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Organometallic chemical vapor deposition of compound semiconductors

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Abstract

Nano-sized zinc oxide (ZnO) was prepared by metal organic chemical vapor deposition (MOCVD) in a sulfonated polystyrene matrix. The effects of ultraviolet light irradiation on the growth of ZnO was examined. Scanning electron microscopy (SEM) analysis reveal that the ZnO nanoparticles have polycrystalline hexagonal wurtzite structure. The photodeposited films showed lower resistivities relatively to the non-irradiated films at 150 °C. Quantum chemistry was used to investigate the possible reactions of diethylzinc (DEZ) on PS-SO_3H surface. The semiempirical simulations at PM3 level indicates strong interactions of DEZ with the polymeric surface and may be able to explain the growth of the highly crystalline ZnO on the polymeric substrate, as observed experimentally.

Keywords: Zinc oxide; Organometallic vapor deposition; Thin films; Polymeric substrates

1. Introduction

In recent years a large number of techniques have been developed to the production of nanocrystaline zinc oxide (ZnO) since this II–VI semiconductor is a very prosperous material extensively used in catalysis, rechargeable batteries, fuel cells, gas sensors, photocells, electrochromic devices and varistors [1–4].

The metal organic chemical vapor deposition (MOCVD) of compound semiconductors represents today one of the most important research area of nanotechnology. It provides an efficient synthetic rout for the production of materials in nanometric scale with desirable physical properties that are often inaccessible by conventional routes of materials synthesis.

Nowadays, there is a great interest in replacing glass by polymer substrates, particularly in flat-panel display technology where low volume, light weight, robustness and flexibility are relevant properties [5]. In the present work, we have attempted to evaluate the potential of sulfonated polystyrene (PS-SO_3H) films as substrate to the ZnO deposition by MOCVD technique.

2. Experimental

Sulfonated polystyrene films were obtained after immersion of polystyrene films (100 μm of thickness) in chlorosulfurous acid ($HClSO_3$) for 2 h at 25 °C followed by ultrasonically cleaning and drying in N_2 atmosphere at 60 °C for 24 h. The 10% sulfonation degree was estimated by FTIR spectroscopy.

A high-pressure mercury lamp (500 W and λ = 280 nm) was employed as a UV light source for the photo-MOCVD ZnO deposition onto sulfonated polystyrene films.

Diethylzinc (DEZ, $Zn(C_2H_5)_2$) and O_2 reactant gases were alternatively fed in the reaction chamber with argon as carrier gas. The pressure in the chamber during photo-MOCVD ZnO deposition was 101.3 kPa and the PS-SO_3H temperature was varied from 373 to 473 K.

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Semiempirical calculations for the PS-SO_3:Zn(C_2H_6)$_2$ charge transfer complexes were done using the PM3 parameterization (MOPAC 2000).

The DC resistivity properties of the deposited ZnO films were measured by the four-point probe measurement (610C-Keithley) and the crystal morphology was analyzed by scanning electron microscopy (SEM, Phillips XL30).

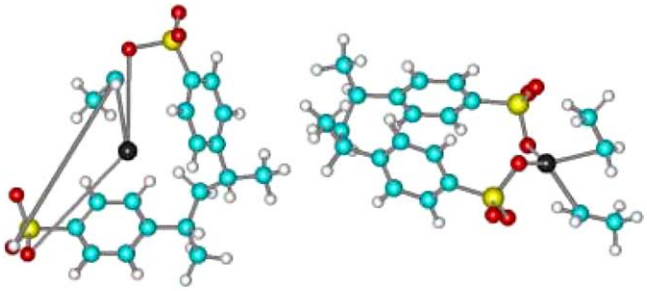
3. Results and discussion

Fig. 1A shows the SEM micrography of the photo-MOCVD deposited ZnO films. It shows a hexagonal morphology characteristic of the polycrystalline ZnO.

The resistivity dependence of the photo-MOCVD ZnO deposition on PS-SO_3H temperature was examined and the results are shown in Fig. 1B. The observed lower resistivities may be attributed to the better crystallinity of the ZnO photodeposited as demonstrated by XRD spectroscopy analysis in Fig. 1C. The diffraction peaks can be indexed to the wurtzite structure (hexagonal phase) with cell constants of a = 3.24 Å and c = 5.19 Å. At the same time, no diffraction peaks from other species could be detected, which indicates that all the precursors have been completely decomposed.

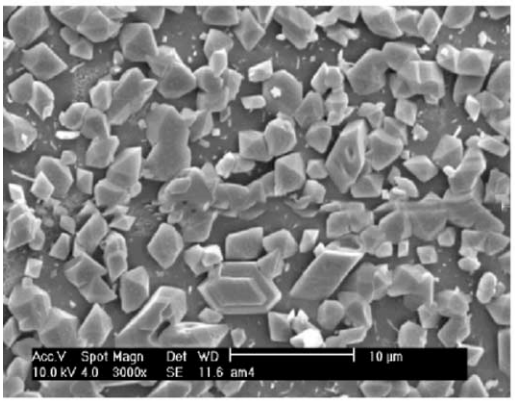
The nucleating capability of PS-SO_3H may be correlated with the interaction between the diethylzinc and the polymeric matrix, initiating the formation of subcritical nuclei ZnO which grow to the critical size needed for the crystal growth.

The following molecular $C_2H_3ZnSO_3$-PS structures (A) and (B) with optimized geometry minimized on the potential energy surface at PM3 level (MOPAC) may be proposed to explain the formation of ZnO onto PS-SO_3H surface:

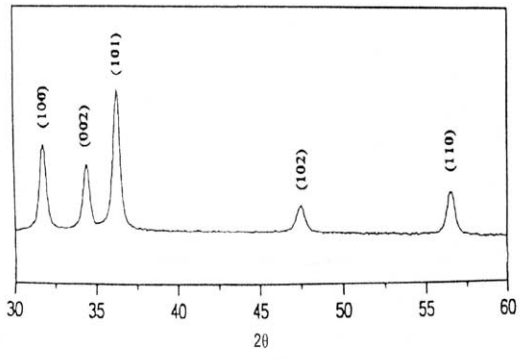


$C_2H_3ZnSO_3$-PS (A) $[C_2H_5]_2ZnSO_3$-PS (B)

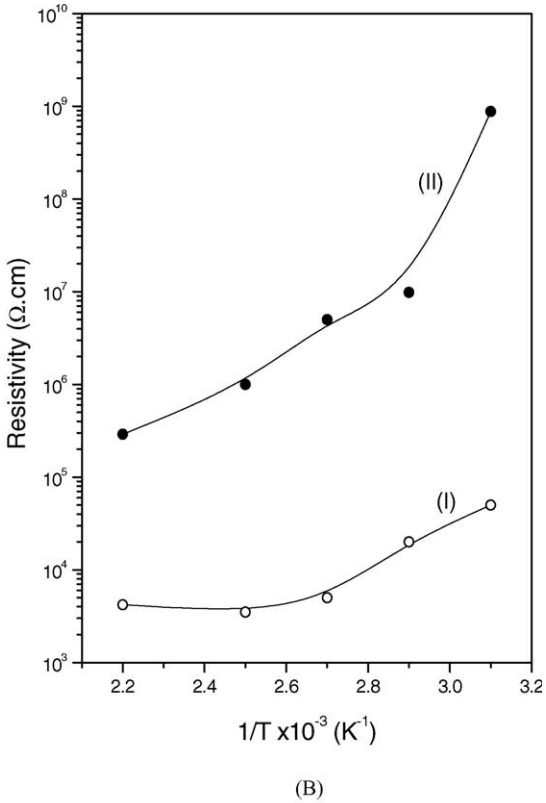
The geometrical structures of $C_2H_3ZnSO_3$-PS and $[C_2H_5]_2ZnSO_3$-PS as two possible precursors molecules for the photo-MOCVD ZnO deposition on the polymeric substrate was investigated in this work. We have calculated both the total energy of the precursor molecules (DEZ) and



(A)



(C)



(B)

Fig. 1. SEM micrograph (A) and XRD pattern (C) of photo-MOCVD ZnO crystals on PS-SO_3H matrix. The resistivity dependence on substrate temperature is shown in (B): thermal MOCVD (I) and UV-MOCVD (II).

the energies of the respective ligands as radicals. The difference can be interpreted as average bond energy of the ligands to the central zinc atom.

The calculated binding energy for $[Zn(C_2H_5)_2]$:SO_3-PS and $C_2H_3ZnSO_3$-PS are 28.00 and 35.7 kJ mol^{-1}, respectively. The results suggest that the formation of adducts of larger dimensions, for example, through the reaction of $Zn(C_2H_5)_2$ with PS-SO_3H, would require overcoming a similar energetic barrier.

The results enables one suggest that the C_2H_3Zn species reduce the charge density in sulfonic groups with the displacement to electronic charge to the Zn atom promoting the formation of the highly polarized ZnO precursor, $C_2H_5ZnSO_3$-PS structure. This results leads to the proposition of the following mechanism to explain the formation of ZnO onto PS-SO_3H surface:

$$Zn(C_2H_5)_2 \rightarrow C_2H_3ZnSO_3{-}PS + C_2H_4$$

$$C_2H_3ZnSO_3{-}PS \xrightarrow[O_2]{h\nu} ZnO : SO_3{-}PS + C_2H_4$$

4. Conclusion

ZnO thin films with good electric properties have been prepared on polymeric substrate (PS-SO_3H) by photo-MOCVD technique. The samples are polycrystalline with a hexagonal wurtzite structure. The good electrical properties and crystallinity structure of the ZnO photo-MOCVD deposition indicate that the PS-SO_3H substrate may serve as a new type of potential substrate for the photo-MOCVD growth thin films.

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