ZnO NANOPARTICLES AND THEIR APPLICATIONS – NEW ACHIEVMENTS

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Abstract

The biggest advantages of ZnO are a low price, good gas sensing properties, photocatalytic activity, antibacterial activity, possibility to prepare structures with interesting optical properties, like photonic crystals, catalytic materials, in small amounts ZnO is not toxic, etc. There is a lot of different methods of ZnO nanostructures preparation, like MOVPE, high temperature evaporation, gas spraying, pulsed laser deposition, sputtering, sol-gel, wet chemical and electrochemical methods. In our laboratory the special research type of MOCVD apparatus combining possibility of plasma exciting oxidizer like N2O, separate branch with DEZn in Ar, UV irradiation of the deposition area, low pressure operation and inertless infrared radiation furnace has been developed. In the study we have investigated the influence of the growth rate on the morphology of ZnO deposited on Si (100), GaP (111) as well as nanoporous GaP substrates. The same apparatus has been used for ZnO nanoparticles preparation with the diameter of individual nanoparticles of about 25 nm.

Keywords: ZnO, nanoparticles, MO CVD, morphology.

1. INTRODUCTION

Zinc oxide is frequently used in several areas of technology. It is worthy to investigate high-quality self-textured ZnO films synthesized on different kinds of substrates. In this study we investigate influence of the growth rate on morphology of ZnO deposited on Si (100) and GaP (111) substrates. Photoluminescence study was used for comparison of the growth condition influence on quality of the deposit.

In the second part of the contribution we try to list some very important new areas of research ZnO. These are in particular : the core–shell nanorods for the photovoltaic dye-sensitized solar cells, transparent conducting oxide thin films, thin film transistors, removal of the hydrogen sulfide from natural gas streams,coal gas and chemical feedstocks, chemical gas sensors, diluted magnetic semiconductors, photocatalysis and toxicity.

2. EXPERIMENTAL

In our laboratory the special research variant of the MOCVD apparatus combining possibility of plasma exciting oxidizer N_2O, separate branch with DEZn in Ar, UV irradiation of the deposition area, low pressure operation and inertless infrared radiation furnace was developed. In this study we investigated influence of the growth rate on morphology of ZnO deposited on Si (100) and GaP (111) substrates. Growth rate was adjusted to changing the vapor phase composition and to obtain the highest growth rates, also the substrate position in gas stream was optimised simultaneously. In our experiments surface morphology of the ZnO/Si (100) and ZnO/GaP(111) structures at relativelly slow growth rate app. 1-3 μm/ hour are nanowalls type. The quantity of rods with diameters up to 500 nm in layers morphology increases when the growth rate increases up to 80 μm/hour. In the surface morphology of more than 10 μm thick ZnO layers on Si (100) and

GaP (111) dominates the hexagonal pyramids with diameter up to 3000 nm, [9]. Generally the surface morphologies of the thick ZnO layers on both substrates are very similar. First part of this ZnO/GaP structures is polycrystalline with small grains dimension. Low temperature photoluminescence studies of the prepared layers confirm significantly deteriorate optical properties ZnO layers prepared on GaP substrates. Similarity in final morphology of the ZnO on both substrates corresponds to the selforganization of numerous ZnO molecules and long-range spatial correlation under non-equilibrium conditions similarly with CdO [1]. It affects morphology of the second stage of the ZnO deposits. Another evidence of the same mechanisms illustrates Fig 1, where identical morphology of ZnO was observed on two perpendicular planes of the Si substrate. The same apparatus has been used for ZnO nanoparticles preparation with the diameter of individual nanoparticles of about 25 nm.

2. 1. Selforganization

Self-organization as very important phenomena in nanotechnology is often observed in non-equilibrium systems as a modification toward the equilibrium. It is very important to know origin, complexity, correlation of self-organization phenomena. Recently, many research works on self-organization have been reported, especially in the fields of quantum dots, nanowires, nanotubes, and other nanostructures [1]. Seo et al. [2] reported a simple, effective, and innovative approach based on ion assisted self-organization. It is used to synthesize size-selected Si quantum dots on SiC substrates at low substrate temperatures. Nakamura et al. [3] prepared two- dimensional nano-arrays of Ge quantum dots with the ability to self-repair by self-organization on Si substrate using an ultra-thin SiO_2 film technique. Choi et al. [4] reported the self-organized pore formation behavior of porous anodic alumina by investigating correlation between morphological change at themetal oxide interface and current–time characteristics during anodization. Tsybeskov et al. [5] investigated strain- induced lateral self-organization in Si/SiO2 nanostructures, and found that the Si nanolayers exhibited a low density of structural defects and were elastically strained with respect to the crystal Si substrate. Ruffino etal. [6] studied Au/Si nanodroplets towards Si nanowires formation,and discussed characterization of the thermal-induced self-organization mechanism. Self-organization phenomena at semiconductor electrodes were also found. Foell et al. [7] reported that anodically dissolving semiconductor electrodes such as Si,Ge,GaAs,InP,or GaP exhibit a number of self-organization phenomena

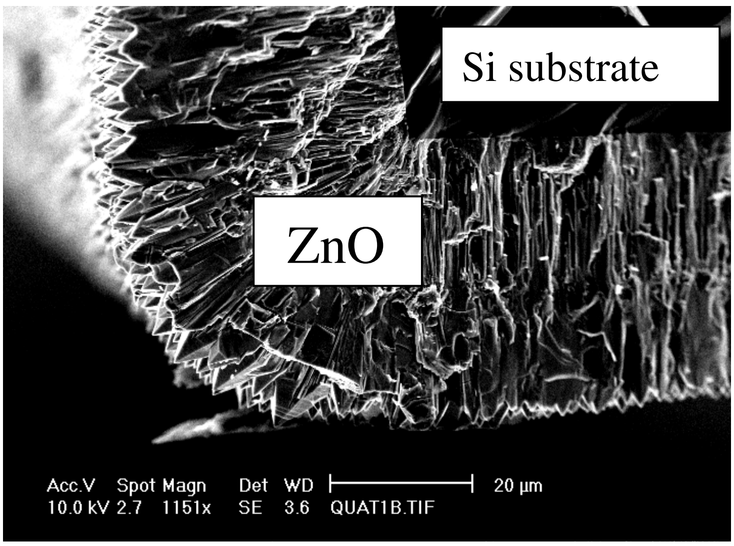

Fig 1. Identical ZnO morfology on two perpendicular plane sof the Si substráte.

such as current oscillations in time and/or in space. List of selforganization studies could be very extended. We suppose self organization of the ZnO particles at the MOCVD deposition as a more important phenomena than substrate pulling effect.

Fig 2. shows near band edge (NBE) photoluminescence spectra at 4 K from ZnO/Si films. The spectra are recorded with 325 nm HeCd laser and excitation densities of 5 W.cm^{-2}. A strong luminescence in the UV region corresponds to the known PL lines for epitaxial and bulk ZnO. The observed NBE PL has a structure corresponding to the lines of bound excitons (BE), two electron satellites (TES) and their LO phonon replica (~72 meV). In our best samples (grown at high growth rate 80 μm/hour) the BE peak at 3.36 eV exhibits FWHM of ~4 meV, while the intensity of the TES peak is substantially lower compared to the BE

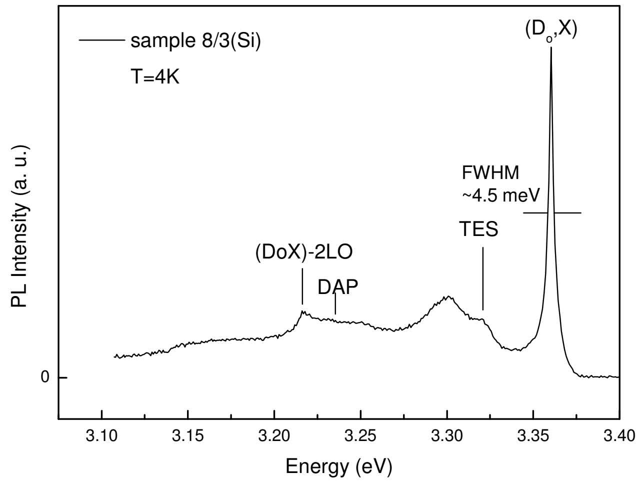

Fig 2. ZnO/Si PL spectra at 4 K.

The same apparatus has been used for ZnO nanoparticles preparation. Dimension of the idividual nanoparticles of ZnO prepared in described apparatus at 15 torr reaction pressure approaches 25 nm.

3. NEW DIRECTION of THE ZnO- NANOPARTICLE DEVELOPMENT

The optimal electrode geometry for the photovoltaic dye-sensitized solar cells (DSSC) is provided by a core–shell nanorod with the conducting core being coated by a TiO2 or ZnO shell that would support the dye on the outside. The roughly parallel nanorod array should be anchored to a substrate that would form the collection electrode. The nanorod surface provides as an effectively large heterojunction area, while the metallic nanorod cores themselves provide an optimal path for the charge carriers to reach the electrodes below. There are till now only very few reports on the fabrication of nanorod arrays with a core–shell structure and their use as a DSSC electrode. Chou et al. [9] first reported a new architecture for DSSCs based on indium–tin–oxide(ITO) nanorods coated with a titania layer. Later Joanni et al. [10] also reported the synthesis of ITO–TiO2 core–shell nanorod arrays by pulsed laser deposition to produce photoelectrode with very high interfacial area followed by Wang et al. [11] who used electrophoretic deposition.Ye et al. [12] have reported the template based fabrication of nanowire– nanotube hybrid array. Latest study of the template-based fabrication of Ag–ZnO core–shell nanorod arrays reports a very general strategy for the fabrication of aligned nanorod arrays with a metallic core and a metal oxide shell, using a combination of electrochemical and wet chemical methods, [13].

The demand of transparent conducting oxide (TCO) thin films has been increasing for applications such as flat panel displays, solar cells and functional windows. Although the indium tin oxide (ITO) thin film has been used in commercial products as transparent electrodes. Research for an alternative material and its thin film deposition technique is required because of the high cost of indium and its limited supply. In recent years, zinc oxide (ZnO) doped with group-III elements has shown promising properties as an inexpensive and alternative TCO material. ZnO films can be modified by the doping of metals, such as aluminum (Al) or gallium (Ga) [15, 16]. Among these metal dopants the Ga doping seems to be the most successful and promising due to its advantages, such as the rather similar ionic radius and the covalent radius (0.62 and 1.26 Ă), as compared to those of Zn (0.74 and 1.34 Ă), respectively [14]. The optical bandgap of ZnO-Ga thin films showed the lower blueshift than the theoretical value of the Burstein–Moss (BM) effect. The shift of bandgap was dependent on the carrier concentration and acquired by combining the nonparabolic BM effect and bandgap narrowing (BGN). The modified BM effect equation was proposed to substitute the nonparabolic BM effect and BGN. The exponent in the modified BM equation was affected by carrier concentration and it was decreased with carrier concentration, [17].

Thin film transistor (TFT) operates as an electronic switch, in which the current flow between source and drain electrode is modulated by the gate electrode. TFT is regarded as an essential element for liquid crystal display, image sensor and many other electric fields. Since future electronics will be a flexible form, organic TFT (OTFT) has regarded as a future flexible electronic modulator and received growing attention from 1986 when the first OTFT was reported by Tsumura and coworkers [18]. Because of their superior compatibility with flexible substrate and easiness of device fabrication,OTFT has another huge advantage which is its ability to be fabricated as a plastic electronic by roll-to-roll processing, which will lead massive production and reduction of cost. Recent progress has been made toward improved performance and stability of OTFT through advanced device architecting and synthesis of new organic material. However, the performance of OTFT is still far lower than that of their inorganic counterparts and required properties for suitable electronic applications an alternative method to prepare printed TFT should be considered. Inorganic oxide semiconductor using solution process has been used to replace organic semiconductors because of their superior properties such as atmospheric stability and relatively high mobility [19-21]. Very encouraging results obtained by gravure printed InGaZnO thin films as an active channel layer in thin film transistors were obtain in [22].

Hydrogen sulfide is a familiar impurity in natural gas streams,coal gas and chemical feedstocks . Due to the fact that it is a very hazardous, toxic, corrosive and pyrophoric gas, the H2S removal has been necessarily studied applying various methods – one of the most well-known of which is adsorption . Zinc oxide is among the most common and promising materials used in H2S adsorption, since it can ensure a satisfactory level of H2S removal [23].

Nanostructure ZnO is a promising material for chemical gas sensors because of its large surface-to-volume ratio, which improves its response. ZnO gas sensors have been recently studied extensively due to the simplicity of its preparation, high chemical stability and it has been prepared by different methods. Many studies had focused on the aceton, etanol, hydrogen etc. sensing properties of ZnO. However, sensors based on ZnO nanostructures were found to have low response. Despite the fact that much work had been offered for ZnO gas sensors, more investigation are still needed, especially to increase the response of the ZnO gas sensors [24].

In recent years, diluted magnetic semiconductors (DMSs) have been found to play an important role in interdisciplinary material science, especially in magneto- and spin-electronics. Spin-electronic devices based on DMSs materials, where the spin degree of freedom has been utilized, have potential application in the fields of new spin-electronic devices such as spin valve, spin light emitting diodes, spin field effect transistors, non-volatile memory, optical isolators, ultra-fast optical switches and quantum computation [26]. ZnO-based DMSs in particular, have widely attracted interest for potential applications since the recent theoretical predictions [27, 28] assumed transition metal (TM)-dopedZnO as one of the most promising candidates for room temperature ferromagnetism.

Aside from TiO2, ZnO is one of the most promising materials for remediation of contaminants and destruction of microorganisms. Both materials exhibit very similar band gaps (ZnO, 3.37 eV; TiO2,3.2 eV) and conduction band edge positions . These semiconductors are well established and there has been considerable interest in their applications to the area of photocatalysis [29]. The general scheme for the photocatalytic destruction of organic compounds involves the following three steps: (i) when the energy hv_ of a photon is equal to or higher than the band gap (Eg) of the semiconductor, an electron is excited to CB, with simultaneous generation of a hole in the VB; (ii) then the photoexcited electrons and holes can be trapped by the oxygen and surface hydroxyl, respectively, to ultimately produce the hydroxyl radicals (•OH), which are known as the primary oxidizing species; and (iii) the hydroxyl radicals commonly mineralize the adsorbed organic substances. However, the photoexited electrons and holes can also recombine to reduce photocatalytic activity of the semiconductor. To overcome this limitation, modification of semiconductors with noble metals is one of the most efficient ways [30]. ZnO/Ag composite structure is now an exciting area in research for developing photocatalytic applications..

ZnO nanoparticles are used in various commercial products such as cosmetics and sunscreens and are known for their anti-bacterial activity. In [25] was shown that semiconductor nano-oxides are much more toxic than nano-oxides that are insulators in bulk, and the presence of dopants in the semiconductor nano-oxides can alter the toxicity. Electronic properties of the nano-oxides, determined by their chemical compositions, and can be modulated by crystalline structure, defect, size, shape, and morphology, may play an important role in the observed cytotoxicity.

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