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Ordered silicon nanowire arrays prepared by an improved nanospheres self-assembly in combination with Ag-assisted wet chemical etching

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Abstract

An improved Langmuir–Blodgett self-assembly process combined with Ag-assisted wet chemical etching for the preparation of ordered silicon nanowire arrays is presented in this paper. The new process is independent of the surface conditions (hydrophilic or hydrophobic) of the substrate, allowing for depositing a monolayer of closely packed polystyrene nanospheres onto any flat surface. A full control of the morphology of the silicon nanowire is achieved. Furthermore, it is observed that the formation of porous-Si at the tips of the nanowires is closely related to the release of Ag nanoparticles from the Ag mask during the etching, which subsequently redeposit on the surface initially free of Ag, and these Ag nanoparticles catalyze the etching of the tips and lead to the porous-Si formation. This finding will help to improve the resulting nano- and microstructures to get them free of pores, and renders it a promising technology for low-cost high throughput fabrication of specific optical devices, photonic crystals, sensors, MEMS, and NEMS by substituting the costly BOSCH process. It is shown that ordered nanowire arrays free of porous structures can be produced if all sources of Ag nanoparticles are excluded, and structures with aspect ratio more than 100 can be produced.

Keywords: Ordered silicon nanowire array; Langmui–Blodgett; Porous silicon; Nanosphere lithography; Ag-assisted wet chemical etching

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1. Introduction

Silicon nanowire arrays attracted considerable attention during the last years because of their superior electrical [1–3] and optical properties [4] compared to bulk silicon. Ordered SiNWs with specific morphologies (regarding diameter, spacing, density, and length of the nanowires) are highly desired and have a wide range of applications in optics [5] as special grating or photonic crystals [6,7], as anti-reflection layer in photovoltaics [8], for sensors and detectors [9,10], to micro-electro-mechanical systems (MEMS) or nano-electro-mechanical systems (NEMS) [11,12].

However, the fabrication of such highly ordered SiNW arrays is very challenging and usually done by costly electron beam lithography [13] and deep reactive ion etching (also known as BOSCH process or its variants) in a vacuum chamber [14]. The vacuum-based process significantly limits the throughput, and hinders

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the application for a mass production. Alternatively, nanosphere (NS) lithography has been used to fabricate ordered arrays. In this case the length of the SiNWs is limited by the resist covering the area which is supposed not to be etched.

Recently, low-cost NS lithography in combination with a metal-assisted wet chemical etching process was developed and its superior ability in producing high aspect ratio (AR) ordered SiNW array was shown [15–17]. Metal-assisted wet chemical etching presents a non-vacuum, high throughput, low-cost route for the preparation of SiNWs, in which noble metal nanoparticles such as Ag, Au and Pt are used as catalyst [18] to accelerate a local etching of silicon wafers. In this process the noble-metal free area remains practically unetched, leaving behind a densely packed array of SiNWs. Ag-assisted wet chemical etching has been mostly used due to its easy handling. It shows the unique ability to produce high AR channels as narrow as tens of nm [19]. Such structures are highly desired for many devices such as capacitors, where no other technologies can compete with it at present. This technology allows transferring any pattern, predefined by a Ag mask, into a high AR structure. This method was soon adopted in the micro- and nano- fabrication of high AR micro- and nanostructures for MEMS applications [12], as it is a promising candidate for low-cost non-vacuum mass production of micro- and nanostructures interested in the above listed fields.

However, there are still great issues regarding this novel technology, preventing it from real-world large-scale applications. First of all, the routine Langmuir–Blodgett (LB) process for preparing the NSs monolayer requires the sample surface to be hydrophilic, so that the NS monolayer can be attached onto it by pulling the sample out of the water. Thus, this approach does not work on hydrophobic surfaces, which could be an issue in specific cases such as on a silicon surface free of native oxide (hydrophobic) [15–17]. Moreover, the reproducibility of the Ag-assisted wet chemical etching is poor due to the formation of porous structures [12,15], in which the areas initially free of Ag often gets porous [15–17], which prevents the application of this technology in the MEMS and NEMS fabrication. The same applies in case of optical components such as gratings, photonic crystals and functional electronic devices, where the porous structure destroys the periodic assembly and increases the surface recombination. Up to now, the formation of porous structures is not well understood, and no direct evidence is given in the references.

In this work, we have solved the aforementioned problems by an improved LB process in combination with a low-cost Ag-assisted wet chemical etching for the fabrication of ordered SiNW arrays. The new process is independent of the surface conditions (hydrophilic or hydrophobic) of the substrate, and hence allows fabricating a closely packed hexagonally ordered monolayer of polystyrene NSs on any flat surface. Central issues regarding the mask preparation are addressed. Furthermore, we have observed that the release of Ag nanoparticles from the mask and their subsequent accumulation on the area initially not covered by Ag is the main reason for the formation of the porous silicon structures.

2. Experimental

Silicon (100) wafers with doping levels of $\sim 3 \times 10^{15}\,\mathrm{cm}^{-3}$ in size of $2.5 \times 2.5\,\mathrm{cm}^2$ were used. The wafers were cleaned by a sequence of baths in acetone/isopropanol/diluted HF (2%) and subsequently rinsed in deionized water, followed with a Piranha treatment (H_2SO_4 (98%):H_2O_2 (30%) solution = 1:1) at 80 °C to remove any remaining contamination on the surface. Mono-dispersed polystyrene NSs purchased from Microparticles GmbH Berlin with nominal diameters of 608, 1030, and 2390 nm suspended in water were used, and the polystyrene NSs have a weight ratio of 10% in the suspensions. From this set of experiments, the results based on the 608 nm NSs will be mainly presented. In detail, to 100 μl of the NS suspensions, 100 μl ethanol and 5 ml hexylamine (5%) were added and sonicated for 30 min. The amphiphilic hexylamine serves as an intermediate to functionalize the NSs [20], so that the self-assembly to prepare the monolayer of the NSs can take place on the water surface. The samples were placed on a stage immersed in deionized water as shown in Fig. 1a. For comparison, the routine LB process by pulling the sample out of the solution is sketched in Fig. 1b. Guard rings with a diameter of 4.5 cm floating on the water surface can be used to constrain the NS film and can be shifted to adjust the position above the silicon wafers. Drops of the NS suspension were carefully added on the water surface inside the guard ring by a syringe. The spread of the NSs on the water surface can be observed by bare eyes, and the NSs forms subsequently a loose monolayer at the interior edge of the guard ring which can be visualized by the light interference on the ordered NSs. A distance between the syringe and the existing monolayer should be guaranteed to avoid a pile-up (or multilayer formation) of the NSs, and this can be controlled visually by slowly adding the suspension. To obtain a closely packed monolayer of NSs on the water surface, several drops of anionic surfactant,