ZnO flowers by forced hydrolysis of ammonium zinc complex on hot glass substrates

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A simple solution growth method for preparing nanostructured ZnO flower-like particles has been developed. The method is based on the forced hydrolysis of aqueous solution of tetra ammonium zinc complex [$Zn(NH_3)_4^{+2}$] on hot glass substrate kept at 80 ^oC. Scanning electron microscopic studies reveal that these flowers consist of a c-axis oriented round rod of around 500 nm diameter with five or six triangular petals of length ~ 500 nm. The diameter of each flower is about 1.5 μm. X-ray diffraction studies show that particles are out-of-plane textured along c-axis.

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1. Introduction

Hydrolysis of aqueous solution of tetra ammonium zinc complex yields ZnO as given by the reaction [1]:

$$Zn(NH_3)_4^{+2} + 2OH^- \longrightarrow ZnO + 4NH_3 + H_2O \quad \text{..... (1)}$$

This has been the basis for solution growth of textured ZnO thin films [2-7] and nanostructured particles [1,8]. Films are formed on substrates by heterogeneous nucleation of ZnO. The deposition temperatures of 50 ^oC and above have been reported [2-6] for films. Above 80 ^oC deposition of ZnO film is due to forced hydrolysis (Eqn. (1)). Chaudhuri et al. [2] reported the chemical bath deposition (CBD) of ZnO films on glass above 80 ^oC. These films were out-of-plane textured along c-axis with 1-2 μm conical shaped grains. ZnO buffer layers for $CuInS_2$ solar cells were deposited by Ennaoui et al. [3] from $Zn(NH_3)_4^{+2}$ solution at 65 ^oC. Later, Yamada et al. [4] also developed CBD ZnO films as buffer layers for $Cu(InGa)Se_2$ solar cells. They deposited c-axis oriented ZnO films on glass from an aqueous solution of $Zn(NH_3)_4^{+2}$ at 50 ^oC. Preparation of c-axis textured ZnO films on glass from of $Zn(NH_3)_4^{+2}$ solution at 50 ^oC was reported by Shinde et al. [5] . $Zn(NH_3)_4^{+2}$ aqueous bath is also used for deposition of ZnO films by successive ion layer adsorption and reaction (SILAR) by Mitra and Khan [6]. In this process a substrate is first coated with a complex layer by dipping in $Zn(NH_3)_4(OH)_2$ bath at room temperature. The complex layer is then converted to ZnO film by dipping the coated substrate in hot water at near boiling point. During the hot-water dip (at ~ 95 ^oC) $Zn(NH_3)_4^{+2}$ decomposes to ZnO as per Eqn. (1). Recently, preparation of out-of-plane textured and microstructured ZnO films on glass from $Zn(NH_3)_4^{+2}$ bath at above 80 ^oC has been reported by Chaudhuri and Kothari [7]. ZnO flower-like particles have been also deposited from $Zn(NH_3)_4^{+2}$ solution by forced hydrolysis [1,8,9] above 80 ^oC.

It is clear from earlier investigations [1,2,6-9] that ZnO can be produced by forced hydrolysis of aqueous solution of $Zn(NH_3)_4^{+2}$ above 80 ^oC. It implies that some deposition is likely to occur if $Zn(NH_3)_4^{+2}$ solution is brought in contact with a hot substrate above 80 ^oC. Exploratory experiments showed that a thin ZnO layer did form on hot glass substrate and the layer consisted of nanostructured flowers. This brief note reports a simple method of preparing a layer of nanostructured flowers of ZnO by forced hydrolysis of $Zn(NH_3)_4^{+2}$ solution on hot glass substrate. ZnO flowers are characterized by Scanning electron microscope (SEM) and X-ray diffraction (XRD).

2. Experimental

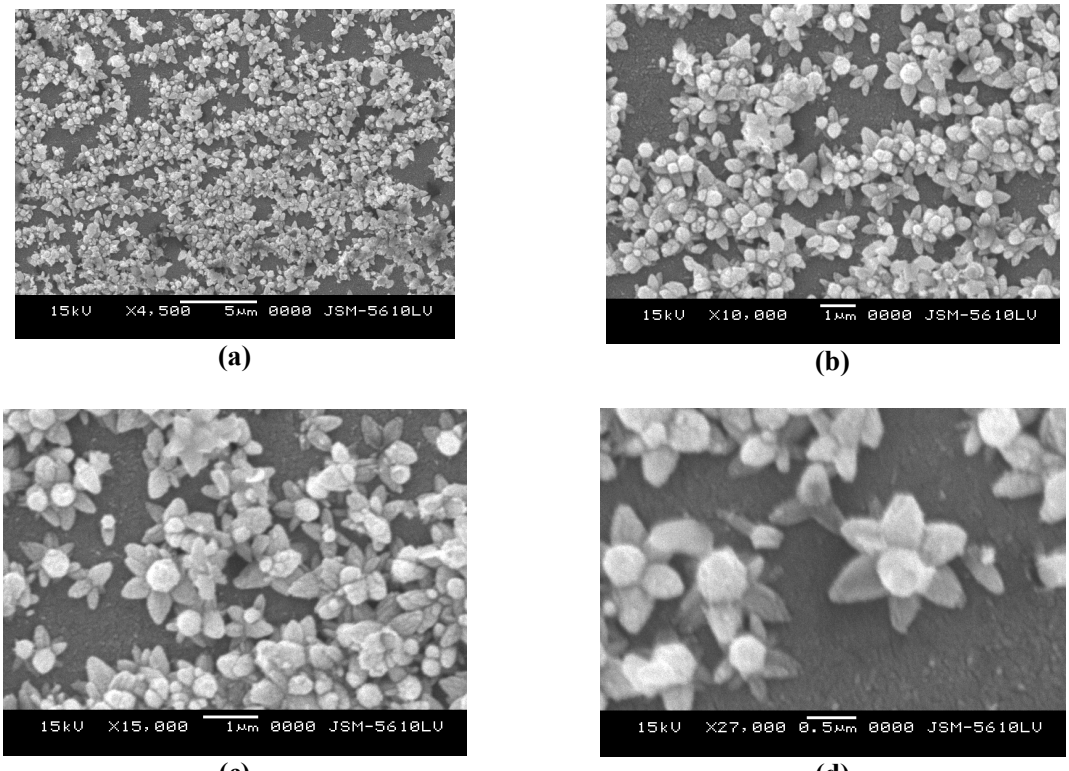
Precursor solution of $Zn(NH_3)_4^{+2}$ was prepared from aqueous solutions of $Zn(CH_3COO)_2.2H_2O$ (0.1667 M) and NH_4OH (5%) as described earlier [2,6]. 60 mL of $Zn(CH_3COO)_2.2H_2O$ solution was taken in a 100 ml beaker and NH_4OH was poured slowly into it. The content of the beaker was vigorously stirred by a magnetic stirrer. At first, curd-like white precipitate was formed which slowly dissolved on further addition of NH_4OH. NH_4OH was added till the solution became clear. The final volume of deposition solution was about 85 mL with pH of around 10. The final solution was continuously stirred for 5 min. The chemicals used were of analytical grade supplied by Merck Ltd., Mumbai, India.

A glass substrate was kept on a hot plate and heated above 80 ^oC. About 2 mL of $Zn(NH_3)_4^{+2}$ solution was spread on the substrate. After about 5 minutes the substrate was removed, washed in distilled water and dried in an oven at 100 ^oC. A whitish semi-transparent film was deposited. Cleaned glass slides of size 7.5 × 2.5 × 0.145 cm^3 (Blue Star, Polar Industrial Corporation, Mumbai, India) were used as substrates. The substrates were ultrasonically cleaned in chromic acid, distilled water, acetone, methanol and dried in warm air.

The morphology and structure of the films were studied with a Jeol (JSM-5610LV) Scanning Electron Microscope. The composition and texture of the films were determined from XRD plots (θ - 2θ) recorded with a Philips (X'Pert) X-ray Diffractometer (using Ni-filtered CuKα radiation) from 20 to 80^o. Transmission spectra of the films were measured from 300 to 1100 nm with a Shimadzu (UV-1700) spectrophotometer.

3. Results and discussion

A whitish translucent ZnO film forms on a hot glass substrate (kept at > 80 ^oC) from a layer of $Zn(NH_3)_4^{+2}$ solution. The SEM microphotographs of this film are presented in Fig.1.



(a) **(b)** **(c)** **(d)**

Figure 1 Scanning electron micrographs of ZnO flowers deposited on hot glass

It can be seen from Fig.1 (a) and (b) that the film is essentially an array of particles that are like flowers. Each particle is a well formed flower. The size of each flower is about 1.5 μm across. Fig. 1(c) shows a closer view of few such flowers. Each flower (particle) consists of a central round rod of about 500 nm diameter with five or six radially aligned triangular petals arranged in a plane. The lengths of these petals are about 500 nm with bases of about 400 to 500 nm. Fig.1(d) gives a closer view of such nanostructured flowers.

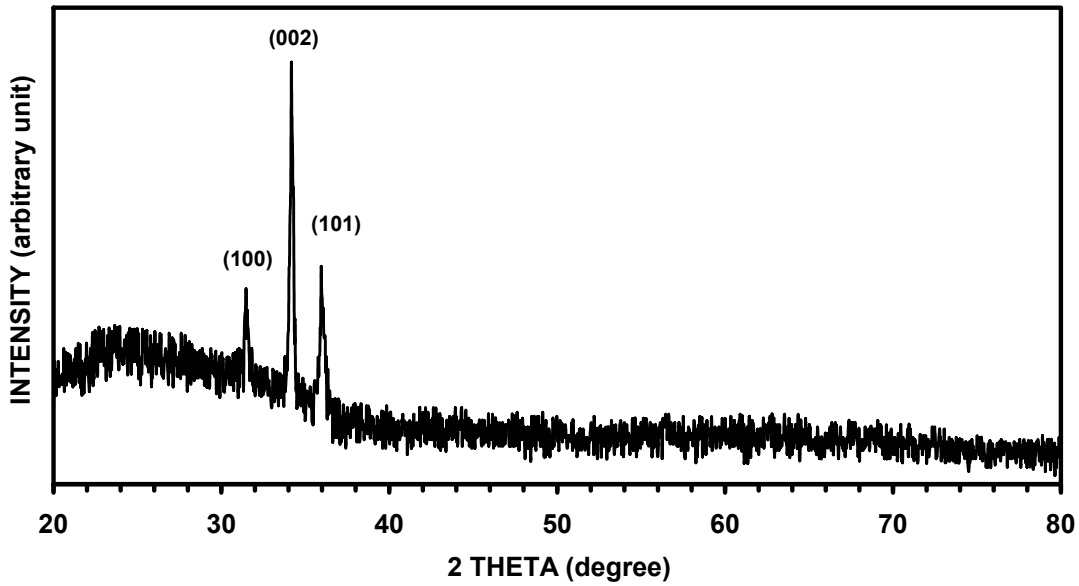


Fig. 2 X-ray diffractograph of ZnO film deposited on hot glass.

The XRD plot of a typical film is shown in Fig. 2. The XRD lines are identified to be (100), (002) and (101) of hexagonal ZnO (JCPDS File No. 36-1451). Strong (002) line indicates that the film is out-of-plane textured along c-axis. XRD study and SEM images suggest that the central rods are c-axis oriented and out-of-plane aligned.

The transmission (T) spectrum of a typical ZnO film in the wavelength range 300 to 1100 nm is presented in Fig. 3. T of these films is below 60 % due to granularity. A sharp decrease in T below 400 nm is also observed which is because of energy band edge (3.37 eV) absorption.

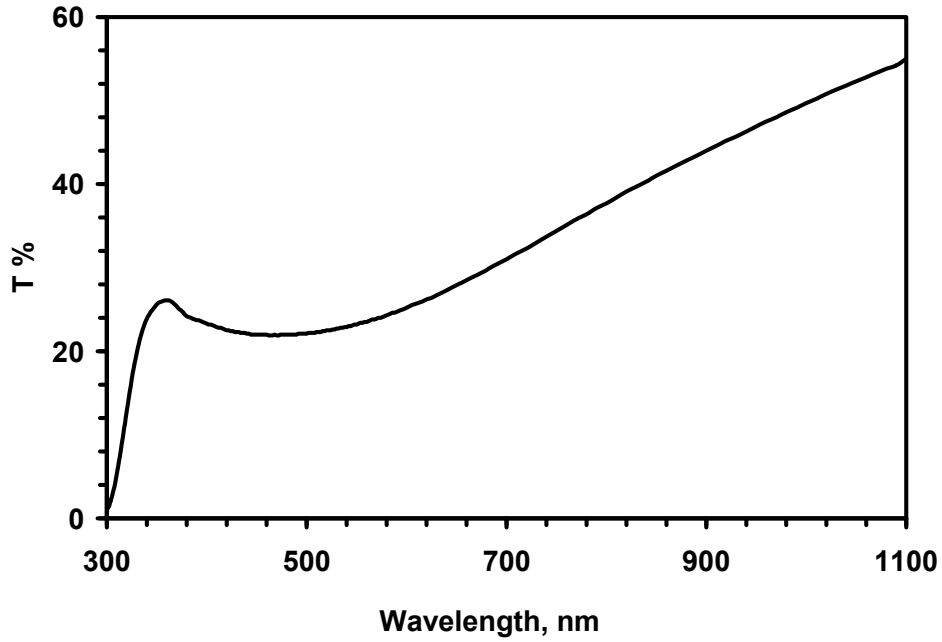


Figure 3 Transmission spectrum of ZnO film deposited on hot glass.

It was observed that adding NH_4OH to an aqueous solution of $Zn(CH_3COO)_2.2H_2O$ produced curd white precipitate which dissolved on further addition of NH_4OH. The precipitate is due to the formation of $Zn(OH)_2$ according to the reaction :

$$Zn(CH_3COO)_2 + 2\,NH_4OH \rightarrow Zn(OH)_2 + 2\,NH_4(CH_3COO) \quad .....(2)$$

Adding more NH_4OH to the solution dissolves $Zn(OH)_2$, forming tetra ammonium zinc hydroxide

$$Zn(OH)_2 + 4NH_4OH \rightarrow Zn(NH_3)_4(OH)_2 + 4H_2O \quad .....(3)$$

This resulted in a clear solution of $Zn(NH_3)_4(OH)_2$. The overall reaction leading to formation of $Zn(NH_3)_4(OH)_2$ is (adding (2) and (3)):

$$Zn(CH_3COO)_2 + 6NH_4OH \rightarrow Zn(NH_3)_4(OH)_2 + 2NH_4(CH_3COO) + 4H_2O \quad .....(4)$$

$Zn(NH_3)_4(OH)_2$ dissociates as

$$Zn(NH_3)_4(OH)_2 \rightarrow Zn(NH_3)_4^{+2} + 2OH^- \quad .....(5)$$

ZnO particles are formed by forced hydrolysis of $Zn(NH_3)_4^{+2}$ as depicted by the reaction

$$Zn(NH_3)_4^{+2} + 2OH^- \rightarrow ZnO + 4NH_3 + 2H_2O \quad .....(6)$$

When $Zn(NH_3)_4(OH)_2$ solution is heated above 80 ^oC, the ionic product exceeds the solubility product and precipitation occurs on the substrate and in the solution to form ZnO nuclei and thus ZnO particles deposit on the substrate by forced hydrolysis.

Solution processed ZnO particles with varied flower- or star-like nanostructures have been reported [1,8,10] earlier. However, these particles generally consisted of spherical arrangement of needles or rods which is in contrary to well-defined flowers observed in the present investigation. ZnO has a hexagonal lattice, with an a : c axial ratio of 1 : 1.6. The most common morphologies observed are either rod-like or needle-like crystals, elongated in the c-axis direction and with hexagonal prismatic faces. ZnO crystals also exhibit twinning and fourling [10] growth. The formation of flower-like particles is attributed to this property.

The deposition of ZnO particles on hot glass substrate may be explained as follows. When surface of hot glass (~80 ^oC) substrate comes in contact with $Zn(NH_3)_4^{+2}$ solution, ZnO nucleation centres are created by forced hydrolysis as mentioned in Eqn.(6). Later the whole mass of solution on the substrate attains 80 ^oC and ZnO molecules are formed again by forced hydrolysis. These ZnO molecules attach

themselves to the nucleation centres produced earlier resulting in c-axis oriented growth of particles. The high tendency of twinning leads to formation of flower-like structure.

4. Conclusion

A simple method for synthesis of nanostructured ZnO flowers has been developed. The method utilizes the forced hydrolysis of aqueous solution of $Zn(NH_3)_4^{+2}$ on a hot substrate at temperature above 80 ^oC. Each flower consists of a c-axis oriented round rod of around 500 nm diameter with five or six triangular petals of length ~ 500 nm.

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