



Electrostatic interaction induced nucleation and growth of self-assembled nanostructures

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Received 10 July 2014; received in revised form 23 August 2014; accepted 31 August 2014

Available online 8 September 2014

Abstract

We performed in-situ growth of self-assembled nanostructures (SANs) by a wet chemical technique, and demonstrated that electrostatic interactions could be exploited for the initiation of nucleation and growth of SANs at a solid–liquid interface. The formation of SANs of cobalt compound on a Si substrate together with their morphology and structure were investigated. The creation of nucleation sites was attributed to electrostatic adsorption, and in principle a specific adsorption approach could also be invoked for the preparation of SANs. It was found that the SANs of different sizes and shapes could be obtained by varying the concentration of cobalt solution and reducing agent.

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Keywords: Self-assembled nanostructures; Electrostatic interaction; Cobalt; Adsorption

1. Introduction

Self-assembled nanostructures (SANs) are important for fundamental investigations as well as for applications including light emitting devices, plasmonics, and photonics [1–3]. The study on self-assembled growth techniques on suitable platforms is therefore vital for exploiting the potential of nanostructures. Traditionally, SAN growth has been achieved through vapor phase or molecular beam epitaxy techniques by depositing a desired material on a substrate having a definite crystallographic relationship [1] or by metal-assisted deposition [4]. Nanostructures with various morphologies and dimensions are easily synthesized by wet chemical routes in which self-assembly is attained by functionalizing surfaces with charged molecules such as DNA [5], proteins [6,7], polymers or long chain hydrocarbons [8] followed by coating using different methods [5–8]. Although SANs may be prepared by a template-assisted sol–gel technique, the in-situ growth of SANs by wet chemical routes still remains a great challenge [9].

The study of epitaxial single crystal thin films and nanostructures on lattice-matched substrates by wet chemical growth has been going on for nearly two decades. Most often the studies on the structural properties of such films/nanostructures were based primarily on structural compatibility with the substrate and supersaturation conditions [10,11]. However, the influence of interactions between the growth species and the substrate on nucleation has been invoked only occasionally and tentatively [11]. Recently, it was proposed that by employing charged impurities the aspect ratio of nanostructures could be manipulated by selective electrostatic control of growth faces [12]. The role of electrostatic interaction has been exploited for the fabrication of hybrid polyelectrolyte films [13]. The significance of such charge-mediated interaction for the adhesion of mussel protein has recently been reported [14]. These studies, therefore, suggested that the Coulombic interaction between ionic complexes and a given surface (substrate) could significantly affect nucleation sites.

The study of adsorption processes and mechanisms is an important area of science and technology since the phenomena play vital role in understanding the corrosion processes and preparation of materials for coating, purification of the ambient atmosphere, liquid effluents and synthesis of supported

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catalysts [15]. The studies on the adsorption of ionic complexes have demonstrated that the process was strongly influenced by the electrostatic interaction between the adsorbent and adsorbate, among many other factors [16]. This fact has been exploited to choose adsorbents having a proper isoelectric point, and to control the pH of the ionic solution to maximize the adsorption [16,17]. Though the adsorption capability of an adsorbent varies with surface area, the surface potential and ionic adsorption preferences display similar trends [18]. The complexes adsorbed on a substrate can act as nucleation sites if a reaction is initiated. It is therefore envisaged that SANs can be prepared by taking advantage of such interactions, i.e., by letting a desired solute be adsorbed onto a suitable substrate induced by electrostatic interaction and subsequently performing suitable growth as required. Under such conditions, heterogeneous nucleation is expected to be initiated at the adsorbed ionic complex at the liquid–solid interface along with homogeneous nucleation in the bulk solution.

In this study, cobalt (Co(II)) adsorption on Si substrate was examined because this system is of interest to researchers in the fields of catalyst preparation and those focused on modeling the adsorption and desorption of transition-metal ions in etching. Co(II) is a useful probe ion for determining the types of adsorption sites on Si surfaces because it can be easily distinguished in the substrate. In addition, compared to other first-row transition metals, Co is easy to maintain in a single oxidation state (Co(II)). Furthermore, Co(II) complexes adsorbed on single crystal supports have been reported to display behavior similar to micro porous particles [17,18]. The dominant cobalt species considered to be non-specifically adsorbed on oxide supports is $\text{Co}(\text{H}_2\text{O})_6^{2+}$ [17–19].

The aim of this work is to examine the growth of SANs of a cobalt compound in aqueous solution using a wet chemical process. The growth of SANs of cobalt ion adsorbed on a single crystal Si substrate, along with their morphologies and structure, are discussed in detail here. The nucleation and subsequent growth were carried out by the well-established reduction approach. The sizes of the nanostructures depended upon the ratio (R) of reducing agent concentration (aqueous sodium borohydride, NaBH_4) to the initial Co ion concentration, and this finding was strongly supported by atomic force microscopy (AFM) analysis. The ability to grow such size-controlled nanostructures is an attractive feature of self-assembly. Therefore, we believe that this work could be further extended to other transition metals.

2. Experimental method

Single crystal p-Si (100) was used as the substrate for growth of the SANs. All substrates were cut to approximately $1 \times 1 \text{ cm}^2$ and cleaned sequentially in acetone, ethanol and deionized water under ultrasonic agitation for 30 min and dried with nitrogen gas. Doubly ionized water was used for preparation of precursors. Fig. 1 depicts schematics of the adsorption and growth technique for the self-assembled nanostructures. In a typical experiment, 200 mL of aqueous cobalt nitrate ($\text{CoNO}_3 \cdot 6\text{H}_2\text{O}$) solution of appropriate concentration was added to a

500 mL beaker. The cleaned Si substrate was placed into the cobalt solution so that the polished surface faced downward by fixing it to the insert of a Teflon stand. The Si substrate was left inside the solution (contacted) for 2 h with mild stirring to ensure uniformity of the solution. Afterwards, a calculated amount (volume) of freshly prepared aqueous sodium borohydride (NaBH_4) solution (conc. 0.10 M) was added under rapid stirring. Subsequently, the Si substrate was removed from the solution and then blown dry with nitrogen for further analysis. All of the experimental steps were performed under ambient temperature and pressure.

After growth, the samples were analyzed by X-ray photoelectron spectroscopy (XPS) using a monochromatic Al $K\alpha$ (1486.6 eV) line, AFM in tapping mode and transmission electron microscopy (TEM). For TEM analysis, the samples were collected from the solution after 5 min of reaction and directly dropped onto a carbon-coated TEM grid. The TEM samples were prepared by ion milling for cross-section analysis of the nanostructures. This combination of techniques

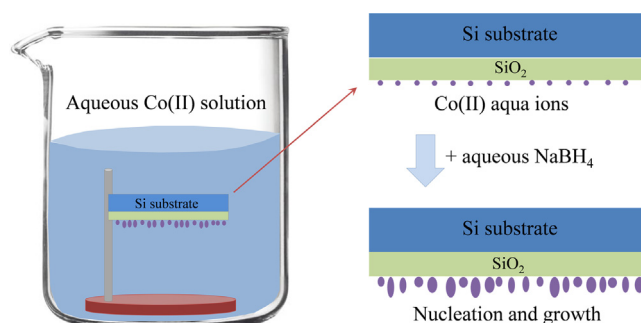


Fig. 1. Schematic diagram of the adsorption and growth technique for self-assembled nanostructures.

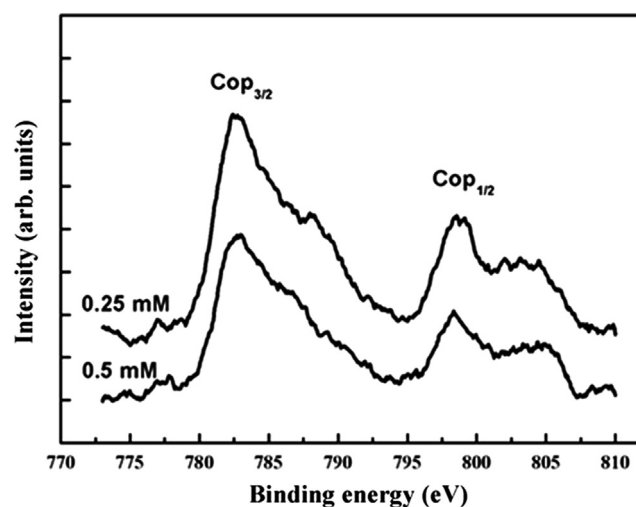


Fig. 2. XPS spectra of Co(II) aqua complexes adsorbed on the p-Si(100) substrate. Adsorption was performed by placing the Si substrate in an aqueous cobalt nitrate solution for 2 hours followed by drying under ambient conditions. The binding energy of 782.5 eV is attributed to $\text{Co}_{2p_{3/2}}$ core electrons and indicates the adsorption of Co(II) hydroxyl complexes from the aqueous solution. Concentrations of solution used for adsorption were (a) 0.5 mM and (b) 0.25 mM.

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