MOCVD Growth of ZnO Nanostrutures Using Au Droplets as Catalysts

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ABSTRACT

ZnO nanostructures were synthesised by Metal Organic Chemical Vapor Deposition growth on Si (100) and c-Al_2O_3 substrates coated with a 5nm thick layer of Au. The Au coated substrates were annealed in air prior to deposition of ZnO so as to promote formation of Au nanodroplets. The development of the nanodroplets was studied as a function of annealing duration and temperature. Under optimised conditions, a relatively homogeneous distribution of regular Au nanodroplets was obtained. Using the Au nanodroplets as a catalyst, MOCVD growth of ZnO nanostructures was studied. Scanning electron microscopy revealed nanostructures with various forms including commonly observed structures such as nanorods, nanoneedles and nanotubes. Some novel nanostructures were also observed, however, which resembled twist pastries and bevelled-multifaceted table legs.

1. INTRODUCTION

ZnO is a remarkable multifunctional material with a distinctive set of properties including a direct bandgap of ~3.37eV, high transparency over the visible spectrum, a very wide range of obtainable conductivities and a remarkably high piezoelectric response. Thus ZnO has many established and emerging applications including varistors, contacts, light emitting diodes [1] and surface acoustic wave devices [2]. Unidimensional ZnO structures, such as nanowires and nanoneedles, also have many potential applications based on this same property set augmented with quantum phenomena of the nanoworld [3].

ZnO nanowires are often synthesised by vapor transport based on a vapor–liquid–solid (VLS) growth mechanism using a metal catalyst such as Au or Cu droplets [4,5,6]. In this case, the metal catalyst can act to both promote alignment of the ZnO nanostructures and to provide a template for their size and distribution [3]. Thus a method for obtention of a regular array of metallic nanodroplets of homogeneous form/size is required. However, recent studies show that well-aligned ZnO nanorods can be grown by Metal Organic Vapor Deposition (MOCVD) without using a metal catalyst [6].

This work reports on preliminary studies into the preparation and use of self-forming Au droplets as catalysts for the MOCVD growth of ZnO nanostructures.

2. EXPERIMENT

5 nm thick Au layers were deposited on 1cm x 1cm Si (100) and c-Al_2O_3 substrates using thermal evaporation. Thermal annealing was employed in order to promote the formation of Au nanodroplets. The anneals were conducted at atmospheric pressure in air using a horizontal tubular furnace. The impact of annealing on the Au layer was studied as a function of annealing time (from 30s to 5 min) and temperature (from 300°C to 800°C).

ZnO was deposited by MOCVD in a water-cooled vertical quartz reactor with an inner diameter of 40mm in the growth zone. Dimethyl zinc triethylamine ($(CH_3)_2Zn\text{-}N(CH_2CH_3)_3$) was used as the Zn source and N_2O gas was used as the as an O source. The carrier gas was N_2 and the flow rate was 500 sccm. The substrate was placed in the middle of the reactor on a graphite susceptor, which was inclined at 45° to the vertical. The susceptor was heated to 800°C during film growth using a radio frequency (rf) spire.

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The sample morphology was studied using a Hitachi S4800 Field Emission-Scanning Electron Microscope (FE-SEM). The local composition was investigated in situ in the SEM using an Energy Dispersive X-ray (EDX) micro fluorescence system. "IMAGE-J" software was used in order to do statistical analysis of the Au droplet distribution [7].

3. RESULTS

3.1 Annealing of the Au-Coating

Figure 1 shows SEM pictures of Au-coated Si (100) as a function of annealing temperature from 300°C to 800°C for an annealing time fixed at 5 minutes.

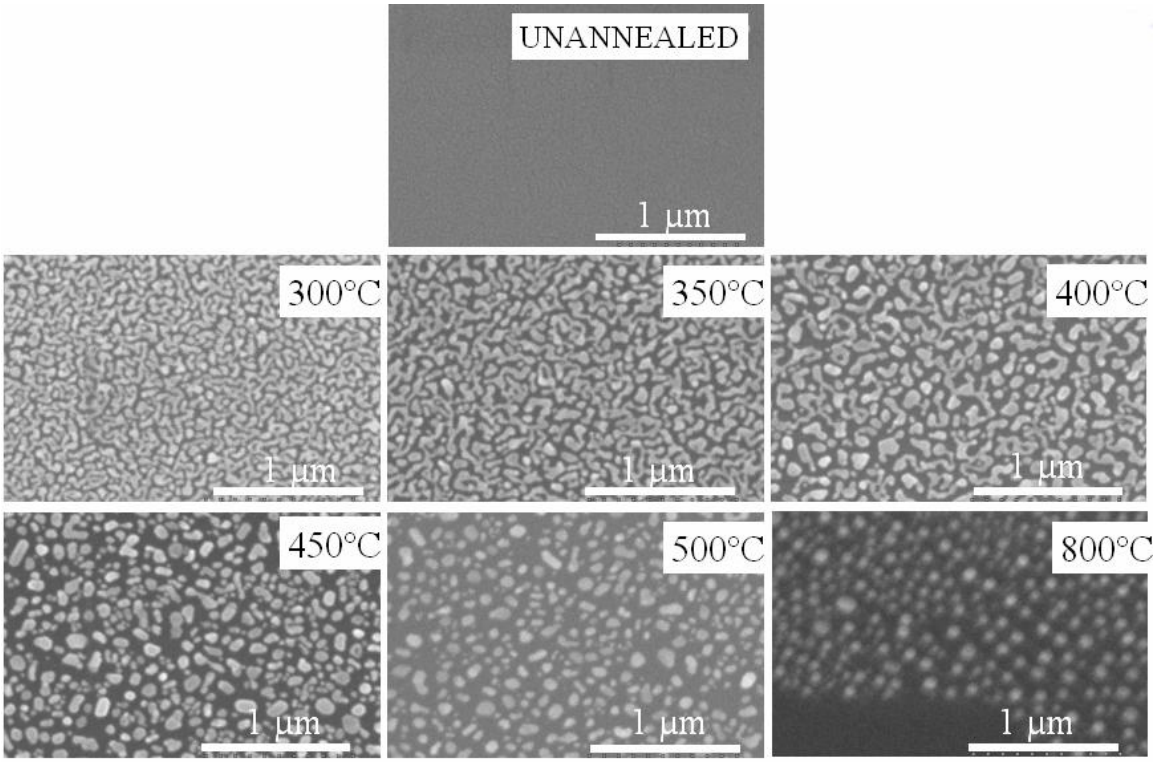

Figure 1. Morphological evolution of the Au layer as a function of annealing temperature.

Figure 2 shows the mean size (top-down cross-sectional area as calculated by "IMAGE J" software) of the Au nanodroplets as a function of annealing temperature.

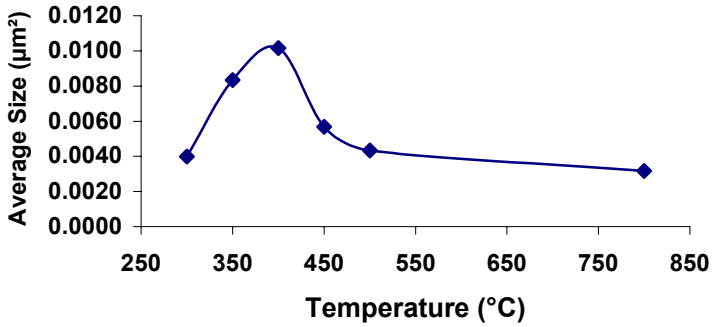

Figure 2. Mean size of the Au nanodroplets as a function of annealing temperature

The average size of the nanodroplets increases with annealing temperature between 300°C and 400°C. The corresponding SEM images (Figure 1) show that this corresponds to the Au film progressively breaking up into discrete Au droplets. Above 400°C the average size of the Au droplets drops off rapidly with increasing annealing temperature up to about 475°C then falls off much more slowly with increasing temperature up to 800°C. This process can be explained as the result of Au droplet surface energy minimisation considerations dominating over the sticking coefficient with the substrate. The associated standard deviations in droplet size decreased gradually with increasing anneal temperature, as might be expected for Ostwald ripening [8]. Thus 800°C was chosen as the best temperature for obtention of the finest and most regular distribution of nanodroplets.
Figure 3 shows SEM pictures of the Au-coated Si (100) as a function of annealing time for an annealing temperature of 800°C.

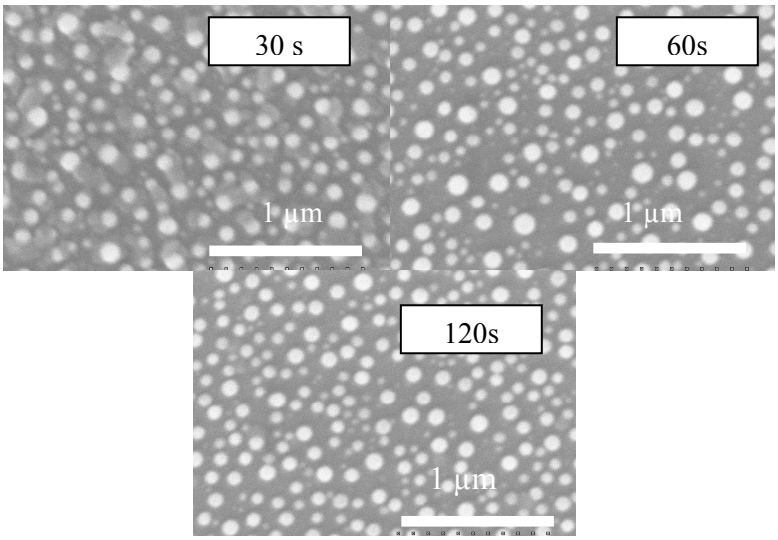

Figure 3. SEM pictures of the morphology of an Au-coated Si (100) substrate for annealing times from 30s to 120s.

Figure 4 shows the evolution of island size with annealing time. After 60s of annealing the average size of the nanoislands remained the same.

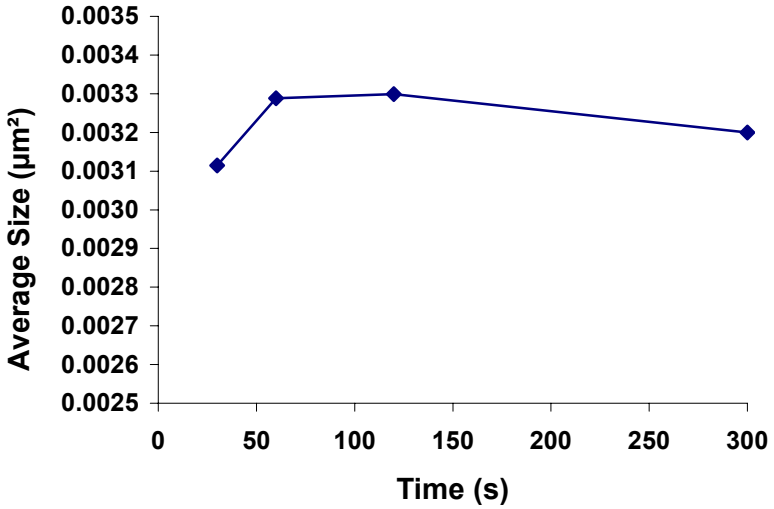

Figure 4. Mean size of the Au nanoislands as a function of annealing time.

Between 60s and 300s, annealing time does not appear to strongly influence the average nanodroplet size. The standard deviation in droplet size occurred at 60s, however, so an anneal of 60s at 800°C was adopted.

3.2 ZnO Deposition by MOCVD

The second step of the process was to grow ZnO by MOCVD. A growth temperature of 800°C was chosen based on previous experience. Three different substrates were used for the MOCVD deposition process:

1) Au-coated c-Al_2O_3 which was not pre-annealed
2) Au-coated Si (100) which was not pre-annealed
3) Au-coated Si (100) which was pre-annealed at 800°C for 1 minute.

3.2.1 MOCVD Growth at 800°C of ZnO on Au-coated Al_2O_3 (without pre-annealing)

Figure 5 shows an SEM image of some ZnO nanostructures obtained on the Au-coated c-Al_2O_3 which was not pre-annealed.

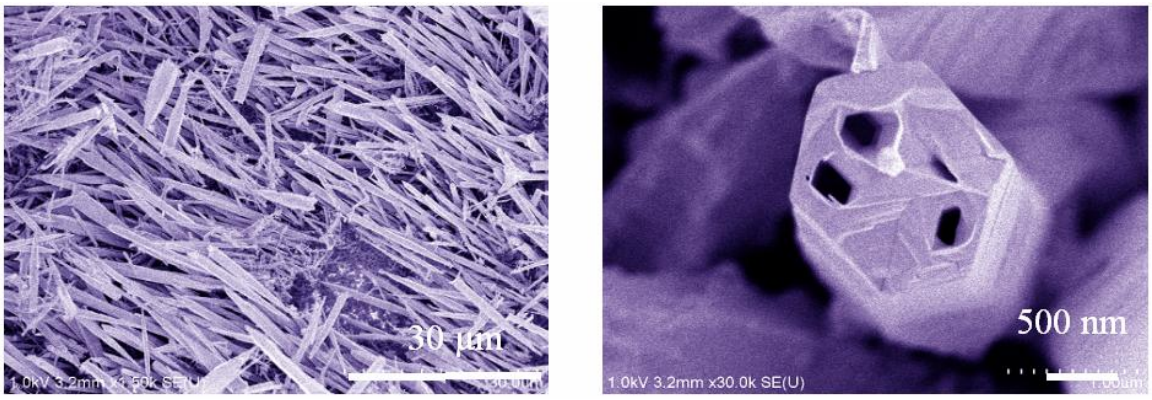

Figure 5. SEM Pictures of ZnO on Au-coated c-Al_2O_3 which was not pre-annealed.

In the image on the left hand side of Figure 5 we can see a forest of nanocolumns/wires of rather uniform diameter and length (typically 1.5 and 30 microns respectively). The majority of the columns appear to have a preferred orientation perpendicular to the substrate plane. The higher magnification image on the right side reveals that some of these nanostructures are partially-hollowed such that the best description of their form might be hexagonally-faceted nanotubes. The origin of this hollowing is unclear.
EDX analysis of these nanotubes revealed strong Zn and O signals and a trace amount of Al but no trace of Au. Thus the location and the role of the Au is also unclear.

3.2.2 MOCVD Growth at 800°C ZnO on Au-coated Si (without pre-annealing).
A variety of different nanostructures was observed on this sample. Figure 6 shows some representative SEM images.

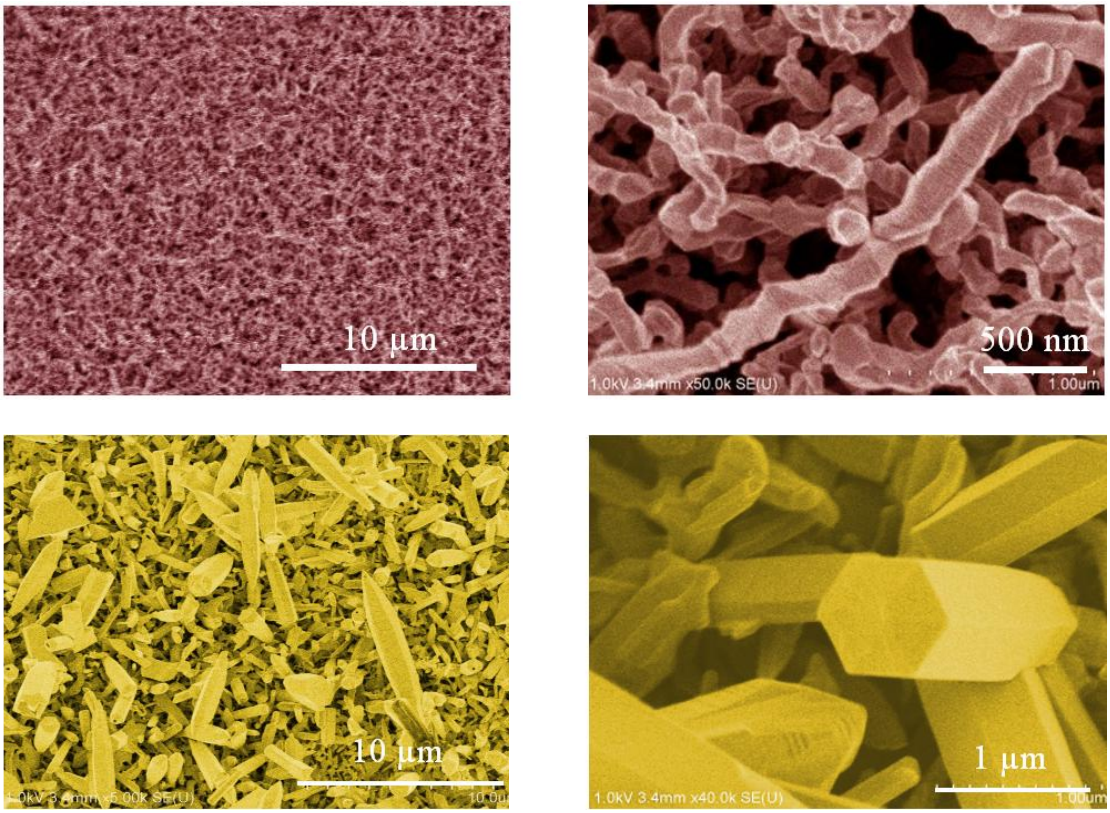

Figure 6. SEM pictures of ZnO nanostructures grown by MOCVD on Au-coated Si without pre-annealing

The nanostructures in the upper part of Figure 6 were observed at the centre of the sample while those in the lower part were observed near the edge of the sample. The nanostructures in the centre of the sample resemble interwoven jointed twisted-cords (they might also be described as twist-pastry-like). They have no obvious preferred orientation and they are relatively long, although their length is difficult to estimate. Their diameter is quite homogeneous, between approximately 100 and 200nm.
The nanostructures from near the edge of the sample are hexagonally faceted and resemble nano-needles or nanocolumns/rods. They are of various lengths and diameters (up to 10 microns and 1.5 microns respectively) and appear to have random orientation.
As well and Zn, O and Si, EDX analysis of these nanostructures showed traces of Au. It is not possible to deduce where it is located but the signal indicates that the Au does not evaporate under these growth conditions.

3.2.3 MOCVD Growth of ZnO at 800°C on pre-annealed Au-coated Si (100)

Figure 7 shows SEM pictures of the ZnO nanostructure obtained on top of the Au-coated Si substrate which was pre-annealed at 800°C for 1 minute prior the MOCVD process.

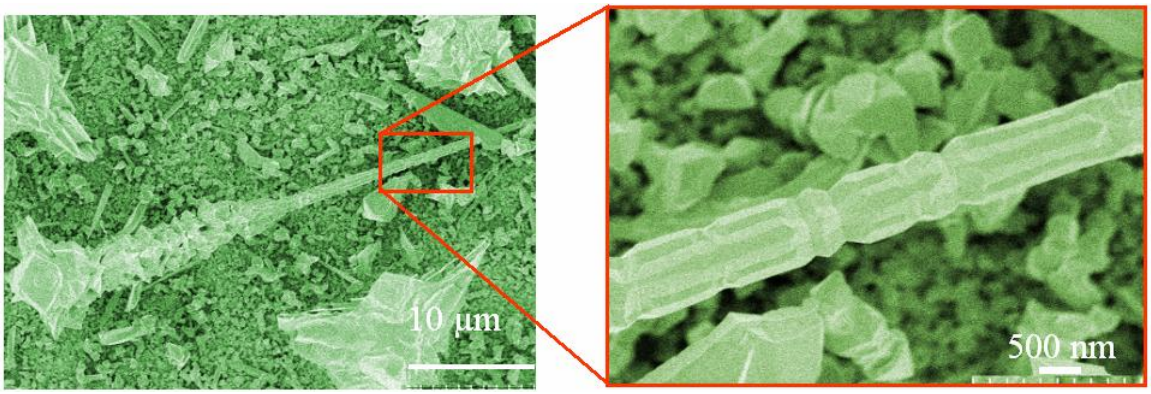

Figure 7. SEM images of ZnO grown on pre-annealed Au-coated Si

A wide range of nanostructures, of varying form and size, was observed in this sample. Of particular note was a region expanded in Figure 7 which showed a remarkable nanorod with 12 fold faceting and a bevelling which resembles a table leg. EDX revealed Zn, O and Si plus trace amounts of Au.

4. CONCLUSIONS

The influence of air annealing on 5nm thick Au films on Si (100) and c-Al_2O_3 substrates was studied as a function of temperature and duration. Au nanodroplets formed and grew spontaneously. The finest droplets and most regular distribution were obtained for an anneal of 60s at 800°C.
ZnO nanostructures were grown on the Au-coated Si (100) and c-Al_2O_3 by MOCVD. Even after pre-annealing, a regular distribution of preferentially oriented ZnO nanocolumns was not obtained. A myriad of other nanostructures was observed, however, including well-known ZnO nanostructures such as hexagonal nanorods, nanoneedles and nanotubes. Some novel ZnO nanostructures were also observed, including beveled & faceted table-leg-like structures and twist pastry like structures.
EDX analysis showed that the Au was still present after the MOCVD ZnO growth but it could not be localized. It is not clear whether or not the Au plays the role of a catalyst or not in these ZnO growths. Further investigations are underway.

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