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Zinc oxide Chemical Bath Deposition on Functionalized organic thin films: Formation of nanorods, nanorockets and nanoflowers

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ABSTRACT

Controlling the morphology of nanostructured materials is critical for their use in technological applications including in sensing, electronics and energy harvesting. In this paper we investigate the reaction pathways involved and their dependence on reactant concentrations in the formation of ZnO nanomaterials on –COOH terminated self-assembled monolayers using a simple chemical bath deposition process which employs zinc acetate, which acts as the Zn source, and ethylenediamine, which acts as both the O source and a complexing agent for Zn^{2+}. At a deposition temperature of 318 K (45 °C) our data shows that the concentration of Zn^{2+} as well as the deposition bath pH, which is controlled by the ethylenediamine concentration, is critical in determining the ZnO morphology. Above 0.01 M zinc acetate at low bath pH (~7.7–8.5), nanorods and nanorockets are observed to form. The nanorods exhibit a clear interface in the middle indicating that they are composed of two crystals. At lower zinc acetate concentrations over a wide pH range (~8.0–10.5) nanoflowers form. The nanorockets and nanoflowers grow via a modified La Mer mechanism in which there are multiple nucleation and crystallization steps. The initial nuclei are spherulites (nanoflowers) or nanocrystallites (nanorockets). Since the reagent concentrations limit the reaction, for these initial precursor crystallites to increase in size, it is required dissolution and re-precipitation must occur. Thus at later times nanorockets or nanoflowers develop.

1. Introduction

Nanostructured films exhibit a wide range of novel electrical, chemical, optical and mechanical properties which result from surface and quantum confinement effects [1–3]. Such films have potential applications in areas including sensing [1,3–5], energy conversion [6,7] and electronics [1,5]. Gas phase reactions are often employed to prepare nanostructured films [1,2,5]. However, these methods are expensive and incompatible with some substrates because they require high temperatures (> 773 K) and are performed in vacuo. An attractive alternative approach is to employ aqueous deposition methods, such as chemical bath deposition (CBD). These techniques generally be performed at low temperatures (≤ 323 K) and do not require the use of expensive vacuum equipment [8,9].

To date most solution-based synthesis methods have produced films of nanorods, nanotubes or nanoflowers with or without the use of organic modifiers [3,4,10–12]. However, the pathways for transformation and formation of these nanomaterial morphologies are often poorly understood. Zinc oxide, which is an important II-VI semiconductor, has been synthesized from aqueous solutions with morphologies including hexagonal rods [12–15], star-like crystals [9,15,16], nanoflowers [10,17,18], nanoplates [9,14,17], ellipsoids [18], nanoneedles [15,16] nanotubes [3] and even smooth films [10]. Further it is well known that the chemical, optical and electrical properties of ZnO are critically dependent upon the film surface area and microstructure [1,6,19–21]. It is therefore crucial to have precise control over these variables in designing ZnO-based systems for practical applications. In general the growth kinetics of ZnO nanostructured films are described using growth-dissolution-recrystallization. However, the analysis is complicated by the use of different complexing agents [15,22], organic additives [12] and experimental conditions such as deposition temperature [15,16] and the application of ultrasound [10].

In this paper we systematically investigate how the morphologies of ZnO crystallites vary with reactant concentrations in a simple CBD process using zinc acetate and ethylenediamine on –COOH terminated self-assembled monolayers (SAMs) at a deposition temperature of 318 K. In CBD a controlled ion-exchange precipitation reaction is used to deposit a thin film [8]. The reaction rate is generally controlled by the concentration of the "free" metal ion, which here is Zn^{2+}. In this deposition, ethylenediamine (en) has two roles. First, ethylenediamine hydrolysis leads to an increase of pH and thus OH^- concentration. This leads to a critical concentration of OH^- ions and precipitation of ZnO. In the plating solution:

$$NH_2(CH_2)_2NH_2 + 2H_2O \leftrightharpoons \left[NH_3(CH_2)_2NH_3\right]^{2+} + 2OH^-$$

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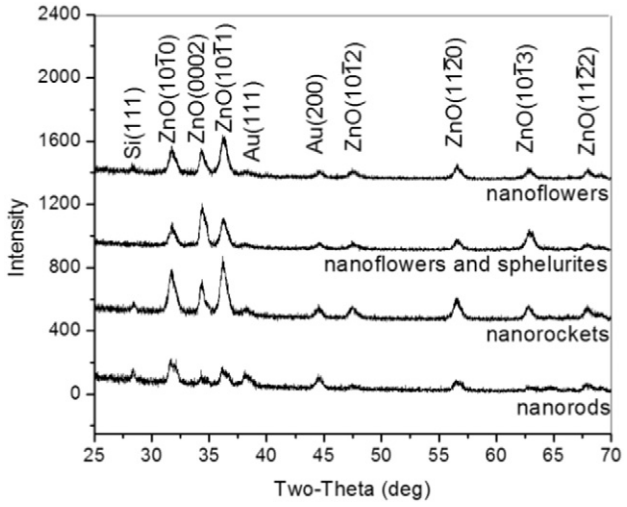

Fig. 1. XRD pattern of ZnO crystallites deposited on –COOH terminated SAM surface. Reaction conditions: deposition time 1 h, deposition bath temperature 318 K.

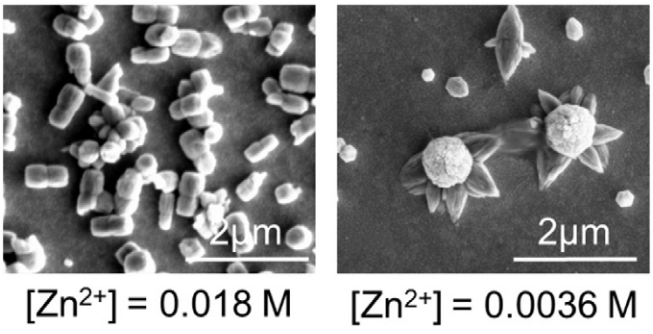

Fig. 2. SEM images after ZnO chemical bath deposition for 1 h on –COOH terminated SAMs at 318 K and [en]:[Zn^{2+}] = 1.25. The concentration of Zn^{2+} is varied from 0.018 M to 0.0036 M.

The ethylenediamine also acts as a complexing agent for Zn^{2+} ions. Under our reaction conditions, previous studies indicate that dominant species present in the solution are $Zn(en)_x^{2+}$ (x = 1–3) [23]. Once the solubility product (K_{sp}) of $Zn(OH)_2$ is exceeded a precipitation and dehydration reaction occurs and ZnO is deposited. For –COOH terminated SAMs, the CBD reaction proceeds via a mixed ion-by-ion deposition and cluster-by-cluster growth [10]. The deposition is strongly temperature dependent; at 318 K deposition is observed but at room temperature there is no ZnO [10]. The ion-by-ion deposition leads to an underlayer of uniform nanocrystals strongly which strongly adhere to the substrate. In contrast, there are larger ZnO nanocrystals which are deposited by cluster-by-cluster deposition. These larger crystals exhibit many different morphologies and do not strongly adhere to the substrate. Although the ZnO CBD process appears to be simple, we observe that the nanocrystals formed by cluster-by-cluster deposition follow a complicated reaction pathway. At low Zn^{2+} and OH^- concentrations nanorods form. These nanorods grow slowly suggesting that there is a low supersaturation concentration close to the surface [15]. At higher reagent concentrations, ZnO deposition occurs via multiple nucleation and growth steps. In this regime more complex ZnO nanocrystals, nanoflowers and nanorockets, are observed.

2. Experimental

2.1. Materials

Zinc acetate dihydrate (≥98.0%), mercaptohexadecanoic acid (99%) and ethylenediamine (≥99.5%) were acquired from Sigma Aldrich (St. Louis, MO). Gold and chromium were purchased from Alfa Aesar Inc. (Ward Hill, MA) and were of 99.995% purity. All reagants were used without further purification. Silicon wafers (<111> orientation) were obtained from Addison Engineering Inc. (San Jose, CA) and prior to use etched using piranha etch (H_2SO_4:H_2O_2 = 3:1).

2.2. Self-Assembled Monolayer preparation

The –COOH terminated SAMs were prepared and characterized using to previously published procedures [24–26]. In brief, a Cr adhesion layer (~ 50 Å) followed by a Au layer (~1000 Å) were sequentially thermally deposited onto freshly etched Si wafers. The prepared Au substrates were immersed into a 1 mM ethanolic solution of the mercaptohexadecanoic acid for 24 h at ambient temperature (294 ± 2 K) to form well-organized –COOH terminated SAMs on Au substrates. For each batch, one sample was taken and characterized using single-wavelength ellipsometry (Gaertner Scientific Corp., Skokie, IL) and time-of-flight secondary ion mass spectrometry (TOF SIMS) to ensure that the SAMs were free of significant chemical contamination.

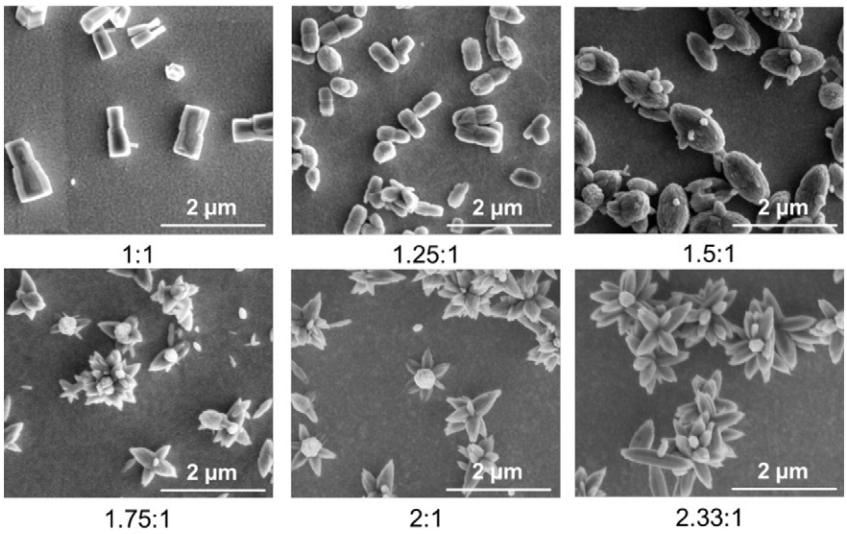

Fig. 3. SEM images after ZnO chemical bath deposition for 1 h on –COOH terminated SAMs at 318 K and [Zn^{2+}] = 0.018 M. The ratio of [en]:[Zn^{2+}] is varied from 1:1 to 2.33:1.