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Air annealing induced growth of self-assembled ultra long ZnS microwire: Structural and photoluminescence studies

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ABSTRACT

In an attempt to facilitate annealing assisted self assembly, we have grown amorphous ZnS films using rapid vacuum evaporation technique and followed by air annealing at an elevated temperature for longer duration. It has been found that ultra long microwires were formed as a consequence of air annealing assisted asymmetric mass flow. However on further increase in annealing temperature the microwires were found to be squeezed, forming larger macromolecules. XRD studies revealed the gradual transition from amorphous to crystalline phase with preferential orientation along (008) hexagonal phase. Photoluminescence studies revealed multiple defect transition caused by annealing.

1. Introduction

Zinc sulphide has been one of the most promising wide band gap semiconductor owing to its numerous potential applications in optoelectronic device fabrication, namely, as buffer layer in solar-photovoltaics [1], thin film phosphors for electroluminescent device applications [2], non-linear optical device [3] nano-wire based UV photodetector, sensor, IR window, photocatalysis etc [4–6]. Transitional metal doped ZnS would give rise to bandgap tailoring which finds its application in fabricating light emitting diode and electroluminescence devices [7]. Various techniques have been employed to deposit ZnS thin films, including MBE (molecular beam epitaxy) [8], CBD (chemical bath deposition) [9,10], CVD (chemical vapor deposition) [11] and spray-pyrolysis [12], thermal evaporation [13,14].

Considering thermal evaporation deposition technique, much work has been devoted on studying ZnS film properties as a function of substrate temperatures. Fang et al. [13] demonstrated the growth of various kinds of ZnS nanostructure (with different morphologies and size) as a function of catalyst and substrate temperature. Chen et al. [14] reported the synthesis of branched architecture of ZnS as the functional material for specific optoelectronic applications. Kurbatov et al. [15] stated that substrate temperatures is one of the important characteristics in determining the structural and sub-structural properties of ZnS. However few reports are there to study the effect of annealing temperature on structural and morphological configuration of ZnS; particularly where the amorphous natures of the thin films were involved and how significant structural change to be realized owing to self assembly. ZnS nano-materials like nano-wires, nano-rods or nano-ribbons exhibit special optical and electrical properties [16,17]. Lin et al. prepared hexagonal ZnS nano-wires on Au-coated Silicon substrate by VLS (vapor-liquid-solid) method [18]. Growth of such ZnS nanostructures by thermal evaporation has been reported to be facilitated by the formation of intermediate Au-ZnS nano-composite; which is believed to be responsible for the growth of ZnS nano-wires [19]. Unlike previous studies, which essentially involve the growth of nano-structured ZnS with the assistance of either temperature or catalytic support during the growth stage; we investigate the structural and morphological transformation to be taken place owing to post growth annealing. In this work, the as-grown ZnS films were made to be amorphous and subsequent post-growth, air-annealing was carried out at elevated temperatures ranging from 350 °C to 550 °C in a box-furnace to facilitate self-assembly and improvement in crystal quality. The impact of rapid thermal annealing would possibly trigger local molecular reorganization and self assembly, giving rise to structural and morphological transformation. So in this process, annealing was carried out by inserting the samples in the box furnace at the specified temperature without allowing the molecules to readjust themselves. Furthermore, we used amorphous phase of the ZnS material, with relatively higher molecular mobility, as compared to polycrystalline phase, when subjected to heat treatment. The samples were subjected to structural, morphological and optical analysis. The results were properly investigated and co-related. To the best of our knowledge, no paper has yet been published on annealing induced structural transformation from amorphous to crystalline phase compounded with morphological transformation into microwire by self assembly

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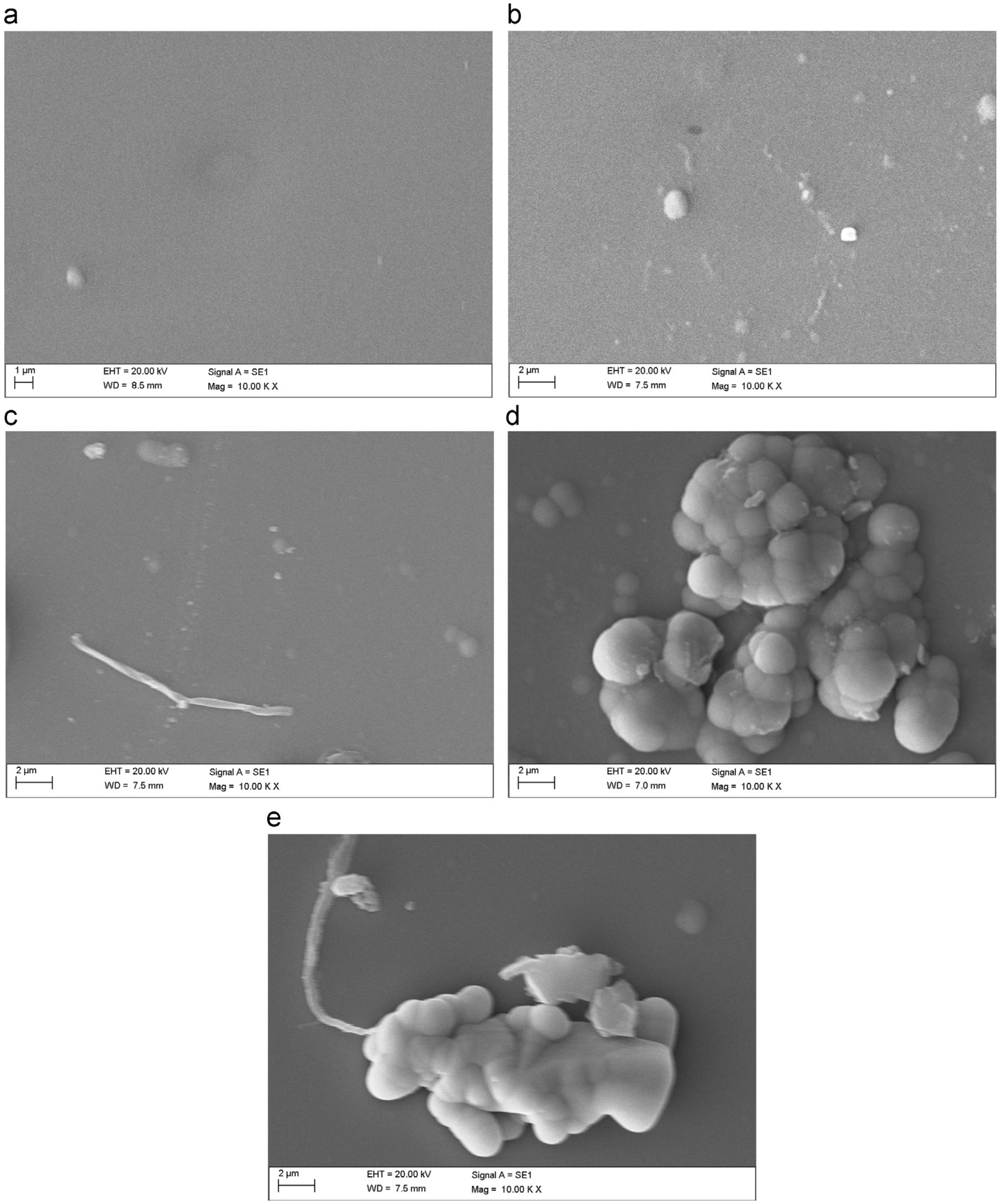

Fig. 1. a-e: Representative SEM images of air annealed ZnS thin films (T_2–T_5), d and e represents SEM images of T_5 at two different locations.

2. Experimental

ZnS thin films were grown on sodalime glass-substrates, using vacuum evaporation technique. The glass slides (74 mm × 24 mm × 1.3 mm) were initially sonicated in water-ethanol solution (3:1 v/v) for 10 min and then etched in 37% HCl acid for 30 min. High purity (99.99%) ZnS powder (Sigma Aldrich– 10 µm) was evaporated from a quartz crucible, placed inside molybdenum crucible-holder by applying constant supply current of 145 A for 2 min. The deposition was carried out at a base pressure of 10^{-5} mbar, with a source-to-substrate distance of 17 cm. The high current would initiate higher deposition rate, which in turn would give rise to amorphous nature of as-grown film as confirmed from XRD analysis (to be discussed later). The depositions were carried out without any substrate heating, as substrate heating too can induce improved crystallinity of the as-deposited films. The as-grown films were smooth, pinhole free and strongly adherent to the substrate. The thickness of the films was measured using weight difference method and was found to be around 300 nm. The samples were annealed in box-furnace in presence of air at around 350 °C, 450 °C, 500 °C and 550 °C for 2 h each. Henceforth, the as-grown and annealed samples would be referred to as T_1, T_2 T_3, T_4 and T_5 respectively.