



Surface pinning of catalyst nanoparticles for enhanced size and position control of 1D nanostructures growth

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ABSTRACT

Catalyst nanoparticles are required in most established synthetic routes for the growth of carbon nanotubes (CNTs) and semiconductor nanowires (NWs). A simple and widespread method to coat a substrate with metal nanoparticles is based on the dewetting of a thin metal film, often induced by a process of thermal annealing, and resulting in the formation of fine droplets. However, the control of the sole thermodynamic parameters affecting the dewetting results in a rather broad size distribution and random positioning of the catalyst. Efforts aiming at a better control of size and position of the catalytic seeds by top-down and bottom-up patterning techniques are well documented. However, patterning the catalyst may be a useless process step if, once approaching the temperatures at which the growth of nanowires and CNTs is catalyzed, nanoparticles become mobile on the substrates, displacing from their position and altering the initial size distribution due to coalescence. Moving from this observation, we propose a simple and general method to prevent the diffusion of the catalyst during annealing steps or the initial stage of the synthesis of NWs and CNTs. Its principle consists of confining the catalyst nanoparticles on top of vertical columnar structures. This can be achieved by etching the substrate all around the nanoparticles by dry anisotropic etching using the nanoparticles themselves as etch masks. Nanoparticles thus sitting on top of nanopillars result effectively confined, even at temperature at which they are found highly mobile on flat substrates of the same material, due to surface tension effects. Experimentally, we demonstrate this principle with iron nanodots obtained on silicon by lift-off starting from a P(MMA-*b*-S) diblock-copolymer template. The iron nanodots isolated on top of columnar nanostructures, were found to be stable at 600 °C, temperature suitable for the growth of CNTs.

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1. Introduction

Ordered and vertically aligned CNTs and nanowires of semiconducting alloys (of the IV, III–V and II–VI groups) are candidate building blocks in many applications as field emitters in displays [1], light emitting diodes in lighting systems [2], highly sensitive detectors in biosensors [3], carrier channels in vertical transistors [4,5] and cantilevers in nanoelectromechanical systems [6]. In most cases, the growth of such 1D structures is catalyzed by metal nanoparticles. Commonly, the formation of catalytic seeds on the growth substrates is obtained by evaporating a thin metal film on a surface; up to a certain film thickness and opportune conditions, metal nanodroplets can be obtained. By treating the substrates with a thermal annealing in vacuum or controlled atmosphere, it is possible to modify the size and the distribution of the nanoparticles [7–9]. It is evident that for many potential applications the control on the size and position of the 1D

nanostructures grown from the catalysts would be highly desirable: size changes produce changes in the desirable physical and chemical properties, possibly leading to device failure: the control on the size, shape and arrangement on the substrate of the metal clusters becomes fundamental.

In principle top-down fabrication methods, such as UV, e-beam, nanoimprint and soft lithography [10], or by bottom-up “templating” techniques, such as self-organization of diblock-copolymer or porous anodic alumina [11–14] are presently available. However, also in the case of accurately pre-patterned catalyst seeds the control on their geometrical parameters may be lost once the substrate approaches the temperatures suitable for the synthesis of NWs or CNTs, due to diffusion and coalescence. We observed this phenomenon in particular during the preparation of the iron nanoparticles on silicon as catalysts for the growth of CNTs. There, the local hexagonal order and the narrow size distribution of iron nanoparticles on flat silicon inherited via a metal lift-off from P(MMA-*b*-S) diblock-copolymer templates (Fig. 1) was lost in annealing steps at temperature above 600 °C. We present here a simple and general method that allows circumventing such a problem. In principle,

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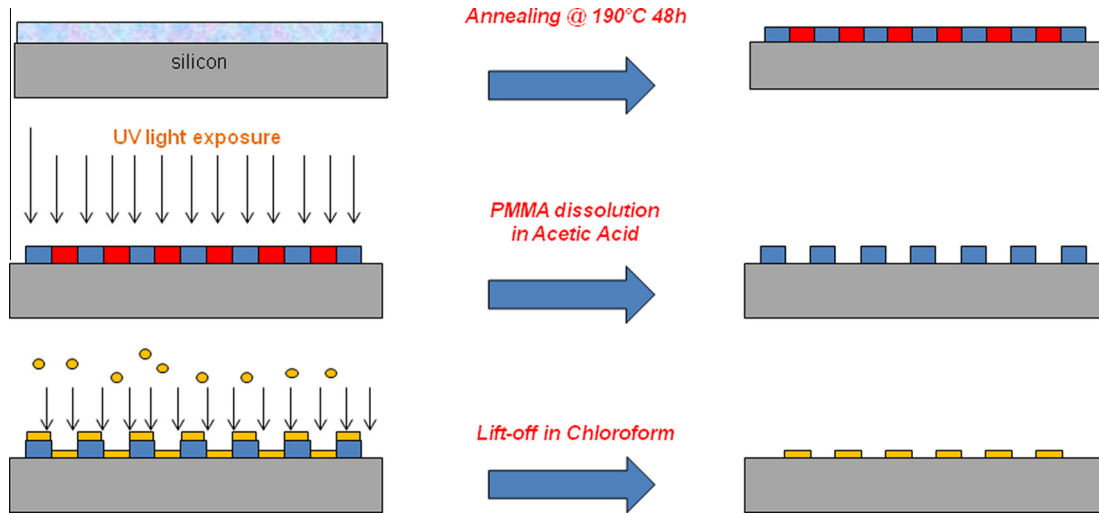


Fig. 1. Fabrication scheme of the patterning process of Fe nanodots arrays by diblock-copolymer lithography and lift-off.

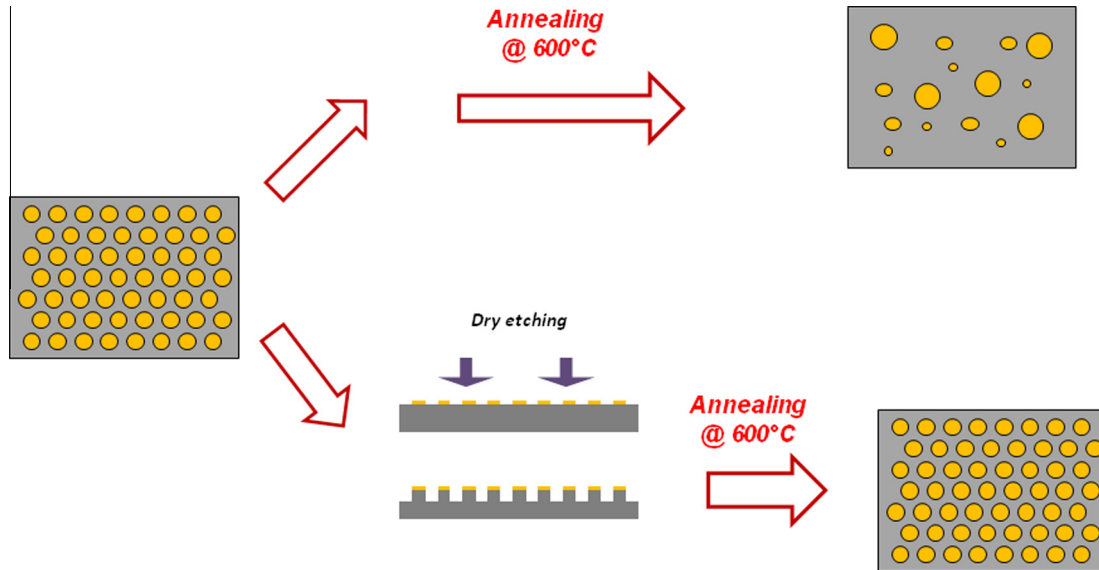


Fig. 2. Schematic representation of the effect of thermal annealing (600 °C, 5 min) on Fe nanodots arrays on flat surface (up) and if capped on Si nanopillars (down) fabricated by anisotropic dry etching process.

catalyst seeds can be effectively confined in areas delimited by sharp steps in the substrate, as an effect of surface tension. In particular, metal nanodots can be effectively confined on top of vertical columnar structures. In practice, catalyst nanodots pre-patterned on a flat surface becomes the capping of nanopillars after a dry etching step in which the metal seeds themselves act as a mask (Fig. 2). Owing to surface tension effects, nanoparticles remain effectively confined on the top of nanopillars, even at temperature at which they are mobile on flat substrates of the same material.

2. Experimental method

We demonstrate the process for the inhibition of catalyst nanoparticles diffusion in the case of iron on silicon. The patterning of the catalyst was obtained by lift-off of iron in a P(MMA-b-S) diblock copolymer template.

We choose block copolymer lithography since this represents a convenient strategy to pattern large areas with structures of size in

the 10–50 nm range [15]. These dimensions are compatible with the dimension of the catalyst nanoparticles generally employed in the growth of CNTs and nanowires. Locally ordered hexagonal packed cylindrical PMMA domains of 20 nm diameter and 40 nm center-to-center spacing surrounded by PS were obtained following well established protocols [16].

Shortly, a silicon substrate was cleaned in “Piranha” solution ($\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ 3:7, 90 °C), rinsed in deionised water and dried, and transferred into a nitrogen filled glove box. The substrate was subsequently surface functionalized in a 1 mM solution of 3-(methoxyphenyl) propyltrichlorosilane (MPTS) for 2 days, in order to control the interfacial energy between the silicon substrate and the diblock copolymer film (~30 nm) which was spin-coated from a solution of PS-b-PMMA (PS MW 96.5 k, PMMA MW 37.5 k, MW/MN 1.14) 1% w in toluene. After thermal annealing (at 190 °C in low vacuum for 3 days), the segregated PMMA in the self assembled cylindrical nanodomains was degraded by exposure to 2.1 J/cm² UV light with main peak at 254 nm wavelength and dissolved in glacial Acetic acid, resulting in a thin PS film with holes (fig. 3).

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