Growth of ZnO nanostructures in a chemical vapor deposition process

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Abstract

Shape-controlled ZnO nanostructures (nanorods, nanotips, nanonails, nanowires, nanoropes and nanolawns) were synthesized by metalorganic chemical vapor deposition at relatively low growth temperature (400–500°C) via assistance of colloidal gold (Au) nanoparticles dispersed on SiO\textsubscript{2}/Si substrates. The shape variation of the nanostructures was sensitive to the density of the Au nanoparticles on substrates as well as the growth temperature, allowing the effective shape control of the nanostructures by handling those parameters. The grown ZnO nanostructures were found to have negligibly weak deep-level emission, as evidenced by photoluminescence (PL) measurements. The strong PL emission band, which originate from free-excitons in shape-controlled ZnO nanostructures indicates that the shaped–controlled ZnO nanostructures by this method have high optical quality.

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1. Introduction

ZnO with a wide band gap (3.37 eV) has a large exciton binding energy of 60 meV and biexciton binding energy of 15 meV, which is more than two times larger than those of GaN (24 and 5.7 meV) or ZnSe (21 and 3.4 meV)\textsuperscript{[1–4]}. This fact allows us to expect high-efficiency lasing by contribution of exciton to the optical gain. Binding of excitons can be strengthened by enhanced exciton confinement in low-dimensional structures. In this regard, recently, studies on ZnO nanostructures have been extensively carried out\textsuperscript{[5-7]}. Especially, one-dimensional ZnO nanostructures such as nanowires\textsuperscript{[6]}, nanobelts\textsuperscript{[8]} and nanorods\textsuperscript{[9]} have been intensively focused on due to their promising applications for novel multi-functional nanodevices such as ultra-violet nanolasers and nanosensors for chemical and biological species. Various kinds of ZnO nanostructures which have ever been reported were realized by vapor–liquid–solid (VLS) processes\textsuperscript{[6,10,11]}, thermal evaporation\textsuperscript{[12,13]}, electrochemical decomposition\textsuperscript{[14]}, metalorganic chemical vapor deposition (MOCVD)\textsuperscript{[9]} and so on. In most of these techniques, gold (Au) seeds on a substrate play a key role for the formation of nanostructures\textsuperscript{[6,11]}. However, high temperature (900–1000°C) processes have been generally required in order for forming the Au seeds and for growing the ZnO\textsuperscript{[11,15]}. This seriously limits the applicable substrate materials and enhances thermal strain and damage in the structures.

In the present work, we propose to fabricate the initial Au seeds by spin coating of colloidal solution of Au nanoparticles, whose size has been strictly controlled during their formation processes. This allows room-temperature formation of Au seeds for the ZnO nucleation fairly uniform in their sizes with a certain density, decided by the density of Au nanoparticles in the solution as well as the spin coating conditions, on the substrate. By appropriate tuning of these parameters, we could control the shapes of nanostructures fabricated...
by MOCVD at relatively low growth temperatures from 400 to 550 °C.

2. Experiments

A commercially available colloidal solution of Au nanoparticles with average diameter of 20 nm was spin-coated onto SiO$_2$/Si substrates. Two series of substrates S$_1$ and S$_2$ were prepared, where the coating with Au nanoparticles has been made under different conditions. One (S$_1$) is prepared by three-times iteration of a spin-coating and air-drying process of colloidal Au nanoparticles onto SiO$_2$/Si substrates. The other (S$_2$) is made by six-times iteration of the process. On these substrates, either S$_1$ or S$_2$, the MOCVD growth of ZnO has been carried out in a vertical reactor at a pressure of 200 Torr for 30 min. Typical flow rates of source materials, diethylzinc and N$_2$O were 2 and 1250 μmol/min, respectively. For comparison to references, untreated SiO$_2$/Si substrates were also placed near the substrates S$_1$ and S$_2$ during the growth run.

3. Results and discussion

Figs. 1(a) and 2(a) show field-emission scanning electron microscope (FE-SEM) images of Au nanoparticles dispersed on substrates S$_1$ and S$_2$ where their densities were about $4 \times 10^9$ and $3 \times 10^{10}$ cm$^{-2}$, respectively. At the growth temperature of 400 °C, vertically aligned ZnO nanorods and nanotips were formed on the substrates S$_1$ and S$_2$, respectively, as shown in Figs. 1(b) and 2(b). Lengths of the nanorods and nanotips are in the range of 540–600 nm and 700 nm–1.3 μm, respectively. In addition, diameters of the ZnO nanorods and nanotips range from 100 to 180 nm and from 110 to 160 nm, respectively. However, in case of the ZnO nanorods shown in Fig. 1(b), we could not observe any significant differences in shape between the ZnO nanorods on the substrate S$_1$ and those on an untreated SiO$_2$/Si substrate [16], showing that Au nanoparticles on the substrate S$_1$ did not play an important role in nucleation of ZnO at this relatively low growth temperature of 400 °C. This fact indicates that nucleation of ZnO on the SiO$_2$ surface rather than that of ZnO on the Au nanoparticles with low density governs entire growth of ZnO at the low growth temperature. On the other hand, as shown in Fig. 2(b), ZnO nanotips with narrow shafts and sharp ends were fabricated on the substrate S$_2$. The average length of the ZnO nanotips on S$_2$ is longer than that of the ZnO nanorods on S$_1$ in spite of the same growth run. However, the diameter of the ZnO nanotips on the substrate S$_2$ is over five-times larger than that of the ZnO nanorods on S$_1$ in spite of the same growth run. These results suggest that shape controllability of ZnO nanostructures is a function of the

![Fig. 1. FE-SEM images of the Au nanoparticles (a) and shape-controlled ZnO nanostructures (b–d) on the substrate S$_1$. Density of Au nanoparticles is about $4 \times 10^9$ cm$^{-2}$ and average diameter of the Au nanoparticles is 20 nm. (b) The image of the nanorods was taken at a tilt angle of 45°. Plan-view FE-SEM images of nanonails (c) and nanopins (d). MOCVD-growth temperatures of nanorods, nanonails and nanowires are 400, 500 and 550 °C, respectively.](image-url)
number of Au nanoparticles at this growth temperature of 400 °C.

We have also observed ZnO nanonail [17] and nanorope structures by increasing the growth temperature. Figs. 1(c) and 2(c) are the plan-view FE-SEM images of the typical ZnO nanonails and nanoropes grown on the S1 and S2, respectively, at 500°C. The nanonails grown on the substrate S1 are somewhat perpendicular to a surface of the substrate as shown in Fig. 1(c). The lengths of the nanonails are in a range of 600–900 nm. Although the caps of the ZnO nanonails do not have perfect hexagonal shape, they are basically comprised of hexagonal facets [17]. Existence of caps on the nanonails indicates that growth of ZnO nanonails is governed by not a VLS process, but a vapor–solid (VS) one. In addition, because we could not observe any ball-shaped solid-solution of Zn–Au upon the caps of the nanonails in FE-SEM images, we could conclude that ZnO was directly nucleated on the Au nanoparticles dispersed onto the SiO2 substrate and grew into ZnO nanorods. Namely, the Au nanoparticles did not act as catalysts for a VLS process but acted as nucleation centers for formation of ZnO by a VS one. High eutectic temperature of a Zn–Au binary system could be an additional evidence of our suggestion to the growth mechanism.

After the nucleation of ZnO at the initial stage of growth, nanorods grow from the Au nanoparticles. Columnar growth of ZnO for nanorod formation is mainly due to a high growth rate along the c-axis of ZnO. ZnO is a polar semiconductor, with (0 0 0 1) planes being Zn-terminated and (0 0 0 1) being O-terminated. These two crystallographic planes have opposite polarity, hence have different surface relaxation energies, resulting in a high growth rate along the c-axis [18]. Zn and O radicals in the MOCVD reactor deposit epitaxially on both the trunk and the top-surface of the nanorod. The top-surface of the nanorod has a higher probability to absorb the Zn and O radicals than the bottom (a surface of SiO2), resulting in the formation of hexagonal cap [17].

On the other hand, ZnO nanoropes on the substrate S2 were grown as shown in Fig. 2(c) although the growth was carried out at the same growth condition of the nanonails which are presented at Fig. 1(c). A large quantity of ZnO nanoropes with typical lengths up to several tens of micrometers are presented in Fig. 2(c). Diameters of the nanoropes are quite uniform in the range of about 20–24 nm, which might be attributed that ZnO nucleates directly on Au nanoparticles with high density dispersed upon the substrate S2 and, then, the continuous supply of Zn and O radicals results in the formation of nanoropes. This result shows that a diameter of nanoropes is a critical function of size and density of Au nanoparticles. To clarify the growth mechanism of the nanoropes, we prepared another substrate (Si3) dispersed by Au nanoparticles with large variation in sizes. In Fig. 3(a) which represents the surface of the substrate, the Au nanoparticles with sizes of
around 500 nm–1 μm as well as those of about 20 nm are clearly seen. Fig. 3(b) shows ZnO nanorope networks that were grown on the substrate S3. It is suggested that the nanoropes were mainly stretched out from the Au nanoparticles with large sizes of around 500 nm–1 μm. Therefore, we could conclude that the ZnO nanostructures in this study were mainly governed by not a VLS process, but a VS one.

At the temperature of 550 °C, ZnO nanowires (Fig. 1(d)) and nanolawns (Fig. 2(d)) were grown on S1 and S2, respectively. We attribute that the formation mechanism of the ZnO nanowires is quite similar to that of the ZnO nanonails shown in Fig. 1(c); ZnO nanowires with diameters in a range of 20–60 nm grow on Au nanoparticles as the shaft of the nanopin. However, the formation of the nanowires with irregular growth directions at 500 °C is not clear. In addition, we do not know why ZnO nanolawns (shown in Fig. 2(d)) with diameters in a range of 20–50 nm and very short lengths of about 400–700 nm grow on the substrate S2 compared with the formation of the ZnO nanoropes present at Fig. 2(c) even though the difference of the growth temperature is only 50 °C. On the other hand, flower-like ZnO structures were densely formed at the same growth temperature of 550 °C on a bare SiO₂/Si substrate without Au nanoparticles. This result strongly suggests that Au nanoparticles played an important role in the formation of ZnO nanowires and nanolawns at this growth temperature. No Au–alloyed tips which generally observed on the top of the ZnO nanowires grown by the VLS mode in high growth temperatures (over 900 °C) were observed in FE-SEM measurements, clearly indicating that the formation of the ZnO nanowires and nanolawns in this work is mainly the result of a VS process.

In order to characterize optical properties of shape-controlled ZnO nanostructures, we carried out photoluminescence (PL) measurements. The ZnO-nanowire sample presented at Fig. 1(d) was used for the PL measurements. The temperature dependences of spectra and integrated intensity of PL are shown in Figs. 4 and 5, respectively. A peak labeled “EX” (3.375 eV) and another peak labeled “D°X” (3.362 eV) are attributed to free exciton emission and neutral donor-bound exciton emission, respectively, in the PL spectrum excited by a He–Cd laser at 10 K as shown in Fig. 4. The emission bands labeled “X-1LO and X-2LO” which originate from the radiative recombination of first
and second phonon replicas of free excitons, respectively, considering the energy separation of each emission band of about 64 meV. This ZnO-nanowire sample exhibited a negligible deep-level emission band (not shown), indicating high quality of the ZnO nanowires.

As the temperature increases, the EX emission becomes dominant in comparison to the D’X emission due to thermal dissociation of the donor-bound-excitons. In usual ZnO films or bulk crystals, EX emission is not clearly observed at low temperatures due to the localization of excitons at impurities. At higher temperature usually over the range of 60–80 K, EX emission appears because of the ionization of impurities that used to bound excitons at low temperatures. The clear observation of dominant EX emission in the emission spectrum even at 50 K suggests that the impurity incorporation was very low in the sample. The clear observation of EX emission even at low temperatures and the high-internal quantum efficiency might be attributed that formation of individual ZnO nanostructures (nanowires) with the lower density of defects such as a dislocation compared with that of a ZnO thin film and enlarged surface areas emitting photons by nanostructuring.

4. Conclusions

In summary, we have successfully synthesized shape-controlled ZnO nanostructures (nanorods, nanotips, nanonails, nanowires, nanoropes and nanolawns) by MOCVD by means of assistance of colloidal Au nanoparticles dispersed on SiO$_2$/Si substrates. The FE-SEM measurements clearly showed that various types of ZnO nanostructures can be realized by controlling the density of Au nanoparticles even at low MOCVD-growth temperatures of 400–550 °C. Supposing all of the carriers radiatively recombine at 10 K, the internal quantum efficiency of the ZnO-nanowire sample was estimated to be about 13% at 300 K. The clear observation of free-exciton emission indicates that the shape-controlled ZnO nanostructures in this study are of high optical quality.

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