

## The effect of growth parameters on the aspect ratio and number density of CuO nanorods

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 8531

(<http://iopscience.iop.org/0953-8984/16/47/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 19:09

Please note that [terms and conditions apply](#).

# The effect of growth parameters on the aspect ratio and number density of CuO nanorods

Ashwani Kumar, A K Srivastava, Pragya Tiwari and R V Nandedkar

Synchrotron Utilization Division, Centre for Advanced Technology, Indore 452 013, India

E-mail: ashwani@cat.ernet.in

Received 20 August 2004, in final form 19 October 2004

Published 12 November 2004

Online at [stacks.iop.org/JPhysCM/16/8531](http://stacks.iop.org/JPhysCM/16/8531)

doi:10.1088/0953-8984/16/47/007

## Abstract

We have studied how different growth conditions, namely, oxygen flow rate, annealing temperature and annealing time affect the diameter, aspect ratio and number density of CuO nanorods using scanning and transmission electron microscopy. CuO nanorods are synthesized by thermal annealing of thin copper foil. It is observed that while the diameter and number density of nanorods depend critically on the oxygen flow rate and annealing temperature, the aspect ratio and dispersion in diameter of nanorods can mostly be improved by thermal annealing for extended time periods. The growth mechanism of the nanorods is inferred from the evolution of observed microstructural changes. It is proposed that the growth of nanorods takes place from triangular shaped pyramids due to the relaxation of stress accumulated in oxide film during the process of oxidation and annealing.

## 1. Introduction

Ever since the discovery of carbon nanotubes [1], there has been a steadily growing interest in the studies of one-dimensional (1D) nanostructures, such as nanowires and nanorods. By definition, 1D nanostructures are anisotropic nanocrystals with large aspect ratio (length/diameter) and diameter in the range of 1–200 nm. These 1D nanostructures not only open new opportunities in the field of microelectronics but also provide models for studying the effect of dimensionality and size confinement on electrical, transport and mechanical properties. For example, transport properties of a single SnO<sub>2</sub> nanowire exhibit strong correlation effects in comparison to the bulk or thin films of SnO<sub>2</sub> whose temperature dependent conductivity is well described by the thermal activation model [2]. During the last 3–4 years, nanowires of various inorganic materials have been synthesized due to the realization of their applications in different fields. High capacity, longer cycle life and higher C-rate performance compared to the bulk have been reported for SnO<sub>2</sub> nanofibres used as the anode material for Li ion batteries [3]. Similarly, a lower lasing threshold has been observed for ZnO nanowires [4].

Cupric oxide (CuO) is a p-type narrow band semiconductor. It has been widely studied for being the basis of several high  $T_c$  superconductors as well as for its applications as a heterogeneous catalyst, electrochemical cell, photothermal and photoconductive material [5]. Moreover, in its nanoform it is perceived to have applications in field emitters [6] and gas sensors [7]. During the last couple of years 1D nanowires, nanorods, nanowhiskers, nanosheets of CuO have been synthesized by adopting various strategies such as using precursors, for example  $\text{Cu}(\text{OH})_2$ , or basic copper salts for sacrificial templates [7–12], solid state reaction [13], self-catalytic growth processes [14], thermal evaporation and thermal annealing [15, 16]. One of the crucial factors in the synthesis of 1D nanostructures is the control of composition, size and crystallinity. Moreover, from the point of view of studies of their fundamental properties as well as their applications, the method of preparation of the 1D nanostructures should be simple, suitable for producing bulk quantities and amenable to control of diameter and length. In comparison to complex chemical methods, thermal annealing of copper foil provides a simple, convenient and fast method for synthesizing CuO nanorods.

In this paper, we report the dependence of the diameter, aspect ratio and number density (number of nanorods per unit area) of CuO nanorods synthesized by thermal annealing of copper foil under different growth conditions of oxygen flow rate, annealing temperature and annealing time. Although nanorods synthesized by this method are always found to be almost perpendicular to the surface of the copper foil, only under certain growth conditions is the formation of nanorods spread over a large area observed. Further, it is observed that while the diameter and number density of nanorods are critical functions of oxygen flow rate and annealing temperature, the length of nanorods depends mainly on the annealing time. Thus, these experiments reveal that by varying either the oxygen flow rate or the annealing temperature or both, CuO nanorods of different diameters can be synthesized. The length and hence the aspect ratio of these nanorods can be enhanced by increasing the thermal annealing time. In the last section a possible mechanism of growth of CuO nanorods by thermal annealing is discussed.

## 2. Experimental details

The synthesis of the CuO nanorods was carried out by thermal annealing commercial grade copper foil of 0.1 mm thickness. The foil of about 1 cm  $\times$  1 cm was first cleaned by dipping once in dilute HCl acid to remove the native oxide layer. The foil was then thoroughly rinsed with deionized water. Finally, it was cleaned with methanol in an ultrasonic bath for about 5 min. The clean copper foil was kept in a quartz tube, which was loaded into a horizontal resistive furnace. The thermal annealing of clean copper foil was carried out for different oxygen flow rates, annealing temperatures and annealing times. The sample temperature was monitored by placing a K-type thermocouple in the near vicinity of the sample. In all the experiments, unless otherwise mentioned, the rate of heating of the copper foil was  $\sim 10^\circ\text{C min}^{-1}$  and cooling was carried out by just switching off the furnace. The oxygen flow rate was kept constant during the complete cycle of heating, annealing and cooling during each experiment. Samples were removed from the quartz tube only after the sample temperature was below  $\sim 50^\circ\text{C}$ .

In order to study the effect of various growth conditions on the synthesis of CuO nanorods the following strategy was adopted. First, the annealing temperature and time were kept constant at  $500^\circ\text{C}$  and 30 min, respectively, and only the oxygen flow rate was varied. The optimum oxygen flow rate thus determined is  $150\text{ ml min}^{-1}$ . Preliminary results obtained from this study are reported in our earlier publication [17]. In the second step, the oxygen flow rate was kept fixed at its optimum value and the annealing time at 30 min and the effect

of temperature on the growth of nanorods was studied. Finally, the temperature and oxygen flow rate were kept fixed at their optimum values of 400 °C and 150 ml min<sup>-1</sup>, respectively, determined from the above two steps, and we studied how the annealing time affects the aspect ratio and number density of CuO nanorods. The data generated from all these experiments revealed that a combination of different growth parameters results in CuO nanorods with different diameters and lengths. Samples prepared under similar growth conditions gave CuO nanorods of similar diameter and length indicating that this method is reproducible. Further, this method was found to be very robust in the sense that the nanorods of other transition metal oxides can also be prepared just by annealing the foils of their respective transition metals [18].

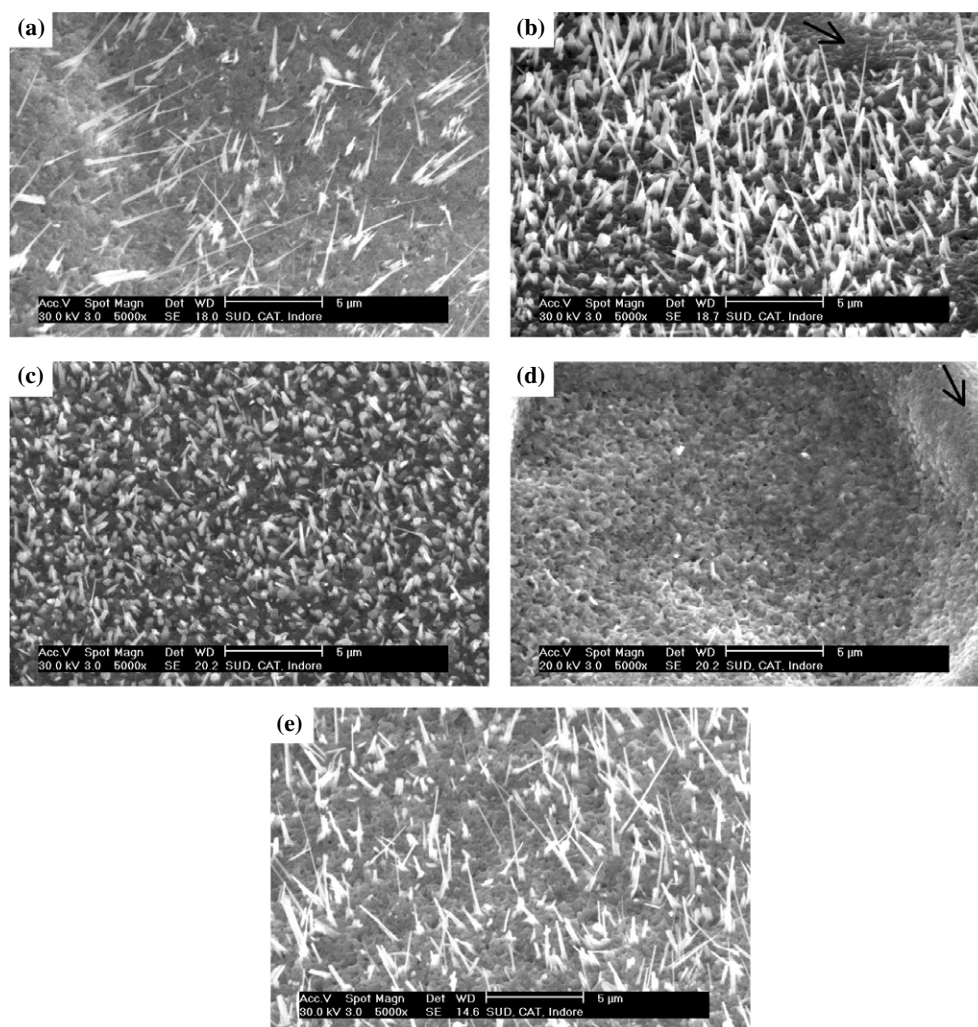
The morphology of the nanorods was characterized in a Philips XL30CP scanning electron microscope (SEM) operated at 30 kV. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies were carried out on the samples in a Philips CM200 microscope operated at 200 kV.

### 3. Results

In the following subsections, experimental results obtained from the study of the influence of various growth parameters on the evolution of CuO nanorods obtained by the method of thermal annealing of copper foil are presented.

#### 3.1. The effect of the oxygen flow rate

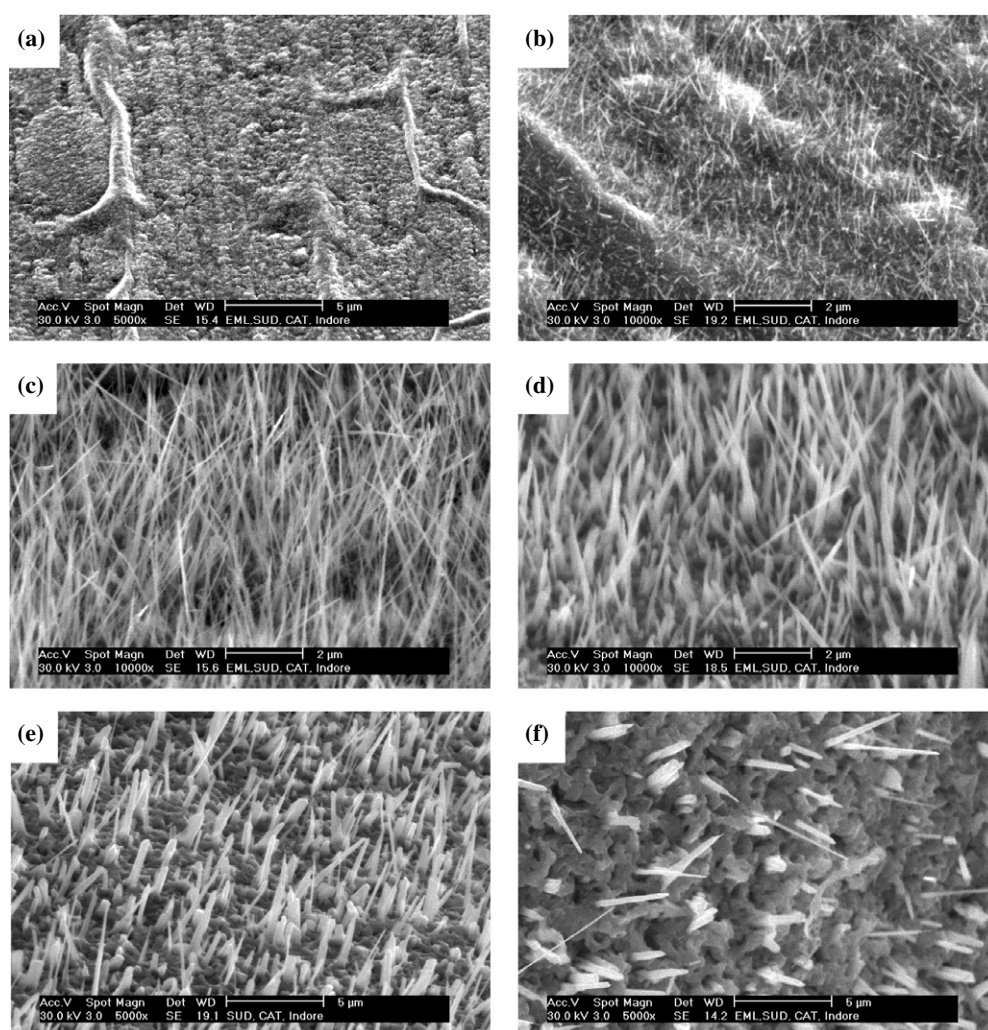
The effect of the oxygen flow rate on the growth of CuO nanorods was studied by thermally annealing the copper foil at 500 °C for 30 min under different oxygen flow rates of 35, 150, 300, 500 ml min<sup>-1</sup> and in atmospheric air. A representative SEM image for the flow rate of 35 ml min<sup>-1</sup> is shown in figure 1(a). The growth of the nanorods can be seen through the protrusions in the substrate, i.e. the oxide layer formed on the copper foil during the process of thermal annealing. While the average diameter of these nanorods is ~115 nm, the length varies between 1 and 3 μm. In figure 1(b), an SEM image of the sample obtained for a flow rate of 150 ml min<sup>-1</sup> is shown. It is obvious from the figure that, compared to the case for the 35 ml min<sup>-1</sup> flow rate of oxygen, the number density of nanorods is much higher. The nanorods are almost perpendicular to the surface of the substrate and uniformly cover the entire surface. The average diameter of these nanorods is about 135 nm and their length ranges from 2 to 5 μm. At the oxygen flow rate of 300 ml min<sup>-1</sup> (figure 1(c)), the number density of the nanorods is almost the same as the one found for the oxygen flow rate of 150 ml min<sup>-1</sup>. However, in contrast, the length of most of these nanorods is <2 μm and their average diameter increases to ~150 nm. Thus, the aspect ratio of nanorods formed at this flow rate is much less than that for the nanorods formed at a flow rate of 150 ml min<sup>-1</sup>. On further increasing the oxygen flow rate to 500 ml min<sup>-1</sup>, almost negligible creation of nanorods is observed, as is revealed by the SEM image shown in figure 1(d). The formation of nanorods is also observed when the copper foil is annealed in atmospheric air at 500 °C for 30 min (figure 1(e)). The average length and diameter of these nanorods are 3 μm and 200 nm, respectively. We would like to point out here that during the process of thermal annealing of the copper foil, the formation of hill and valley structure is observed invariably, as can be clearly seen in figures 1(b) and (d); the hills are marked by arrows in these figures. The formation of nanorods preferentially takes place in valleys. This is a generic feature; it is independent of the oxygen flow rate, annealing temperature and annealing time. Nevertheless, it is apparent from these experiments that the oxygen flow rate influences not only the growth of nanorods but also their number density and aspect ratio; the highest aspect ratio and number density of nanorods are observed when the oxygen flow rate is 150 ml min<sup>-1</sup>.



**Figure 1.** SEM images of CuO nanorods grown at different oxygen flow rates: (a) 35 ml min<sup>-1</sup>, (b) 150 ml min<sup>-1</sup>, (c) 300 ml min<sup>-1</sup>, (d) 500 ml min<sup>-1</sup> and (e) in atmospheric air. The annealing temperature and time were kept constant at 500 °C and 30 min, respectively.

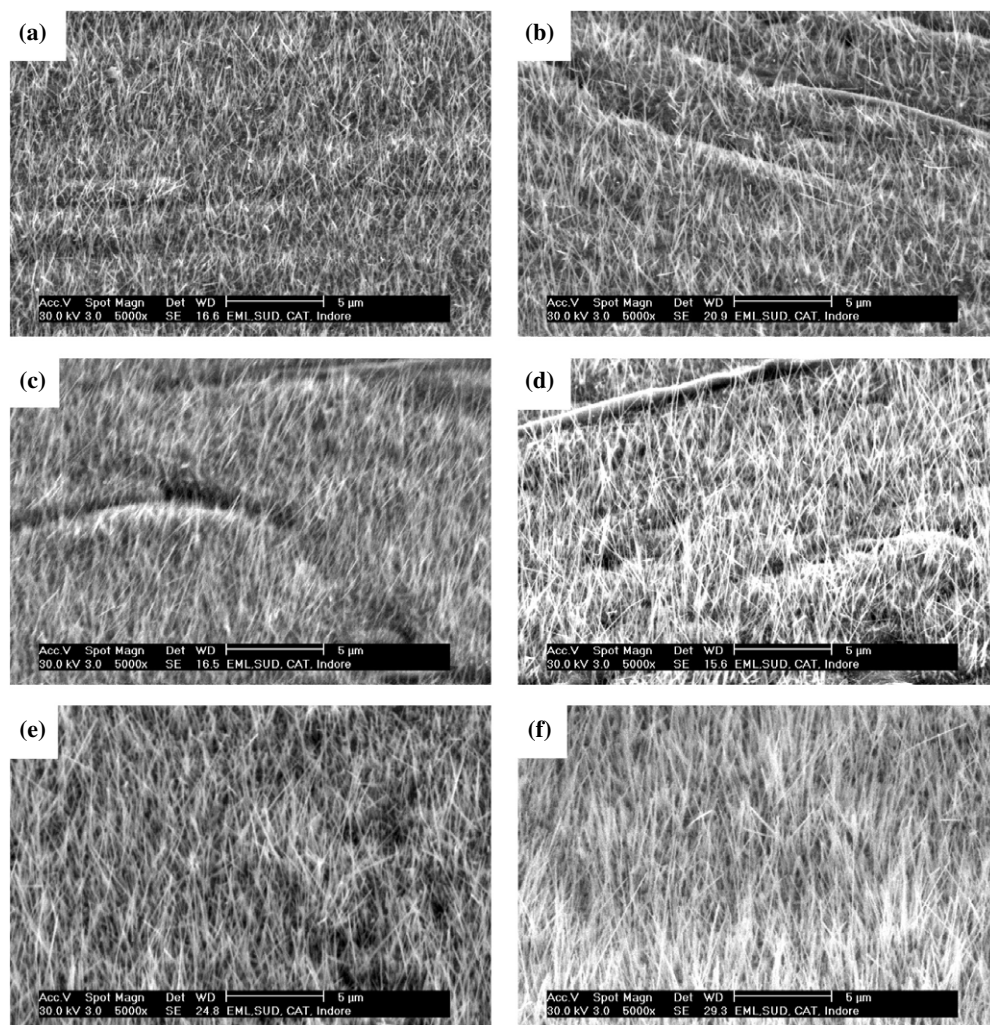
### 3.2. The effect of the annealing temperature

To study the influence of the thermal annealing temperature on the growth of CuO nanorods, copper foil was annealed for 30 min at different temperatures, namely, 300, 350, 400, 450, 500 and 600 °C. The oxygen flow rate was maintained at 150 ml min<sup>-1</sup>. In figure 2(a), an SEM image of the sample obtained by thermally annealing at 300 °C is shown. From the figure, it is evident that although the formation of hill and valley structure along with protrusions or humps in the valleys has taken place, there is no indication of formation of any nanorod. When the temperature is increased to 350 °C, formation of very small nanorods of length ~1 μm, covering almost the complete area of the substrate, is observed (figure 2(b)). The average diameter of these nanorods is 30 nm. A large number density of nanorods is observed at 400 and 450 °C, as is apparent from figures 2(c) and (d), respectively. Nanorods at these two temperatures have almost the same length, ~4 μm. Although the number densities and



**Figure 2.** SEM images of CuO nanorods grown at different temperatures (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C, (e) 500 °C and (f) 600 °C. The oxygen flow rate and annealing time were kept constant at 150 ml min<sup>-1</sup> and 30 min, respectively.

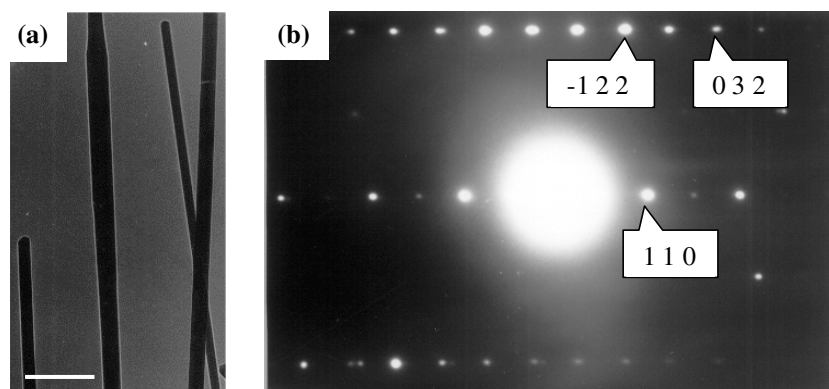
average lengths at these two temperatures are similar, the average diameters of nanorods are 47 and 90 nm, respectively. Thus, when all the other growth parameters are the same, the aspect ratio of the nanorods formed at 400 °C is about 40% higher compared to that of the ones which are formed at 450 °C. On further increasing the annealing temperature to 500 and 600 °C, a consistent decrease in number density of nanorods is observed (figures 2(e) and (f)); at 600 °C only a few nanorods are observed. While the average length of the nanorods is ~3 and 2 μm at 500 and 600 °C, respectively, the average diameter is about 135 and 260 nm, respectively. These experiments thus reveal that, like the oxygen flow rate, the annealing temperature influences both the number density and the aspect ratio. Nanorods are always nearly unidirectional and are almost perpendicular to the surface of the substrate. Under similar conditions of annealing time and oxygen flow rate, the highest aspect ratio and number density of nanorods are observed when the thermal annealing temperature is 400 °C.



**Figure 3.** SEM images of CuO nanorods grown by annealing a copper foil at 400 °C in an oxygen flow of 150 ml min<sup>-1</sup>. The annealing time is (a) 5 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 60 min and (f) 120 min.

### 3.3. The effect of the annealing time

The question of how the annealing time affects the aspect ratio and number density of CuO nanorods was investigated by annealing copper foil at 400 °C under an oxygen flow rate of 150 ml min<sup>-1</sup> for 5, 10, 20, 30, 60 and 120 min. In figures 3(a)–(f), SEM images for the samples prepared with these annealing times are shown. From figure 3(a), it is obvious that just 5 min of thermal annealing is sufficient to produce a large number of nanorods, which not only cover the complete surface of the substrate but are also almost unidirectional. This observation indicates that the creation of nanorods takes place almost spontaneously under optimum conditions of oxygen flow rate and annealing temperature. Although the average length of these nanorods is  $\sim 1.5 \mu\text{m}$ , the average diameter is 47 nm, which is similar to the diameter of nanorods obtained by annealing for 30 min. On further increasing the annealing



**Figure 4.** (a) A bright field TEM image of CuO nanorods; the scale bar corresponds to 250 nm. (b) A selected area electron diffraction pattern from a single nanorod. The diffraction pattern is indexed with the lattice parameters for CuO.

time, the average length of the nanorods is found to be 2, 3, 4, 6, 8  $\mu\text{m}$  for annealing times of 10, 20, 30, 60 and 120 min, respectively. However, the average diameter of the nanorods is found to be the same, i.e. 47 nm, irrespective of the time of annealing. Thus, annealing time does not seem to have an effect on the average diameter of the nanorods and affects only their length; the longer the time of thermal annealing, the longer the nanorods. Moreover, it is also evident from figures 3(a)–(f) that the number density of nanorods is also almost independent of the annealing time.

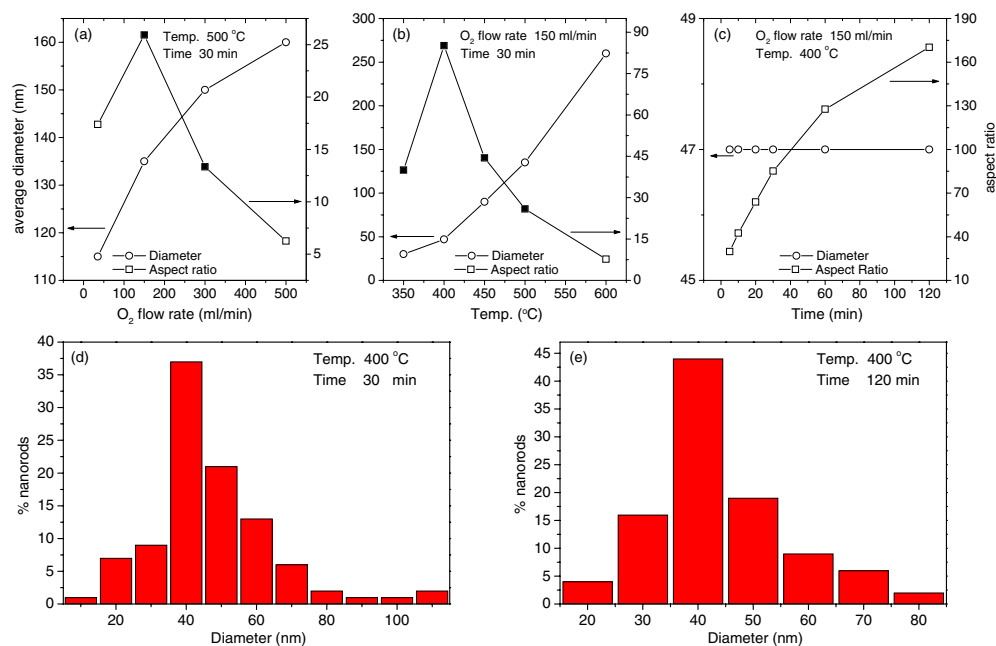
#### 3.4. TEM

A typical bright field TEM image of nanorods grown at 500 °C is shown in figure 4(a). It is apparent from the figure that while the outer surface of the nanorods has smooth morphology, the inner one seems to be solid. The phase purity and the crystalline nature of the nanorods was confirmed by SAED. The diffraction patterns collected from various nanorods prepared under different experimental conditions revealed that all the nanorods are single phase and single crystalline. In figure 4(b), a representative electron diffraction pattern collected from a single nanorod is shown. From the diffraction pattern, it is evident that the nanorod is single crystalline. The diffraction pattern is indexed with lattice parameters for CuO,  $a = 4.684 \text{ \AA}$ ,  $b = 3.425 \text{ \AA}$ ,  $c = 5.129 \text{ \AA}$  and  $\beta = 99.47^\circ$ , indicating that these single-crystalline nanorods are indeed of CuO. The zone axis of the electron diffraction pattern for the nanorod has been found to be  $[\bar{2}2\bar{3}]$ .

#### 4. Discussion

One of the most crucial factors in the synthesis of nanowires or nanorods is to have control of their diameter to study the effect of dimensionality and size confinement on various physical properties. Further, it is also important that these nanostructures are unidirectional, have high aspect ratio and crystalline purity and are easy to synthesize for commercial exploitation and device applications. In the past, various techniques mostly involving different precursor templates have been used for the synthesis of CuO nanorods. For example, CuO nanorods having the average diameter of 10 nm have been synthesized [7] by first fabricating precursor  $\text{Cu}(\text{OH})_2$  polycrystalline nanowires, which act as both reactant and template for the growth





**Figure 5.** The effect of the different growth conditions, namely, (a) oxygen flow rate, (b) annealing temperature and (c) annealing time, on the diameter and aspect ratio of CuO nanorods. The dispersion in the diameter of the nanorods prepared under an oxygen flow rate of  $150 \text{ ml min}^{-1}$  and for annealing times of (d) 30 min and (e) 120 min at  $400 \text{ }^\circ\text{C}$ .

(This figure is in colour only in the electronic version)

of CuO nanowires. Jisen *et al* [13] have used different procedures, each involving various steps of grinding the chemicals together, washing, distilling and heating to produce CuO nanorods having diameters of 10, 15 and 20 nm, respectively. However, the length of the nanorods in each case is less than a couple of hundreds of nanometres. Similarly, Xu *et al* [10] obtained nanorods of CuO having diameters in the range of 30–100 nm and lengths of 1–3  $\mu\text{m}$  by thermal decomposition of precursor  $\text{CuC}_2\text{O}_4$ , which was obtained by chemical reaction between  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  and  $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  in the presence of surfactant NP-9/5. Thus, the techniques based on precursor templates require a deep knowledge of the chemical reactions for adopting/discovering a variety of procedures for producing various precursors for synthesizing nanorods having a choice of diameters. Moreover, normally the lengths of the nanorods produced by these methods are also less than a micron and there does not seem to be a way to control the length and hence the aspect ratio of these nanorods. In contrast with these complex chemical methods, the procedure for synthesizing CuO nanorods by thermal annealing of copper foil is much simpler, faster and more convenient for the preparation of nanorods of different diameters and aspect ratios with high number density.

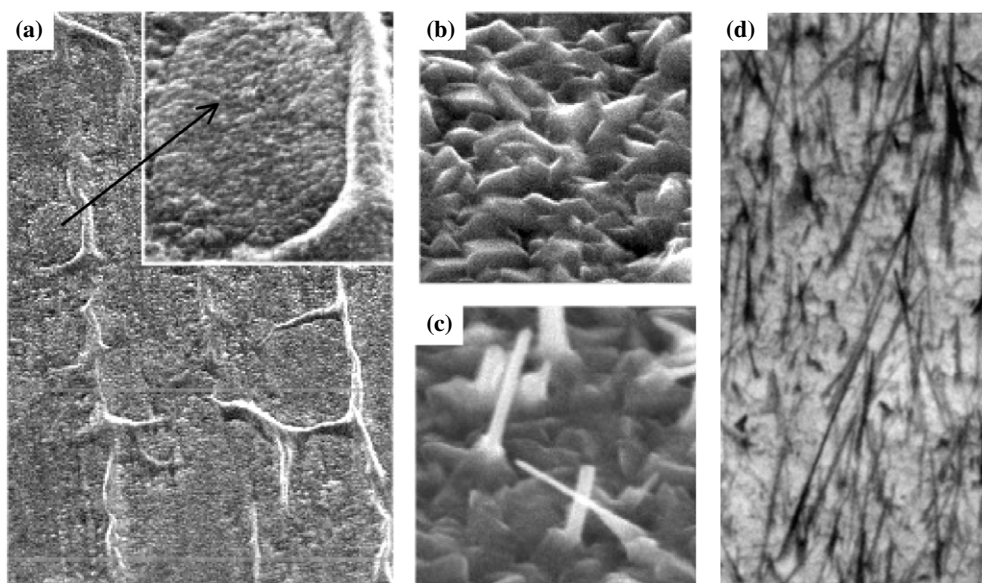
In figures 5(a)–(c), the average diameter and aspect ratio of CuO nanorods are plotted as a function of oxygen flow rate, annealing temperature and annealing time. Filled squares in figures 5(a) and (b) correspond to values of oxygen flow rates and annealing temperatures, respectively, at which high number densities of nanorods ( $\sim 10^6$ – $10^8 \text{ cm}^{-2}$ ), covering almost the complete surface of the substrate, are observed. From these two figures, it is clear that the diameter of the nanorods increases monotonically with both oxygen flow rate and annealing temperature. Moreover, under similar conditions of annealing time, there is an optimum value

of temperature for each oxygen flow rate or vice versa at which the aspect ratio of the nanorods is maximum. For example, we find that the optimum temperature is 400 °C for an oxygen flow rate of 150 ml min<sup>-1</sup>. Similarly, Huang *et al* [15], who synthesized CuO nanorods at different annealing temperatures but at a constant oxygen flow rate of 50 ml min<sup>-1</sup>, observed the maximum number density and aspect ratio of nanorods at 600 °C. Thus, it is apparent that while nanorods of different diameters can be synthesized with high number density by varying either the annealing temperature or the oxygen flow rate or both, a high aspect ratio of nanorods synthesized at any annealing temperature or oxygen flow rate which is conducive for the creation of nanorods can be achieved by increasing the annealing time (figure 5(c)).

In order to obtain an estimate of the dispersion in the diameters of nanorods, we plot the percentage of nanorods with different diameters synthesized by thermal annealing at 400 °C under an oxygen flow rate of 150 ml min<sup>-1</sup> for 30 and 120 min in figures 5(d) and (e), respectively. Although the mean diameters of the nanorods are almost same for the two annealing times, the dispersion in the diameter of the nanorods is considerably less for the annealing time of 120 min compared to that for the annealing time of 30 min. At 120 min of annealing time, almost 80% of the nanorods have their diameters in the narrow range of 30–50 nm. The standard deviation in the diameter of the nanorods at these two annealing times is found to be 18 and 12 nm, respectively. Recently, Hsieh *et al* [14] synthesized nanorods by first producing a template of copper nuclei having uniform diameter and then performed thermal annealing under an oxygen flow rate of 300 ml min<sup>-1</sup> at 500 °C to grow CuO nanorods from these pre-deposited copper nuclei. Two sets of nanorods produced by this method had diameters in 50–60 and 100–150 nm ranges. The observed standard deviation of 12 nm for nanorods with a mean diameter of 47 nm is thus comparable with these results, indicating that it may be possible to further narrow down the distribution in diameter by annealing for longer time periods. In our recent experiments, we have observed that the dispersion in the diameter of the nanorods can also be further controlled either by maintaining a slow heating rate of copper foil at ~1 °C min<sup>-1</sup> or by the application of an electric field [19].

The growth mechanism of the CuO nanorods has rarely been reported in the literature. Although both Huang *et al* [15] and Hsieh *et al* [14] have attributed the formation of CuO nanorods to the vapour–solid model, details of the growth mechanism are still lacking. In order to elucidate the thermodynamical and kinetic aspects of the growth mechanism, we show the evolution of the observed microstructural changes in figure 6, which illustrates the different stages leading to the formation and growth of CuO nanorods. Although these SEM images were obtained under different experimental conditions of oxygen flow rate, annealing temperature and time, we believe them to represent a possible route to the formation and growth of CuO nanorods when a copper foil is thermally annealed in an oxygen atmosphere.

In all our experiments, irrespective of growth conditions, the formation of hill and valley structure illustrated in figure 6(a) is observed during the process of annealing of the copper foil. This appears to be the first step, which occurs when the foil is annealed in an oxygen atmosphere or air. The foil used during all the experiments is a polycrystalline copper foil, which is strongly textured along the (220) crystallographic direction. The grain growth temperature for cold-worked copper foil is ~200 °C [20]. During thermal annealing of copper foil in an oxygen atmosphere at annealing temperatures higher than 200 °C, in addition to the recovery and recrystallization, grain growth would also occur along with the oxidation of the foil. Previous studies on single crystals of Cu have revealed that an oxide layer grows epitaxially and the rate of oxidation is different on different crystallographic orientations of copper surface [21, 22]. Oxide film replicates the grain structure of polycrystalline Cu and it is not uniform in its thickness due to the different orientations of grains. Further, due to the higher surface energy at grain boundaries compared to that of grains themselves, it is expected that the growth rate



**Figure 6.** The evolution of microstructural changes in the oxide film on thermally annealing the copper foil in an oxygen atmosphere: (a) formation of the hill and valley structure, (b) three-dimensional triangular pyramids, (c) formation and (d) growth of CuO nanorods.

of oxide would be higher on grain boundaries. The observed different heights of oxide film on different grains and the thicker oxide layer along the grain boundaries, as seen in figure 6(a), lead us to conclude that the hill and valley structures are formed by the grain boundaries and the grains, respectively.

In the inset of figure 6(a), a magnified image of one of the grains marked by an arrow in the main figure is shown to illustrate that even the oxide layer on the grain itself is not uniform; it consists of 'nanogranules'. In contrast, the oxide layer on the grain boundaries hardly shows any signatures of formation of such structures. These 'nanogranules' grow bigger, having the morphological structure of triangular pyramids, on further annealing, as is evident from figure 6(b). Copper forms two thermodynamically stable oxides, CuO and Cu<sub>2</sub>O, on reaction with molecular oxygen. The oxide scale consists of either Cu<sub>2</sub>O only or Cu<sub>2</sub>O + CuO, depending on the oxidation temperature and ambient oxygen partial pressure. The topmost layer is always of CuO if the oxide scale consists of both Cu<sub>2</sub>O and CuO. The fractional thickness of the CuO topmost layer in this bilayered oxide scale mainly depends on the annealing temperature; it decreases with increase in temperature due to thermodynamically allowed counter-oxidation of CuO to Cu<sub>2</sub>O. Gusakov *et al* [23] reported that while up to 25% of CuO in the oxide scale is formed below ~600 °C, the fractional thickness of CuO being higher at lower temperatures, the amount of CuO is <5% for temperatures above ~600 °C. Similarly, Zhu *et al* [24] in their studies on the oxidation mechanism of copper found that under 0.1 MPa of oxygen partial pressure at 500 °C, the thickness of the topmost CuO layer is ~15% of the total oxide layer. Therefore, it is reasonable to assume that the observed three-dimensional triangular pyramids and the oxide layer in their immediate vicinity are of CuO. Such an assumption is also consistent with the experimentally observed CuO electron diffraction patterns from the bases of nanorods since, as discussed below, nanorods originate from these very triangular pyramids.

CuO has monoclinic structure with  $a = 4.684 \text{ \AA}$ ,  $b = 3.425 \text{ \AA}$ ,  $c = 5.129 \text{ \AA}$  and  $\beta = 99.47^\circ$ . In comparison,  $\text{Cu}_2\text{O}$  is simple cubic with  $a = 4.22 \text{ \AA}$ . Therefore, it may be expected that substantial stress exists on the CuO– $\text{Cu}_2\text{O}$  interface or phase boundaries due to differences in their crystallographic structures, molar volumes and densities. Further, the stress would be high, comparatively, in triangular pyramids, so the interface area is minimized by this triangular shape. As long as the oxidation process continues through the surface diffusion of oxygen, stress is accumulated and after reaching a critical limit the oxide layer relaxes itself by spontaneous growth of nanorods from the triangular pyramids. Nanorods do indeed originate from the triangular pyramids, as is evident from figures 6(c) and (d) where it can be clearly seen that the base of almost every nanorod has triangular morphology. Growth of nanorods occurs until all the stress accumulated in the oxide film is relaxed. The ultimate length that a nanorod can achieve would correspond to complete relaxation of stress, thus explaining the observed saturation in the length of nanorods on increasing the annealing time (see figure 5(c)). The material transport to nanorods during their growth may take place due to diffusion of constituent elements, where copper atoms are supplied from the substrate and oxygen atoms from the environment and the two combine at the tips of nanorods. However, the possibility of growth of nanorods due to diffusion of CuO molecules from the root to the tip of nanorods cannot be ruled out from the present experimental data.

In our experiments, even after 30 min of thermal annealing, formation of nanorods is not observed when the thermal annealing temperature is  $300^\circ\text{C}$ . In contrast, an annealing period of just 5 min was found to be sufficient for the growth of nanorods at  $400^\circ\text{C}$ . However, at  $350^\circ\text{C}$ , although the growth of nanorods was observed after thermal annealing for 30 min, no nanorods could be seen when the foil was annealed for just 10 min. All these experimental facts indicate that an ‘incubation’ period is necessary for the accumulation of stresses as a result of interactions between the oxide film and the substrate. The thermal annealing temperature not only affects the oxidation rate but also influences the interfacial stress, surface and interface energies and elastic properties of the oxide film. At low temperatures, the oxidation rate being low, the growth of the oxide layer and thus the accumulation of stresses in it is slower. Therefore, a longer incubation period and thus longer annealing time is required at these temperatures for the accumulation of stress to a critical limit and hence for the formation and growth of nanorods. At higher temperatures, under otherwise equal conditions, formation of stresses proceeds faster and therefore the incubation period is shorter, thus explaining the formation of nanorods at temperatures between  $350$  and  $600^\circ\text{C}$  even during short durations of annealing time.

Finally, we explain the observed changes in diameter and number density of nanorods with annealing temperature. From the above discussion it is evident that nanorods originate from triangular pyramids. Thus, there must exist a correlation between the diameter and number density of nanorods and the size and number density of triangular pyramids, respectively. In earlier experimental studies on initial stages of oxidation on Cu(001) and Cu(110) surfaces, formation of three-dimensional islands was observed between  $300$  and  $500^\circ\text{C}$  and at an oxygen pressure of 760 Torr; the morphology of the oxide film even for a thickness of  $400 \text{ \AA}$  exhibited three-dimensional triangular islands [25]. It is thus possible that oxide film on a copper surface grows in a multilayer mode rather than in a layer-by-layer mode. A multilayer mode of growth is possible if the size of an island is small compared to the separation between islands, so that nucleation of a second layer occurs on each island before they coalesce. This occurs when there is a sufficiently large energy barrier, known as the Ehrlich–Schwoebel (ES) barrier [26, 27], for the step down diffusion of adspecies at the island edge [28]. Formation of three-dimensional triangular pyramids during oxidation of copper is a strong indication in favour of the existence of such a barrier. The existence of an ES barrier coupled with a steady flux of precursors,

copper atoms from the substrate and oxygen from the atmosphere, would lead to an instability and consequently to the formation of mounds and pyramids on the growth surface. In most of the theoretical and experimental work, the concept of the ES barrier has most often been invoked to describe roughening in metallic systems [29]. However, recently it has also been applied to explain the formation of pyramids in semiconductors, e.g. heteroepitaxy of ZnO on InP(100) [30] and homoepitaxy of ZnO [31]. Therefore, it may be expected that the size and number density of three-dimensional triangular pyramids will be directly proportional to the size and number density of three-dimensional islands formed on copper surfaces during the initial stages of oxidation. At higher temperatures, due to the high mobility of oxygen as well as the lowering of the barrier, attachment of oxygen to existing islands is more probable than nucleation of new islands. At low temperatures, thus, many small islands are formed, whereas at higher temperatures, islands with larger average island size are formed and hence the island density is less. Oxide island density is indeed observed to decrease with increasing temperature following an Arrhenius dependence [25]. This implies that while the average size of islands increases, island density decreases with temperature, thus explaining the increase in diameter and decrease in number density of nanorods with increasing temperature.

## 5. Conclusions

Nanorods of CuO have been grown by thermal annealing of copper foil in an oxygen atmosphere. This method has been found to be simple, efficient and reproducible for growing well aligned single-crystalline CuO nanorods. The influence of various growth parameters on the diameter, aspect ratio and number density of the nanorods has been investigated in detail. It is observed that the aspect ratio and number density of these nanorods are critical functions of various growth parameters, namely, the oxygen flow rate, annealing temperature and annealing time. While the oxygen flow rate and annealing temperature affect both the aspect ratio and the number density, the main effect of the annealing time is on the aspect ratio of these nanorods. A possible growth mechanism based on stress relaxation has been proposed for describing the formation and growth of these nanorods. Various experimental observations have been explained using such a growth model.

## References

- [1] Ijima S 1991 *Nature* **354** 56
- [2] Ma Y-J, Zhou F, Lu L and Zhang Z 2004 *Solid State Commun.* **130** 313
- [3] Li N and Martin C R 2001 *J. Electrochem. Soc. A* **148** 164
- [4] Huang M H, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R and Yang P 2001 *Science* **292** 1897
- [5] Reitz J B and Solomon E I 1998 *J. Am. Chem. Soc.* **120** 11467
- [6] Hsieh C-Te, Chen J-M, Lin H-H and Shih H-C 2003 *Appl. Phys. Lett.* **83** 3383
- [7] Wang W, Varghese O K, Ruan C, Paulose M and Grimes C A 2003 *J. Mater. Res.* **18** 2756
- [8] Zhang W, Wen X and Yang S 2003 *Inorg. Chem.* **42** 5005
- [9] Zhu C L, Chen C N, Hao L Y, Hu Y and Chen Z Y 2004 *Solid State Commun.* **130** 681
- [10] Xu C, Liu Y, Xu G and Wang G 2002 *Mater. Res. Bull.* **37** 2365
- [11] Cao M H, Hu C W, Wang Y H, Guo Y H, Guo G X and Wang E B 2003 *Chem. Commun.* **15** 1884
- [12] Chen D, Shen G Z, Tang K B and Qian Y T 2003 *J. Cryst. Growth* **254** 225
- [13] Jisen W, Jinkai Y, Jinqun S and Ying B 2004 *Mater. Des.* **25** 625
- [14] Hsieh C-Te, Chen J-M, Lin H-H and Shih H-C 2003 *Appl. Phys. Lett.* **82** 3316
- [15] Huang L S, Yang S G, Li T, Gu B X, Du Y W, Lu Y N and Shi S Z 2004 *J. Cryst. Growth* **260** 130
- [16] Jiang X C, Herricks T and Xia Y N 2002 *Nano Lett.* **2** 1333
- [17] Srivastava A K, Tiwari P, Kumar A and Nandedkar R V 2004 *Curr. Sci.* **86** 22
- [18] Kumar A *et al* 2004 at press
- [19] Srivastava A K *et al* 2004 at press

- 
- [20] *ASM Handbook* 1997 vol 4 (Metals Park, OH: ASM International) p 830
- [21] Yang J C, Yeadon M, Kolasa B and Gibson J M 1997 *Appl. Phys. Lett.* **70** 3522
- [22] Ali S I and Wood G C 1968 *Corros. Sci.* **8** 413
- [23] Gusakov A G, Voropayev A G, Zheludkevich M L, Vecher A A and Rapopov S A 1999 *Phys. Chem. Chem. Phys.* **1** 5311
- [24] Zhu Y, Mimura K and Isshiki M 2002 *Mater. Trans.* **43** 2173
- [25] Yang J C, Kolasa B, Gibson J M and Yeadon M 1998 *Appl. Phys. Lett.* **73** 2841
- [26] Ehrlich G and Hudda F G 1966 *J. Chem. Phys.* **44** 1039
- [27] Schwoebel R 1969 *J. Appl. Phys.* **40** 614
- [28] Tersof J, Vandergon A W D and Tromp R M 1994 *Phys. Rev. Lett.* **72** 266
- [29] Zuo J-K and Wendelken J F 1997 *Phys. Rev. Lett.* **78** 2791
- [30] Vasco E, Zaldo C and Vazquez L 2001 *J. Phys.: Condens. Matter* **13** L663
- [31] Baxter J B, Wu F and Aydil E S 2003 *Appl. Phys. Lett.* **83** 3797