INTRODUCTION

Zinc oxide (ZnO), a representative of II-VI semiconductor compounds, is a technologically important material. ZnO has a unique position among the semiconducting oxides due to its piezoelectric and transparent conducting properties, high electrical conductivity and optical transmittance in the visible region. These properties make it ideal for applications such as transparent conducting electrodes in flat-panel displays and window layers in thin-film heterojunction solar cells. Due to these properties, combined with its low cost and nontoxicity, ZnO has been recognized as a promising alternative material to transparent conducting indium tin oxide (ITO). ZnO has a wide band gap (3.37 eV) and a large exciton-binding energy (60 meV), exhibiting many potential applications in areas such as laser diodes, gas sensors, optoelectronic devices and devices for solar energy conversion. The ZnO nanostructures are found to have potential application in nanodevices such as a nano gas sensor. ZnO in the form of nanostructures would enhance the properties of gas sensors due to its high surface area. Apart from this, bio-safe characteristics of ZnO make it very attractive for biomedical applications. A method for economical mass production and determination of conditions favourable for the synthesis of ZnO nanostructures would therefore be very useful. This is why the study of synthesis of ZnO nanostructures and understanding the ZnO nanostructures is of great interest and technological importance [1-7].

Recently, various synthesis techniques have been developed to fabricate ZnO nanocrystals with different shapes, which include metal-catalyzed vapour-liquid-solid (VLS) growth, physical vapor deposition (PVD), chemical vapor deposition (CVD), metal-organic vapor-phase epitaxy, metal-organic CVD, template-assisted growth and oxidation method [4-11]. Many of these techniques however are complicated, needing a high temperature for synthesis and also require a long reaction time. Apart from this, these techniques also utilize toxic components and require expensive experimental setup. The oxidation method on the other hand is a simple low-cost technique and very commonly used for the synthesis of ZnO nanostructures.

Here we have shown that ZnO nanostructures could be very successfully synthesized by the simple method of oxidation. Knowing the exact temperature and holding time required for the synthesis of the ZnO nanostructures by this technique would be of great use. We have tried to ascertain how the morphology of ZnO changes with oxidation temperature. The effect of longer holding time at a particular oxidizing temperature was also studied.

Zhang et al. [8] have successfully synthesized ZnO nanostructures by oxidizing zinc foils at 700°C in air without the presence of any catalyst and carrier gas. Sekar et al. [9] reported that ZnO nanowires were grown on silicon (100) substrates by oxidation of metallic zinc powder at 600°C without the use of a catalyst. Here the ZnO structures synthesized by the simple process of oxidation of pure zinc have been found to have rod-like, belt-like, wire-like and needle-like morphologies. A wide range of morphologies of ZnO nanostructures have been reported previously in the literature [2, 3, 12, 15]. This simple method of oxidation of Zn for the synthesis of ZnO nanostructures is economical as it requires a very simple experimental setup and uses oxygen from the air. Knowledge of the exact parameters required for the synthesis of ZnO nanostructures by this route would be of great technological importance.

An economical and environment friendly route has been used here for the synthesis of ZnO on zinc. Different morphologies of ZnO both nanostructured and microstructured have been achieved by us by controlling the oxidation temperature and the holding time. The change in the morphology of ZnO with oxidation temperature as well as holding time has been tracked. Nanostructures such as nanowires, nanorods, nanobelts and nanoneedles were seen on the metallic zinc substrate. The ZnO formed on zinc has also been found to be highly stoichiometric.
MATERIALS AND METHODS

Specimen Preparation
Zinc having a purity of 99.9% was obtained from RFC Limited (RANKEM), India.

The oxidation of pure metallic zinc was performed by heating the zinc at temperatures of 300°, 400°, 500°, 600°, 700°, 800°, 900° and 1000°C for 2 hours in a muffle furnace to obtain ZnO on the surface of Zn. Zn was also oxidized at 900°C for 0.5 h to find out the effect of holding time on the growth of ZnO. A silica crucible was used for the experiments. The atmosphere in the muffle furnace was air and the oxygen present was used for oxidizing the zinc.

Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy
The morphology of ZnO that was formed on Zn was analyzed using a JEOL JSM-6480VL scanning electron microscope (SEM).

In order to identify the composition of the nanostructures formed at low oxidizing temperatures and the needle like structures formed at high oxidizing temperatures, energy dispersive X-ray spectroscopy (EDX) was performed. The JEOL JSM-6480VL scanning electron microscope was equipped with an INCA PentaFET-x3 X-ray microanalysis system with a high-angle ultra-thin window detector and a 30 mm² Si(Li) crystal.

X-Ray Diffraction and Differential Scanning Calorimetry-Thermogravimetric Analysis
X-ray diffraction (XRD) analysis of the samples was also done in order to track the formation of ZnO with oxidizing temperature. A Philips Pananalytichal X'Pert X-ray diffractometer using Cu Kα radiation (λ = 0.15406 nm) was used.

Differential scanning calorimetry/thermogravimetric analysis (DSC/TGA) of the sample was done in order to find out the temperature at which the oxidation of the pure zinc sample begins.

RESULTS AND DISCUSSION

Nanostructures have attracted the attention of researchers for their many important technological applications. The synthesis of nanostructures is a growing area of research. The synthesis of nanostructures by a low cost process would be of great technological importance [10-17]. The ZnO nanostructures were synthesized by oxidizing pure metallic Zn. Pure metallic Zn was heated at various temperatures ranging from 300°C to 1000°C for 2 h. It should be noted that Zn has a melting point of 419.5°C whereas its boiling point is 907°C. The choice of the range of oxidizing temperature was increased in order to find out the change in morphology from nanostructured ZnO to microstructured ZnO as the oxidizing temperature was increased. The holding time at all heat treating temperatures was either 0.5 h or 2 h.

Zinc has a metallic lustre but after heating, the lustre is lost and it starts to have a white layer on it, which is typical of ZnO. The SEM image in Figure 1 shows the surface of the pure metallic Zn. The morphology of ZnO that was synthesized on Zn by oxidation of Zn was investigated by using a SEM. At 300°C we found that there was no trace of formation of ZnO on the Zn surface (Figure 2a). The EDX analysis in Figure 2b also confirmed that the surface was 100% Zn. From this result we concluded that oxidation of Zn and formation of ZnO structures does not start at 300°C even when the pure Zn was held at this temperature for 2 h. Sato et al. [18] have also reported that highly conductive and transparent aluminium-doped ZnO (AZO) thin films could be prepared only at high substrate temperatures, above 300°C, using conventional d.c. magnetron sputtering. Comparison of the SEM images in Figures 1 and 2a indicates that the surface of Zn oxidized at 300°C shows some changes as compared to the surface of the as-received Zn.

A DSC/TG analysis of the pure Zn sample was done to find out the temperature at which oxidation of Zn starts and the weight gain during oxidation as a function of temperature. The TG curve in Figure 3 shows a gain in weight of 1.09%. At temperatures above 200°C there was sign of weight gain which is due to the oxidation of Zn. At temperatures above 200°C and up to 450°C a weight gain mainly due to the oxidation of Zn could be seen. Below 200°C hardly any gain in weight of Zn could be found. At 416.8°C an endothermic peak corresponding to the melting temperature of Zn can be observed in the DSC plot.
From the SEM image in Figure 4 a, b we confirmed that at the oxidizing temperature of 400°C the surface of Zn shows the formation of ZnO structures. When Zn was held at 500°C for 2 h the SEM image of the surface showed the formation of a wide range of ZnO nanostructures (Figure 5 a, b). EDX analysis of these nanostructures shown in Figure 5c revealed that their composition was almost that of stoichiometric ZnO (21.59 at. % O and 24.51 at. % Zn). At the oxidizing temperature of 600°C also we noted that the surface of Zn was completely filled with nanostructures of ZnO. As can be seen from the SEM image in Figure 6 a, b there was a wide range of nanostructures of ZnO present on the Zn surface. ZnO having structures such as nanowires, nanobelts and nanoribbons could be seen in the samples oxidized at 500°C and 600°C (Figure 5 a, b and Figure 6 a, b). On the other hand the oxidation of Zn at 700°C did not show nanostructured ZnO (Figure 7 a, b). There was a gradual increase in the size of the ZnO structure with further increase in temperature.

Figure 8 a, b show SEM images of Zn oxidized at 800°C for 2 h. Nanostructures of ZnO could not be seen at this oxidizing temperature. The EDX analysis in Figure 7c of the ZnO microstructure formed by oxidizing Zn at 700°C for 2 h shows that the at. % of Zn was 43.57% and that of O was 56.43%, suggesting that highly stoichiometric ZnO was formed at this temperature. The EDX spectrum showed that only O and Zn elements were detected, confirming the formation of pure ZnO. Synthesis of stoichiometric ZnO having high purity has also been reported earlier [12].

The SEM observations show that rod-like or needle-like structures of ZnO formed at temperatures between 700-1000°C and ZnO nanostructures could not be found at these oxidizing temperatures. The ZnO that grew on the surface of the metallic Zn at temperatures between 700-1000°C seems to have a smooth surface and also seems to be highly adhered to the surface of the metallic Zn substrate.

Figure 8 a, b are the SEM images of pure Zn oxidized at 800°C for 2 h. The ZnO rods formed in Zn samples oxidized at 900°C for 2 h were found to be mostly triangular in shape (Figure 10 a, b). Its thickness reduced gradually from the base to the tip. The thickness of the base of the ZnO structures formed on Zn surface after oxidation at 900°C for 0.5 h was less than 1 µm and there were a large majority of the ZnO structures having thickness much less than 1 µm (Figure 9 a, b). Their heights were relatively large and some of the structures were almost 10 µm long. On the other hand the thickness of the base of the majority of the ZnO structures formed on the Zn surface after oxidation at 900°C for 2 h were higher than the ZnO structures formed at 900°C for 0.5 h (Figure 10 a, b). This was possibly due to the longer period of holding time during oxidation which allowed the ZnO structures to grow in thickness. Their heights were comparatively much lower and were in the range of 3-4 µm. The ZnO structures formed by oxidation at 900°C for 0.5 h looked much thinner as compared to the ZnO structures formed by oxidation at 900°C for 2 h. It can be concluded that holding Zn sample for a longer period of time at a particular temperature led to ZnO structures having larger cross-sectional area and relatively shorter height. The diameter of the ZnO structures gradually becomes smaller along the growth direction, leading to a tapered structure with a sharp tip.

The ZnO structures that were formed at 900°C for 2 h were faceted and triangular in shape and seemed to be more needle-like or rod-like whereas the ZnO structures that formed at 900°C for 0.5 h were not triangular and faceted and seemed to have a more leaf-like thinner structure. EDX analysis confirmed that the at. % of O was 52% and the at. % of Zn was 48% in the ZnO formed by oxidizing pure Zn at 900°C for 2 h (Figure 10c). Nearly stoechiometric ZnO could be synthesized by oxidation of Zn in air.

ZnO nanostructures could be synthesized by oxidizing pure metallic Zn for 2 h at temperatures between 400-600°C whereas at oxidizing temperatures above 700°C needle-like or rod-like microstructures could be seen. Clearly, the size of ZnO depends on the oxidizing temperature, i.e. the higher the oxidizing temperature the larger the size of the ZnO structures. Higher temperatures led to more vigorous oxidation and resulted in mostly columnar needle or rod-like structures which were faceted whereas oxidation at lower temperatures resulted in nanostructured ZnO. At oxidation temperatures ranging from 400-600°C nanostructured ZnO having a wider range of structures was found.

The XRD patterns of the Zn samples oxidized at 300°C, 400°C, 700°C and 800°C are shown in Figure 11. The XRD plots showed that all the peaks of ZnO could be traced in the XRD profile of the sample formed by oxidizing Zn at 700°C for 2 h. The diffraction peaks were sharp and no diffraction peak from other impurities were detected in the spectrum, indicating that the as-synthesized product was pure ZnO having high crystallinity and high purity. The formation of ZnO could not be traced in the XRD analysis of samples formed by oxidizing Zn at 300°C and 400°C although SEM image showed the formation of ZnO at 400°C. This is possibly due to the low intensity of the peaks of the ZnO formed at 400°C as they had
1. Subramanyam, T. K., Naïdu, B. Srinivasulu, Uthanna, S. Cryst. Thermogravimetric and SEM analysis suggests that oxidation takes place only above 200°C. The needle-like or rod-like structures of ZnO were found to grow very uniformly in size and shape and were very densely located on the metallic Zn surface at oxidation temperatures ranging from 700-900°C in comparison to the various nanostructured ZnO, which grew less densely and looked more scattered and non-uniform in size and structure. Formation of ZnO was confirmed only at temperatures above 300°C. Comparison of the results of thermogravimetric and SEM analysis suggests that oxidation takes place only above 200°C and structures of ZnO could be seen at oxidizing temperatures above 300°C.


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Figure 10: (a-b) SEM images of pure zinc oxidized at 900°C for 2 hours. (c) EDX analysis of the oxide.