which are probably of little use, PECVD leads to individual thick tree-like stems of CNTs of up to ~ 10 µm height (Fig. 1). These CNTs appear to be the fundamental building blocks on which the formerly envisaged 3D CNT nanoelectronics [19] can be built up, Fig. 2.

Conclusions

It has been shown that nanopores in insulators produced by swift heavy ions are good structural elements for future single ion track electronics (SITE). In combination with nanotubes and nanoclusters the construction of advanced highly dense 3D electronic devices appears possible with the presently available tools. In fact, first examples have already been demonstrated.

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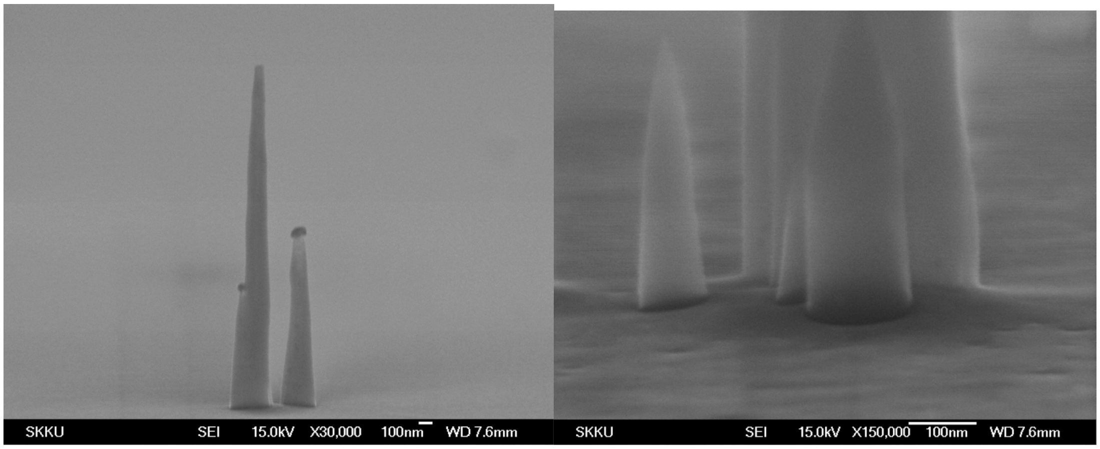

a) b)

Fig. 1: CNTs grown within etched ion tracks. The diameter of the tubes is identical to the etched tracks diameter as the growth-initiating Ni catalyst crystals precipitate at the base of the ion track walls. a) the CNTs grow below the Ni nanoclusters so that the latter are lifted; b) the CNTs growth sets in above the Ni catalysts. The shallow depressions in b) besides the CNTs indicate that CNTs do not emerge from quite a number of the etched tracks.

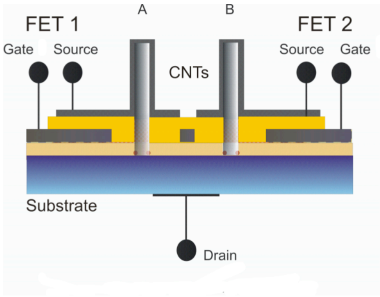

Fig. 2: Principle sketch of a possible 3 D electronic device with CNTs. (Here: two coupled FETs).