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# 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 $SiO_2$/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) [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 [5-7]. Especially, one-dimensional ZnO nanostructures such as nanowires [6], nanobelts [8] and nanorods [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 [6,10,11], thermal evaporation [12,13], electrochemical decomposition [14], metalorganic chemical vapor deposition (MOCVD) [9] and so on. In most of these techniques, gold (Au) seeds on a substrate play a key role for the formation of nanostructures [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 [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

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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 $N_2O$ 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 Au nanoparticles, which indicates that the Au nanoparticles on the substrate $S_2$ as seeds made a partial contribution to the nucleation of ZnO. These results suggest that shape controllability of ZnO nanostructures is a function of the

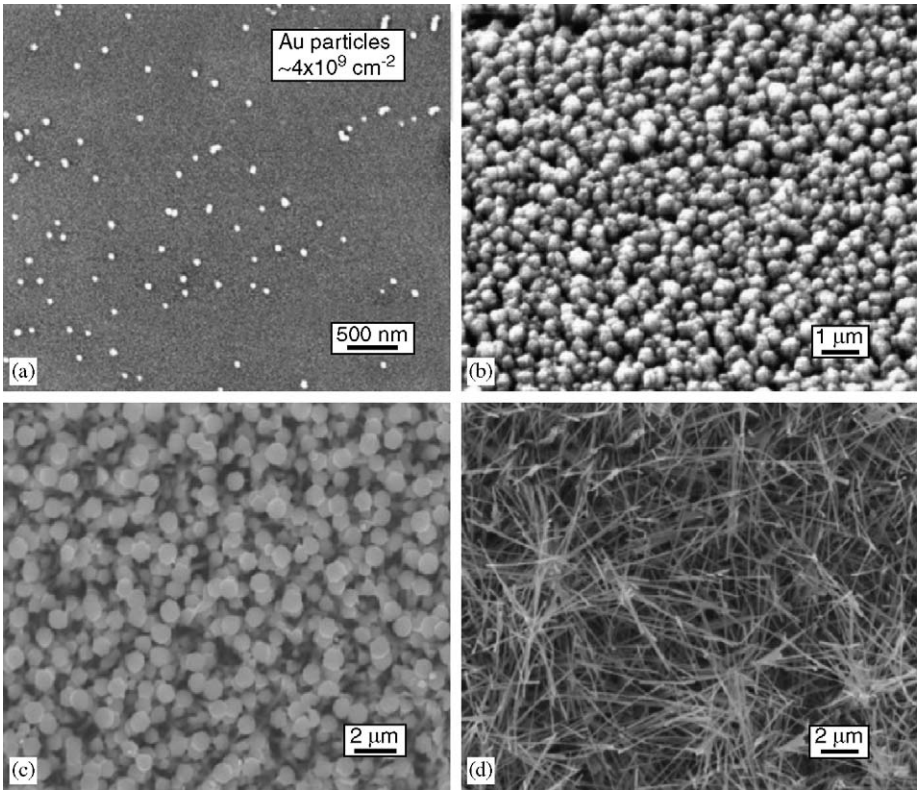


Fig. 1. FE-SEM images of the Au nanoparticles (a) and shape-controlled ZnO nanostructures (b–d) on the substrate $S_1$. Density of Au nanoparticles is about $4 \times 10^9\,cm^{-2}$ and average diameter of the Au nanoparticles is 20 nm. (b) The image of the nanorods was taken at a tilt angle of 45°. 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.