REVIEW ARTICLE: Recent Advances in Nanomaterial Fabrication

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Abstract. As nanostructures with well-controlled dimension, composition, and crystallinity are expected to be a new class of intriguing system for investigating structure-property relations, this review article provides a comprehensive review of researches of these materials and related applications.

1. Introduction
Technology of making small structures, nanofabrication, has evolved greatly over the past decade from a reliance upon clever tricks appropriate for simple structures to a broadly based set of technologies applicable to make complex devices with dimension in the range of one to hundreds of nanometres. Variety of techniques has been used to produce this kind of nanostructures. In this article, the author introduces recent advances in nanofabrication techniques in order to harvest the final nanostructures. The related applications of these nanomaterials are also presented in this review article.

2. Nanofabrication
Relief structures present on the surface of a solid substrate serve as a class of natural templates for generating supported nanostructures. In this regard, decoration of these templates provides a powerful route to the formation of nanowires made of various metals and semiconductors [1, 2, 3, 4, 5, 6, 7]. It can be subsequently transferred onto the surfaces of other substrates. Sugawara et al. have fabricated the arrays of Fe nanowires on the (110) surfaces of NaCl crystals by a shadow deposition method (figure 1) [7]. When the NaCl (110) templates is annealed in a vacuum conditions, the surface becomes faceted with (010) and (100) planes in order to minimize the surface energy. Periodic macrosteps parallel to the [001] direction are then formed. After iron is deposited at a certain degree from the template normal, approximately sixty percent of (100) terraces are exposed to iron flux, and the iron nanowires are formed only near the edge of the ridges.

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By using the same procedure, they have fabricated cobalt dot arrays sandwiched in gold nanowires onto stepped NaCl (110) surfaces [8]. As demonstrated by Kitahara et al., it is also possible to fabricate arrays of gold nanowires onto the surface of NaCl (110) substrates [9]. The author also uses this simple technique to prepare copper nanowires [10]. Briefly, NaCl (110) single crystals are dipped in distilled water before being mounted on the substrate heating stage in an ultrahigh vacuum deposition chamber. A certain thick of homoepitaxial layers of NaCl are deposited after the substrate annealing. A certain thick SiO layers are then deposited as passivation layers. Copper is deposited a certain deposition rate onto the substrate at a certain flux angle with respect to the surface normal to form copper nanowires. On the arrays of nanowires, a certain thick of SiO layers are deposited as protection layers. For Transmission Electron Microscopy (TEM) observation, the copper nanowire arrays sandwiched by SiO layers are separated from the NaCl substrates by dissolving the substrates in distilled water, and mounted these nanowires on copper grids for TEM observation. Using this approach, the author obtains wide-area arrays suitable for both TEM and optical measurements in order to study microstructures and optical properties of self-organized arrays of the nanowires.

Penner et al. have demonstrated the growth of the nanowires by templating against the step edges present on a highly oriented pyrolytic graphite (figure 2) [11, 12]. The noble metal nanowires are found to preferentially nucleate and grow along the step edges present on a graphite surface into a two-dimension parallel array that can be transferred onto the surface of a cyanoacrylate film supported on a glass slide.
Figure 2. Three phases of nanowires electrodeposition at step edges [10]. 1. Metal nuclei forms along step edges. 2. Nucleation ceases; hemispherical nuclei grows to coalescence with nearest neighbours forming a rough or beaded nanowires. 3. Beaded nanowires grow.

The advantage of this technique is that it is applicable to the mass production of high quality metallic nanostructures and applications requiring large areas without breaking vacuum. One drawback of this technique is that the nanowires cannot be peeled off from the substrate to make freestanding form.

Electron Beam Lithography (EBL) process in figure 3 allows one to deposit metal nanowires of any shape, size, and orientation in any arrangement patterns on the flat substrate as described by Schider et al. [13]. In this process, a master image (resist) is produced onto the thin layer of metals, and it is used in transferring a pattern from a mask to surface of the silicon wafer. Finally, the resist is removed by etching in liquid or gaseous form.

Figure 3. Schematic of main steps of electron beam lithography process.
EBL shows certain benefits over conventional photolithography techniques. It is capable of very high resolution, almost to the atomic level. Typically, EBL has a three orders of magnitude better resolution, although this is limited by the forward scattering of electrons in the resist layer, and back scattering from the underlying substrate. It is a flexible technique that can function with a wide variety of materials and an almost infinite number of patterns. On the other hand, EBL has certain drawbacks. It is slow in operation, being one or more orders of magnitude slower than optical lithography. In addition, it is expensive and complicated, with EBL systems costing many millions of dollars to purchase and require frequent servicing to maintain performance.

Channel in porous membranes provides another class of template for using in the synthesis of nanostructures (figure 4). The nanopores in the template are formed by anodizing aluminum films in an acidic electrolyte. Individual nanopore in the alumina is ordered into close-packed honeycomb structure. The separation between two adjacent pores and the diameter of each pore can be controlled by changing the anodizing conditions. Using this membrane template, nanowires of various types of metals and semiconductors can be fabricated. These nanostructures can be deposited into the pores to form continuous nanowires with large aspect ratio (length-to-diameter ratio) by either electrochemical deposition or other methods such as chemical vapour deposition. When freely standing nanowires are desired, one has to remove the template hosts after forming the nanowires in the templates. This task is accomplished by dissolving away the template materials in suitable solvent. Sandrock et al. have exploited this membrane-based template to grow gold nanowires with a well-defined dimension [14].

![Figure 4. Schematic drawing of an anodic porous alumina template used to form the nanowires by filling the pores with the desired materials.](image)

One advantage of this technique is the possibility of fabricating multilayered structures within nanowires. By varying cathodic potentials in the electrolyte, layers of different compositions can be controllably deposited. This method provides a low-cost approach to prepare multilayered 1-D nanostructures. One disadvantage of this approach for large-scale applications is that anodic porous alumina is a brittle ceramic film grown on a soft aluminum metal substrate. Great care needs to be exercised in the preparation of the aluminum substrate and in the manipulation of the anodic film to
produce pure defect-free porous alumina films that are required to achieve uniform filling of the pores with the nanowires.

Mechanical methods can fabricate the arrays of the atomic-scale metal wires supported on solid substrates by mechanically separating two electrodes in contact. During the separation process, a metal neck is formed between the electrodes due to strong metallic cohesive energy in which is stretched into an atomically thin wire before breaking. One such method is based on a scanning tunnelling microscopy (STM) in which the STM tip is driven into the substrates and the conductance is recorded while the tip is gradually pulled out of the contact with the substrates.

Kawai’s Group has employed Au (111), Au (455) and Au (788) crystals as substrates for the growth of the periodic arrays of manganese nanostructures [15]. The gold substrates are chemically etched and mechanically polished to obtain good metal surfaces. Once introducing into an ultrahigh vacuum chamber, the samples are prepared by the certain cycles of sputtering and annealing processes. After cooling the samples to room temperature, manganese is dosed with an electron beam evaporator. A typical deposition rate was about 0.05 milliliters per minute. The coverage of 1 millilitre is defined as one surface layer of manganese crystal.

The advantage of this technique is that one can fabricate a single or an array of stable nanowires. The method can be automated such that a nanowire with a preset quantized conductance can be produced at will. The nanowires supported on a solid substrate can be removed from the fabrication set-up and used as a stand-alone device or for further investigation using various experimental probes. However, the use of STM in the set-up makes it difficult for mass production. The lifetime of the nanowire is typically less than a few seconds because the gap between the STM tip and the metal surface drifts due to acoustic noise, thermal expansion and mechanical vibrations, which is also undesirable for practical applications.

3. Applications

The nanostructures have received steadily growing interests as a result of their peculiar and fascinating properties, as well as applications superior to their bulk counterparts [16]. The ability to generate such nanostructures is essential to modern science and technology when making new types of nanostructures, or downsizing the existing microstructures into 1 - 100 nanometres regimes. The most success example is provided by microelectronics, where “smaller” has meant greater performance ever since the invention of integrated circuits: more components per chip, lower cost, faster operation, and less power consumption [17]. Miniaturization represents the trend in a range of other technologies. In information storage, for instance, there are many efforts to develop magnetic and optical storage components with critical dimensions as small as tens of nanometres [18]. It is also clear that a new phenomenon is associated with nanometre-sized structures, with the well-established examples including size-dependent excitation of the quantum dot structures [19], and quantization of conductance in the metal contacts [20]. In addition, quantum confinement of electrons by the potential wells of nanoscale structures may provide one of the most powerful means to manipulate the optical, electrical, magnetic, and thermoelectric properties of a solid-state functional material.

So far, nanostructured surfaces such as nanowires, nanorods, and nanotubes become the focus of intensive research owing to their fabrication of nanodevices [21]. These nanostructures provide a good system to investigate the dependence of electrical and thermal transport or mechanical properties on the size reduction. In addition, they are expected to play an important key in the interconnection applications and the functional units in fabrication of electronic and optoelectronic devices.

Although nanostructures can now be produced using a number of advanced nanolithography techniques [22, 23], such as electron-beam, these methods are still not conveniently available to practical routes, and it is also challenging to fabricate nanowires with the widths of a few nanometre. Exploration and development of new techniques for fabrication of large quantities of nanostructures from a diversified range of materials, rapidly, and at reasonably low costs, are desirable. Many deposition techniques described herein are not intended to replace the existing methods, but rather to
provide a simple alternative for generating nanostructures with a well-controlled dimension, and to help the study of their optical properties.

4. Conclusions
Recent advances in nanofabrication techniques have made it possible to produce well-defined nanostructures and each method has its specific merits and inevitable weakness. For instance, some researchers devote the most attention to the method of generating nanostructures based on anisotropic growth [24] directed or confined by the templates. The template-directed methods provide a good control over the uniformity and dimension in which the nominal thicknesses of the nanowires are measured with the sensor plane of the thickness monitor perpendicular to the metal beam direction. However, removal of the template through a post-synthesis process may cause damage to the final nanostructures’ product. Most nanostructures produced using this method is polycrystalline in structure and they may limit their uses in device fabrication and fundamental studies. Therefore, judging against these aspects, some methods described here still need to be improved before it finds widespread use in commercial applications.

5. References
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