Fabrication of ZnO Nanopillars by Atomic Layer Deposition

Mong-Kai Wu1,*, 1Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 106, R. O. China

Jer-Ren Yang1 and Makoto Shiojiri2

1*Corresponding author, E-mail: mjchen@ntu.edu.tw
2Professor Emeritus of Kyoto Institute of Technology, 1-297 Wakiyama, Kyoto 618-0091, Japan

A new method was developed to fabricate high-quality ZnO nanopillars with good uniformity using atomic layer deposition (ALD). The ZnO island seeds were prepared on the (0001) sapphire by the initial 5–20 ALD cycles at 180°C and then heat-treated at 900°C for 1 h. Afterwards, the ALD growth of ZnO at a temperature as high as 300°C proceeds preferentially on the ZnO island seeds over the sapphire substrate, leading to the formation of ZnO nanopillars. The average diameter and height of the nanopillars are about 60 nm and 50 nm, which can be effectively controlled by the numbers of initial ALD cycles and the following high-temperature ALD cycles, respectively. The ZnO nanopillars have high crystallinity with the [0001] orientation, and exhibit a significant ultraviolet luminescence at room temperature.

Keywords: atomic layer deposition, ZnO nanopillars, ultraviolet emission

1. Introduction

ZnO has lately attracted considerable attention as a promising material for ultraviolet (UV) photonic devices owing to its large exciton binding energy of 60 meV and its direct bandgap energy of 3.37 eV at room temperature. Because of the remarkable excitonic properties, significant exciton effects are expected in the ZnO nanostructures. ZnO shows many nanostructural morphologies including nanowires, nanorods, nanobelts, nanocages, nanocombs, nanospheres, nanorings, nanohelices, and nanoparticles.1-3 These ZnO nanostructures have been grown using various techniques including vapor-phase transport process,4,5 chemical vapor deposition,6 and metalorganic chemical vapor deposition.7,8 It is worth noting that another way associated with the growth of high-quality ZnO is atomic layer deposition (ALD).9-11 Unlike other types of chemical vapor deposition, ALD proceeds through reactions solely at the surface of the substrate, leading to a self-limiting and layer-by-layer growth. ALD offers many advantages, including accurate and facile thickness control, excellent conformality, high uniformity over a large area, good reproducibility, dense and pinhole-free structures, and low deposition temperatures. ALD has been used only to deposit a seed layer to grow ZnO nanorods.12-14 Although the nanoscaled control of film thickness is easily achieved by ALD, none have applied ALD to deposit the nanostructures.

In this study, we propose a new ALD method to grow high-quality ZnO nanopillars with good uniformity on the sapphire substrate. The nanostructure has been achieved by the preparation of ZnO island seeds and the preferential growth of ZnO pillars on these seeds. We also demonstrate a significant UV emission from the ZnO nanopillars at room temperature.

2. Procedure for the Fabrication of ZnO Nanopillars

ZnO was deposited using alternating pulses of Zn(C2H5)2 (DEZn) and H2O in the conventional ALD technique. The processing of ALD was similar to that used in our previous experiments, where UV light-emitting diodes composed of n-ZnO/p-GaN heterojunction,15 n-ZnO:Al/SiO2-ZnO nanocomposite/p-GaN:Mg16,17 and n-ZnO/ZnO nanodots-SiO2 composite/p-AlGaAs by ALD18 were fabricated. The ALD process consisted of a number of identical cycles, each of which contained the following sequence: DEZn, 0.02 s → N2 purge, 5 s → H2O, 0.1 s → N2 purge, 5 s. At a low growth temperature of T = 180°C, uniform ZnO films can be deposited on the (0001)-oriented sapphire (c-Al2O3) substrate. However, when the temperature is above 200°C, the DEZn molecules desorb from the c-Al2O3 surface and the growth rate becomes much less than one monolayer per ALD cycle.11 We found that when a ZnO seed layer is prepared by ALD on the c-Al2O3 at T = 180°C and heat-treated at a high temperature, the DEZn molecules can be absorbed on the ZnO seeds at T ≥ 200°C. This indicates that the surface of ZnO seed layer offers stable absorption sites for DEZn molecules at high growth temperatures. On the other hand, it has been pointed out that at the first 20 cycles in the ALD process, the deposition rate is much smaller than one monolayer per ALD cycle.11 This suggests that the island growth mode maintains only in the several initial ALD cycles.20 Nucleation at the reaction sites and the subsequent coalescence form ZnO nanoislands on the surface. These ZnO nanoislands grown by initial ALD cycles can serve as embryos of the seeds for the growth of ZnO nanopillars, accordingly.

Our strategy for the fabrication of the ZnO nanostructure is based on the combined process of the formation of initial island seeds and the preferential growth on the seeds, as illustrated in Fig. 1. At first, we deposited ZnO by ALD of 5~20 cycles to make seed embryos on the c-Al2O3 at T = 180°C. After the deposition, the specimen was heat-treated for 1 h at 900°C in a nitrogen atmosphere to improve their crystallinity and form ZnO island seeds. Subsequently, ZnO ALD of 1000 cycles was performed at T = 300°C. As described above, the ZnO growth occurred preferentially and selectively on the seeds, thus resulting in the growth of ZnO nanopillars.
3. Results and Discussion

Figure 2 shows an atomic force microscopy (AFM) image of the ZnO island seeds. The seeds on the $c$-$\text{Al}_2\text{O}_3$ substrate are dispersed and separated with each other, and have an average diameter of 50 nm and an average height of 4 nm.

In order to investigate the effect of the island seeds, we prepared a specimen of reference by ZnO ALD of 1000 cycles at $T = 300^\circ\text{C}$ directly on the $c$-$\text{Al}_2\text{O}_3$ without the seeds. Figures 3(a) and (b) show the surface morphologies of the two specimens which were prepared by ZnO ALD of 1000 cycles on the $c$-$\text{Al}_2\text{O}_3$ substrates with and without the seeds, respectively. Figure 3(a) indicates high-density nanopillars with the average diameter and height of about 60 and 50 nm, respectively. From AFM observations of various specimens prepared by different conditions, it was found that the diameter of the ZnO nanopillars depends on the size of the ZnO seeds, which can be controlled by the number of initial ALD cycles and the post-annealing conditions. The height of the ZnO nanopillars can be controlled digitally by the number of subsequent high-temperature ALD cycles. Since it is not necessary to control precisely the homogeneity of the precursors in the ALD process, we fabricated the nanopillars uniformly distributed over the entire 2-inch (= 50.8 mm) substrate with good reproducibility. On the other hands, the sample without initial seeds has very rough and disordered surface, as seen in Fig. 3(b). The rough surface indicates that the deposition is no longer in the layer-by-layer growth mode. Instead, the desorption of the precursor molecules takes place and the growth becomes unstable.

Figure 4 shows X-ray diffraction (XRD) patterns of the specimens used in the AFM observation in Fig. 3. The specimen without the seeds exhibits small peaks of the ZnO 0002 and 1011 reflections, while the specimen with the seeds exhibits only a very strong peak of the 0002 reflection. The intensity of the ZnO 0002 reflection from the latter is three orders of magnitude larger than that from the former. This
high-quality ZnO nanopillars with good uniformity on the c-\(\mathrm{Al}_2\mathrm{O}_3\) substrate. Due to the recrystallization caused by the high-temperature heat treatment, the island seeds have better crystallinity, which may facilitate the migration to and nucleation at the proper sites for the following deposition of ZnO.

Figure 5 shows photoluminescence (PL) spectra from the specimens used in the AFM and XRD measurements. PL spectra were measured at room temperature using a fourth harmonic Q-switched Nd:YAG laser (wavelength = 266 nm, pulsewidth = 10 ns, repetition rate = 15 Hz) as the excitation source. Both of the samples exhibit UV emission at 3.24 eV, which is attributed to the radiative recombination of free excitons.\(^{21}\) However, the intensity of UV emission from the ZnO nanopillars is much stronger, about one order of magnitude greater than that of the ZnO deposited on the c-\(\mathrm{Al}_2\mathrm{O}_3\) without the seeds. It indicates that the introduction of the initial island seeds contributes to the formation of the high-quality crystalline ZnO nanopillars.

**4. Conclusion**

In summary, we have provided an ALD process to grow high-quality ZnO nanopillars with good uniformity on the c-\(\mathrm{Al}_2\mathrm{O}_3\) substrate. The ZnO islands grown at the initial ALD cycles followed by a high-temperature annealing were used as the seeds for the growth of ZnO nanopillars. The selective growth of ZnO on the ZnO island seeds and c-\(\mathrm{Al}_2\mathrm{O}_3\) surface was achieved at a high temperature of 300°C due to the different growth rates of ZnO on homo- and heterointerfaces. Thus ZnO nanopillars were formed as a result of the preferential deposition of ZnO onto the seeds over the c-\(\mathrm{Al}_2\mathrm{O}_3\) surface. Because of no need to control carefully the homogeneity of the precursors in the reaction chamber, the ALD process allows the growth of ZnO nanostructures with good uniformity over a large area. The AFM measurement revealed that dimension of nanopillars is 60 nm in diameter and 50 nm in height. The XRD pattern indicated that the ZnO nanopillars have high crystallinity with the c-axis orientation. The ZnO nanopillars also exhibit a predominant UV emission at room temperature. The present result demonstrates that the ALD technique can be used to product high-quality ZnO nanostructures with large-area uniformity, applicable to UV lasers, gas sensors and field emitters.

**REFERENCES**