Synthesis and properties of ZnO multipod structures

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Abstract

We report fabrication and properties of multipod ZnO structures, synthesized from a mixture of ZnO, GeO\textsubscript{2}, and graphite. We studied the morphology, composition, and optical properties of these structures for different ZnO:GeO\textsubscript{2} ratios. The formation mechanism of the multipods is discussed. The multipod structures exhibit significant enhancement of the green emission which can be attributed to the increased surface area. Enhancement of the green emission is of interest for typical applications of ZnO phosphors, such as field emissive display technology.

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1. Introduction

Due to their importance for fundamental physics studies and a number of potential applications in electronic and optoelectronic nanoscale devices, semiconductor nanostructures have been attracting increasing attention in recent years.

ZnO, as a wide band gap (3.37 eV) material with a large exciton binding energy (60 meV), is recognized as a promising candidate for photonic applications in blue and UV spectral range. Up to date, a number of different nanostructure morphologies have been reported for ZnO, such as nanobelts [1,2], nanowires [3–8], tetrapod nanostructures [8–13], tubular nanostructures [14] and whiskers [15], hierarchical nanostructures [16], and nanobridges and nanonails [17]. While a number of synthesis methods were reported for
ZnO nanowires, fabrication of other more exotic shapes has been largely unexplored. Different methods for fabrication of tetrapod-shaped ZnO structures were reported [9–13]. In our recent work [12,13], we fabricated ZnO tetrapod nanorods and tetrapod nanorod/nanowire mixtures by evaporation of Zn at 950 °C in different atmospheres. Tetrapod structures or straight rods or wires are typically formed by evaporation of Zn or ZnO:C mixture in absence of any catalysts or additions to the source material. In order to obtain more complex shapes, such as ZnO hierarchical structures [16] and nanobridges and nanonails [17], the addition of In₂O₃ was necessary. In the former case, hexagonal ZnO nanorods growing on hexagonal In₂O₃ nanowires were obtained [16]. In the latter case, nanobridges were predominantly ZnO and in nanonails there was no indium detected [17]. Therefore, addition of In₂O₃ to ZnO and graphite mixture for ZnO nanostructure fabrication yields novel and complex morphologies [16,17]. Unfortunately, the effects of indium and In₂O₃ on the electrical and optical properties of these structures compared to pure ZnO were not been reported up to date. Since indium acts as a donor in ZnO, changes in the properties with incorporation of indium are expected. Synthesis of ZnO multipod structures was also reported recently [13,19,20]. In this work, we discuss the formation and properties multipod ZnO structures, synthesized from a mixture of ZnO, GeO₂, and graphite. We studied the morphology, composition, and optical properties of these structures for different ZnO:GeO₂ ratios.

2. Experimental section

ZnO:Ge multipod structures were synthesized in a tube furnace (Thermolyne 79400). ZnO and GeO₂ powders (99.99% purity) were obtained from Aldrich, and graphite (> 99.5% purity) was obtained from International Laboratory, USA. A mixture of ZnO, GeO₂, and graphite was used. The percentage of GeO₂ was 2.5%, 5%, and 10%. The furnace was heated to 1100 °C. After the furnace has reached the temperature, a quartz tube (20 cm length, 1 cm diameter, one closed end) containing the material was inserted. Typical reaction time was 13 min. White material was deposited on the walls of the tube. The reaction was performed in air at one atmosphere pressure with no additional gas flow. After the reaction was completed, the tube was removed from the furnace to cool down to room temperature.

The structure of deposited materials was investigated by X-ray diffraction (XRD) using Siemens D5000 X-ray diffractometer, energy dispersive X-ray spectroscopy (EDX) using Philips Tecnai 20 TEM and Leo 1530 field emission SEM, scanning electron microscopy (SEM) using Cambridge-440 SEM, transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) using JEOL 2010F TEM, and selected area electron diffraction (SAED) using Philips Tecnai 20 TEM. Electron paramagnetic resonance (EPR) measurements were performed using Bruker EMX EPR Spectrometer. The room temperature photoluminescence (PL) was measured using HeCd laser excitation source (325 nm). For investigating whether the emission originates from surface defects or not, fabricated nanostructures were coated with a surfactant using following procedure. ZnO nanostructures were dispersed in a 10% dichloromethane solution of n-hexyltrichlorosilane (96% purity, Lancaster Synthesis) in an ultrasonic bath for 1 h. After dispersion, nanostructures were separated using centrifuge and rinsed thoroughly with dichloromethane to remove any residual surfactant and dried in vacuum in a vacuum oven for 30 min at 30 °C. After coating with surfactant, SEM and EDX were performed using Leo 1530 FESEM to check the morphology and composition. It was found that the multipod morphology was preserved after sonication, and EDX confirmed presence of Si and Cl indicating successful attachment of n-hexyltrichlorosilane to ZnO multipod structures.

3. Results and discussion

At 1100 °C, graphite reacts with ZnO resulting in the release of Zn or Zn suboxide vapor [4]. When there is no gas flow, tetrapod-shaped
nanostructures can be obtained [13], similar to previously reported structures synthesized by oxidation of Zn [12]. Exact formation mechanism of ZnO tetrapod nanostructures is not entirely clear. The obtained morphology in pure ZnO nanostructures (i.e. tetrapods, wires, ribbons) is apparently determined by growth kinetics and hence it can be influenced by a number of factors such as position of the substrate, gas flow, geometry of the system and temperature gradient, etc. However, once the growth conditions for obtaining certain type of morphology are established, results are typically very reproducible and the influence of other factors such as the addition of dopants can be studied. With the addition of GeO2 to the starting material, the morphology of the obtained deposition products changes significantly and the multipod structures are obtained. Figs. 1a–d show the representative SEM images of morphologies obtained with GeO2.

For low GeO2 content in the starting material, mixture of multipods and tetrapods was obtained. With the increase of GeO2 concentration, the number of multipods increased but no other new morphologies were found. For 10% GeO2 in the starting material, high yield of ZnO multipod structures was obtained, as illustrated in low-magnification SEM image Fig. 1a. Fig. 2 shows the XRD spectra for ZnO obtained with no GeO2 and ZnO:GeO2 (9:1). It can be observed that in both cases peaks can be identified as hexagonal ZnO. The inset shows representative SAED pattern from a multipod leg. Obtained SAED pattern indicates that the leg grows along (0001) direction, similar to ZnO tetrapod legs [12].

We have investigated the effect of different percentages of GeO2 in the starting material on the Ge concentration in the deposition products using X-ray fluorescence (XRF) and EDX. No obvious relationship between Ge concentration in deposited ZnO structures and GeO2 concentration in the

Fig. 1. Representative SEM images of ZnO:Ge multipod structures. Growth time is 13 min unless specified otherwise. (a) ZnO:Ge multipod structures, low magnification; (b) ZnO:Ge multipod structures, high magnification; (c) ZnO:Ge multipod structures after 6 min growth time; (d) different shape ZnO:Ge multipod structures.
starting material was found. In all cases, Ge concentration determined by XRF was below 1 mol%. Moreover, in majority of the multipod structures examined by EDX, no Ge was detected. Representative EDX spectrum is shown in Fig. 3. Peaks due to C and Cu come from TEM grid. HRTEM image of the multipod leg reveals that the leg grows along [0001] direction and it is covered with a thin amorphous layer on the surface, similar to previously reported results for ZnO nanowires [4].

Since no Ge can be found in the majority of multipod samples, it can be concluded that the addition of Ge apparently induces nucleation of additional legs at the core which would normally develop into a tetrapod structure. Exact process of nucleation of additional legs is not entirely clear. The process has some similarity with the formation of ZnO nanobridge and nanonail structures from mixture of ZnO, In2O3, and graphite [17]. Some indium was found in nanobelts, while no indium was found in nanonails. Gao et al. [19] have reported the formation of multipod ZnO whiskers with the treated ZnO powders (in NiSO4 solution), but no Ni was found in the tips of the whiskers. The whisker formation was explained by small amount of Ni or NiO particles serving as catalysts for the growth of ZnO legs [19]. Sun et al. [20] reported the formation of ZnO multipods from Zn powder etched by CuSO4 solution. Existence of Cu serving as a catalyst or a nucleus was identified as a possible mechanism, even though no Cu was found by EDX while the results from atom emission spectrum indicated presence of Cu [20]. However, simple mixing of Cu and Zn powders produced only tetrapods and the change in the morphology was attributed to the Cu2+ etching process resulting in different morphology of the initial crystal nuclei [20].

In our work, multipods were formed from a simple mixture of ZnO, GeO2, and graphite with no etching of the starting material as proposed in previous studies [19,20]. However, the obtained morphology is very similar to the previously reported results. Also, no Ge was found in our multipods, in agreement with the absence of Ni and Cu obtained in the previous studies [19,20]. We can identify two possible mechanisms responsible for multipod formation. One is presence of small amount of Ge or GeO2, acting as nucleation sites for additional legs. Another is change in the Zn release rate from the source material, which can affect the formation of the initial crystals and the obtained final morphology. It was shown that
the change in the source material can result in significant change of the obtained morphologies of the deposited products [18,21,22]. The morphology difference was attributed to the different Zn vapor yield of different source materials [18,22]. In our experiment, the Zn release rate can be significantly affected by the addition of GeO₂ to the starting material, since graphite in the mixture can react with either GeO₂ or ZnO. Thus, the vapor pressure of Zn and/or suboxide will be different compared to the one resulting from ZnO:graphite source material. The difference in vapor pressure alone can result in the change of the morphology. We have shown recently that structures similar to nanonails can be obtained by varying the rate of release of Zn [18] without any addition of In₂O₃ to the starting material. Therefore, it is possible that the formation of the multipod structures is due to the variation in the partial pressures of oxygen and Zn. Since different vapor pressures will affect the formation of initial crystal nuclei, this mechanism is in agreement with the one proposed by Sun et al. [20] for the growth of ZnO multipods from Cu²⁺-etched Zn powder. However, since we have not been able to obtain multipod structures by varying source material (using different types of carbon, changing the quantity) as well as using different quartz tube sizes, it is possible that presence of Ge plays a role in nucleation of additional legs in multipod structures. Likely, both Ge inducing additional nucleation sites and altering Zn vapor pressure result in the formation of multipod structures. Further study is needed to clarify the exact growth mechanism of these structures.

To investigate the formation of multipod structures in more detail, we have performed SEM on samples obtained for different deposition times. For 6 min deposition time, the sample contains areas where multipods have thinner legs (see Fig. 1c) and in some cases abrupt decrease of leg diameters can be observed. The length of all legs appears similar. These structures in the early stages of the growth are similar to those obtained by oxidation of Zn powder treated with Ni²⁺ containing solution [19]. The structures shown in Fig. 1d are rare and appear in a few isolated places for 6 min deposition. With increase of deposition time, the majority of the sample consists of multipod structures, such as those depicted in Fig. 1b. No abrupt changes in the leg diameter can be observed, and the leg diameters are in the range of 100–250 nm. Also, the structures shown in Fig. 1d become more common with the increase of deposition time, indicating that these are likely to be the later stages of growth of multipod ZnO structures. The obtained results indicate that the multipods form relatively early in the deposition process, and that lateral growth of the multipod legs becomes more pronounced with increased deposition time. Kinetically controlled growth due to different dependence of growth rates in <001> and <100> directions on oxygen partial pressure has been proposed as an explanation for the formation of trumpet-like ZnO tetrapods [11]. It is possible that lateral growth of legs in multipod structures is also due to different dependence of growth rates in different directions on partial pressure of oxygen and zinc. Further study on the formation and evolution of these structures is necessary to confirm the growth mechanisms responsible for observed results.

There have been very few works on studying the doping of ZnO with group IV elements [23–25]. It was found that doping with Si changed tribological properties of ZnO and that it likely created excess Zn [23]. Si and Ge doping also resulted in increased electron concentration in ZnO films [24]. It was also reported that the ZnO:Ge powders prepared by sintering ZnO and GeO₂ mixture exhibited decreasing green emission with the increase of Ge content. However, in this work we found the increase of the green PL with the increased amount of GeO₂ in the starting material. Small (5 nm) red shift can be observed in the UV emission when GeO₂ is added to the starting material. More significant changes can be observed in the green region. The green emission in ZnO synthesized without GeO₂ consists of a typical broad peak centered around ~520 nm. This peak can be fitted as a sum of two Gaussians, one in green and another in yellow spectral range, in agreement with previously reported results for ZnO films [26]. The origin of this green emission is
somewhat controversial. The commonly accepted explanation is that the green emission is due to a transition between singly ionized oxygen vacancy and photoexcited hole [27]. However, other mechanisms such as copper impurities [28], and donor–acceptor complexes [29,30], Zn vacancy and antisite oxygen [31], and recombination of photogenerated electrons with preexisting, trapped holes [32] have been proposed as well. Assignment of the yellow part of the emission is less controversial, and this emission is most likely due to interstitial oxygen [33].

With the addition of GeO$_2$ to the starting material, it can be observed that the green emission becomes more intense and that the peak shifts and becomes centered at around $\sim 500$ nm. The peak can still be fitted with two Gaussian transitions, but the centers of those two Gaussians curves are at $\sim 485$ and $\sim 520$ nm. The emission at 485 nm was previously reported in ZnO [34,35], and it was assigned to the transition between oxygen vacancy and interstitial oxygen [34], and lattice defects related to oxygen and zinc vacancies [35]. Since the incorporation of Ge is very small regardless of the GeO$_2$ concentration in the starting material, enhancement in the green emission is not due to Ge. Furthermore, it was shown that higher incorporation of Ge results in the reduction of green emission, which was explained by Ge atoms replacing Zn vacancies [25]. The morphology of the deposited material changes significantly with addition of GeO$_2$, so that the green peak shift is likely due to dominance of different types of defects. In order to investigate this possibility, we performed EPR measurements. The obtained results for ZnO and ZnO+GeO$_2$ (2.5%) are shown in the inset of Fig. 4. For higher GeO$_2$ content in the source material, the peak position is the same as for the 2.5% sample, but the peak intensity increases. Small shift in the peak position for samples synthesized with and without GeO$_2$ can be observed. The signal $g = 1.96$ actually consists of two lines ($g = 1.955$ and 1.958) which may be caused by different defects [36], which supports the hypothesis that the observed shift of the PL peak is due to different type of defects becoming dominant.

Similar to the origin of the green emission, there is a controversy in the assignment of the origin of $g = 1.96$ EPR signal. It has been assigned to oxygen vacancy [27], shallow donors [28], and free electrons [36]. The origin of the green emission has been assigned to the transition between singly ionized oxygen vacancy and photoexcited hole based on the relationship between intensities of the $g = 1.96$ EPR signal and the green PL [27]. However, it was shown that the relationship between the intensities of the EPR peak at $g = 1.96$ and the green emission is not present in all ZnO samples [13]. In other words, the absence of EPR signal does not necessarily imply the absence of the defect emission. For samples synthesized in the presence of GeO$_2$ in the starting material, we also observed correlation between EPR and green PL intensities (higher GeO$_2$ concentration, higher green PL, and higher $g = 1.96$ EPR signal). It should be noted that there is convincing evidence that the signal $g = 1.96$ does not correspond to singly ionized oxygen vacancy [28,36].

However, there is obvious relationship between the concentration of GeO$_2$ in the starting material and the green PL. Since the concentration of GeO$_2$ in the starting material determines the ratio of multipod and tetrapod structures in the deposited products, the enhancement in the green emission can be assigned to the increased number of

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**Fig. 4.** PL of ZnO:Ge multipod structures for different percentage of GeO$_2$ used during fabrication. PL from pure ZnO tetrapods is also shown for comparison. The inset shows the comparison of the ESR signals for ZnO:Ge multipods and ZnO tetrapods.
multipod structures. It was found that the green PL centers in ZnO are located at the surface, and the green emission was significantly suppressed by coating the ZnO with surfactant (n-hexyltrichlorosilane) [13]. Strong green emission from the ZnO multipod whiskers was also attributed to the increased surface area of the multipod whiskers [19]. Gao et al. [19] also found that there was excess of Zn in their multipod structures, and they attributed the green emission to the oxygen vacancies. However, it should be noted that excess Zn can imply both oxygen vacancy and interstitial Zn. Theoretical calculations predict that the oxygen vacancy is a deep donor [31,37], while interstitial Zn is a shallow donor. Therefore, the predicted energy level of the oxygen vacancy is inconsistent with the green emission. The defect responsible for the green emission could possibly be Zn vacancy [25,31], which is also consistent with the increase of green emission upon annealing in oxygen [31]. The EPR signal is unrelated to the deep level concentration, but it is likely related to the shallow donor concentration [28]. Thus, in the samples exhibiting transition between the shallow donor and deep level instead of the transition between the conduction band and the deep level, some correlation between the $g = 1.96$ EPR peak and the green PL intensities can be observed. Caution is needed in the interpretation of this correlation, since there can be two close EPR signals with $g \sim 1.96$, which may originate from different defects [36]. Further study is needed to identify the deep level causing the green emission.

4. Conclusions

The formation of ZnO multipod structures by addition of GeO$_2$ to the starting material (mixture of ZnO and graphite) was discussed. Addition of GeO$_2$ to the starting material results in nucleation of the additional legs on the core which would normally develop into a tetrapod structure. The multipod structures exhibit enhancement of the green emission which can be attributed to the increase of the surface area. Therefore, the luminescent properties of the material can be adjusted by changing the morphology of the fabricated structures.

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References