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ZnO Nanostructured Arrays Grown from Aqueous Solutions on Different Substrates

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Abstract—ZnO nanostructures were grown from a solution of zinc nitrate hexahydrate and hexamethylenetetramine onto different substrates that were pretreated with an RF sputter coated ZnO seed layer. The choice of substrate was observed to have a direct effect on the morphology, orientation and surface coverage of the nanostructured arrays. Substrates that were covered in a 1.2 μm sputter coated ZnO seed layer, include; 6H-SiC, LiNbO₃, gold, LiTaO₃, ITO (indium tin oxide) glass and plate glass. The ZnO seed layer facilitates the uniform growth of nanostructured arrays of ZnO, without such a layer nanostructure growth was found to be sporadic and unaligned. Under identical reaction conditions, a range of different ZnO nanostructured arrays were observed.

Keywords-component: ZnO; Nanostructure; Array; Nanorod; Aqueous growth; Synthesis; Metal oxide.

I. INTRODUCTION

Research into zinc oxide nanostructures and nanostructured arrays has emerged as popular research choice due to the myriad of morphological forms and diverse range of applications. Applications, include but not limited to; gas sensor technologies [1], solar cell development [2], photonic devices and coatings [3], nanostructured templates and employed as transparent conducting oxides [4].

The aqueous growth of ZnO nanostructures from the hydrothermal decomposition of an equimolar Zn²⁺/hexamethylenetetramine (HMT) solution provides the means for the controlled growth of nanostructured arrays of ZnO. This method is simple, low cost, environmentally friendly, and can be easily scaled to suit larger substrate sizes.

6H-SiC & LiNbO₃ and quartz substrates were purchased as semiconductor grade polished wafers, Au/LiTaO₃ samples were grown on inter-digitated surface, ITO glass was purchased from Sigma Aldrich (10 Ωcm) & the plate glass utilized was of a similar grade to a microscope slide.

Prior to ZnO nanorod growth, substrates were RF sputter coated with a 1.2 μm ZnO seed layer as seen in Figure 1. Such a seed layer, improves the uniformity and orientation of HMT grown ZnO nanostructured arrays.

Nanostructured arrays of ZnO were grown in a sealed reaction vessel via the hydrothermal decomposition of HMT and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) solutions in a modified process first described by L. Vayssieres [5] where Zn²⁺ ions

originate from (Zn(NO₃)₂·6H₂O) and OH⁻ ions are derived from HMT (C₆H₁₂N₄) as written in the equation (1):

deposition of ZnO occurs according to the following equation:

Figure 1. RF sputtered ZnO seed layers

II. EXPERIMENTAL METHODOLOGY

In this process, cleaned sputtered substrates were placed into a sample holder residing inside a reaction vessel filled with an equimolar solution of a 10 mM HMT/ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Vessels were sealed and placed inside a standard laboratory grade oven for 16 to 18 hrs at 80°C. After which the substrates were extricated and washed with DI water to remove any residual zinc salts and dried in a stream of N_2 .

Figure 2. ZnO nanorod growth on 6H-SiC substrate

Under identical preparation and reaction conditions a range of different nanostructured arrays with different surface coverages and morphologies were observed in Figs. 2-7.

III. RESULTS

ZnO growth on 6H-SiC substrates manifests as clusters of nanorods and dispersed thin sheets of ZnO measuring approx 30 nm. These nanosheets grow from the substrate and fold under their own weight, draping over the nanorods. At 10 kV accelerating voltage during SEM imaging, there is sufficient penetration depth associated with the accelerated electrons to pass through the 30 nm nanosheets, interacting with the underlying nanorods. However, this decelerates the electrons as they pass through the nanosheets, such that the interaction with the underlying nanorods is weaker, thus reducing the number of detected secondary electrons, observed as obfuscated regions. Obfuscated regions are those that appear to be out of focus in Figure 2.

ZnO nanorods grown on LiNbO_3 substrates exhibit uniform growth that occurs at relatively low densities as seen in Figure 3. LiNbO_3 substrate bound nanorods have one of the largest variations in width, measuring between approx 125 nm – 200 nm.

ZnO nanorods grow as perpendicular arrays on all substrates, with the exception of ITO coated glass (as shown in Figure 4) displaying no preferential growth angle. Nanorods grown on ITO glass have widths of approx 120 nm with minimal variation between nanorods. Interestingly ITO coated glass has a comparatively rougher surface than the other substrates. It is hypothesized that this roughness may be a contributing factor in the disordered orientation of the nanorod arrays observed in Figure 4.

Figure 3. ZnO nanorod growth on LiNbO_3 substrate

Figure 4. ZnO nanorod growth on ITO glass substrate

Figure 5. ZnO nanorod growth on glass substrate

ZnO nanorod growth on glass substrates shows superior proximal distribution, with excellent substrate coverage (Figure 5). These nanorods are by far the thinnest, with dimensions of approx 100 nm or less. Nanorod growth on quartz, as seen in Figure 6, was found to have excellent

coverage, but suffered from minor deviations in perpendicular growth.

Figure 6. ZnO nanorods grown on quartz

Figure 7. ZnO nanorods on LiTaO₃ & Gold

ZnO nanorods grown on LiTaO₃ and gold (Figure 7) were measured to have identical densities. Despite the fact that different initial sputtered crystallite densities were recorded, this will be discussed overleaf.

IV. DENSITY APPROXIMATIONS

Density approximations were calculated using the ImageJ software package [6]. SEM images of sputtered substrates and the subsequent nanorod growth were employed for density approximation of the sputtered crystallites and the nanorod array as seen in Table 1. These results show that the majority of the samples show a decreasing number of surface bound structures.

Due to the high density of the sputtered crystallites, manually defining the boundaries (Figure 8b) between adjacent sputtered crystallites minimises artifacts in the image and is necessary to prevent the underestimation that occurs when two adjacent sputtered crystallites are interpreted by the software as one, this “necking” phenomenon greatly underestimates the number of sputtered crystallites. The threshold of the manually defined image was then manipulated, rendering only the outlines of the sputtered crystallites visible as seen in Figure 8c. A similar methodology was employed to analyse

nanostructured arrays. This process is highlighted in Figures 8a, 8b and 8c.

TABLE I. ZnO FILM AND NANOSTRUCTURE ARRAY COMPARISON

Density comparison (μm^2)		
Substrate	Sputtered Film	Nanorod Array
Lithium Niobate (LiNbO ₃)	140	96
Lithium Tantalate (LiTaO ₃)	29	146
Gold (Au)	64	146
Glass (SiO ₂)	*	202
ITO Glass (In ₂ SnO ₅ on SiO ₂)	415	123
Quartz (SiO ₂)	244	188
Silicon Carbide (6H-SiC)	1081	71

Densities approximated from SEM images using ImageJ software
* Sputtered crystallites not observed on glass substrate

Figure 8 a) SEM image of ZnO sputter coated on LiTaO₃ substrate, b) boundaries between adjacent crystalrites are manually defined, c) outline map generated from the threshold manipulated image

V. DISCUSSION

As the concentration of free Zn²⁺ ions diminishes, the growth of the nanorods is quenched as governed by Equation (2). Initially the high concentration of Zn²⁺ ions shifts the equilibrium to the right facilitating the growth of ZnO nanorods, however as the concentration of Zn²⁺ ions falls, the

system approaches equilibrium and growth of the nanorods halts. It has been noted in literatures, that in harsher NaOH growth solutions the thermodynamically unfavourable tip of the rod was rendered into a flat top, effectively signalling the point at which the reaction had successfully reached equilibrium [6]. The ZnO nanorods presented in this paper taper to a fine tip, suggesting that the nanorods have not yet fully matured and could possibly grow longer. Additionally, the growth scheme has been modified by increasing the reaction length, a lower reaction temperature (80°C instead of 90°C), and the suspended nature of substrate which may contribute to the tips observed. As a precaution, all reaction vessels were rinsed with weak nitric acid to remove any precipitates that had accrued between consecutive reactions (visible as a hazy film on the inside of the reaction vessel).

It has been reported in literature for reaction times of less than three hours, in high pH solutions that the type and density of ZnO seed layer has no bearing on the densities of nanorod arrays [4]. Furthermore, it has been postulated that the growth of ZnO nanorods from high pH solutions are a direct extension of crystallites that comprise the seed layer [4]. In this study, a mild pH growth solution and longer growth times were employed to investigate if such a hypothesis would be valid. If such a hypothesis was correct, one would expect to see a similar number of nanorods growing to the initial number of sputtered crystallites seen in Table 1.

Figure 9. Ostwald ripening process (dominant pathways denoted in black)

With the exclusion of Au/LiTaO₃ sample, it has been shown that this hypothesis is not valid. This discrepancy is ascribed to Ostwald ripening effects, defined as “the last stage of a condensation transition from liquid to solid”, where smaller particles (sputtered crystallites) can shrink to their critical nucleus size and rapidly vanish because of the thermodynamic instability of subcritical clusters [7]. Initially, the high concentration of [Zn(OH)₂]⁰ is responsible for the growth of perpendicular ZnO nanorods, however as the reaction approaches equilibrium and the concentration of Zn²⁺ ions drops, smaller and less stable ZnO crystallites are dissolved and their zinc content is utilized to fortify the larger more thermodynamically stable nanorods, pictorially illustrated in Figure 9. The small number of sputtered crystallites (i.e. large crystallite sizes such as the Au/LiTaO₃ sample) results in nanostructured arrays that are comprised of nanorod growth regions which are not indigenous to the underlying crystallites size (i.e. more than one nanorod is

capable of growing from a single large seed crystallite). Interestingly, this appears to be linked with a stabilisation effect that occurs when a substrate is patterned with another material. This is evident in the Au/LiTaO₃ samples, where an interdigitated surface was RF sputter coated with a ZnO seed layer, with different seed layer densities for the different underlying substrates. The resultant nanorod arrays appear to have an identical density, regardless of the underlying material upon which they have grown. This may be due to light etching of the seed layer that may occur, which is tied to the release of free hydroxide ions that takes place during the hydrothermal decomposition of HMT in an aqueous environment as seen in Equation (1). This would effectively increase the concentration of free Zn²⁺ ions as ZnO is etched by the hydroxide, driving the reaction to deposit ZnO as seen in Equation (3). Thus, fortifying the arrays via selective re-deposition as defined using Equation (2).

VI. CONCLUSION

In all observations ZnO nanorods grown from HMT solutions exhibit excellent dimensional control, with minimal variation between nanorods. Coverage across all substrates was excellent on a macro scale, with insignificant morphological or density discrepancy on larger scales. Density appears to be substrate dependant with SiC displaying the lowest density of nanorods, whereas glass substrates were found to have the highest nanorod density of any substrate tested. It has been experimentally demonstrated in this work that there are density differences between sputtered ZnO seed layers. It has been derived, that there is non-linear correlation between the number of sputtered crystallites and the number of nanorods grown. This non-linearity is most likely due to the effects of Ostwald ripening. However, it is clear that the growth of ZnO nanostructured arrays from HMT solutions on RF sputter coated ZnO substrates is a function of sputtered crystallite size, with most arrays obeying a decreasing trend between the number of seeds and the number of nanorods grown.

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