Route from ZnO Thin Films to Nanostructures on Si Substrates by Metal Organic Chemical Vapor Deposition

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ZnO thin films and nanostructures were grown on Si substrates in a metal organic chemical vapor deposition (MOCVD) process as a function of growth conditions including source flow rates and growth temperatures. ZnO thin films with smooth surface morphology were grown in growth conditions with low zinc source flow rates and high growth temperatures. On the other hand, the surface morphology of thin films became dramatically rough on increasing the flow rate of the zinc source, resulting in the formation of various kinds of nanostructures such as nanorods, nanotowers, and nanocactuses, depending on the MOCVD growth temperature. This result is mainly due to the strong tendency of ZnO toward a three-dimensional (3D) growth mode with higher flow rates of the zinc source in a MOCVD process, indicating that a route from thin films to nanostructures relies on the 3D growth behavior of ZnO.

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I. INTRODUCTION

ZnO is very promising for applications in optical devices such as light-emitting diodes and laser diodes with high efficiency, covering blue and ultraviolet ranges, due to its wide band gap of 3.37 eV and large exciton binding energy of 60 meV [1, 2]. The large exciton binding energy facilitates low-threshold stimulated emission in ZnO via excitonic recombination, which is a more efficient radiative process than an electron-hole plasma process. Efficient lasing action through excitonic recombination at room temperature has been reported in both ZnO thin films and nanostructures [3–5]. In addition, significant efforts for realization of high-sensitivity nanoscale chemical sensors using ZnO nanostructures have been made [6–8]. Thus, studies on the fabrication and characterization of ZnO thin films [9–12] and nanostructures [13–16] have been extensively carried out.

Si is regarded as one of the most promising substrates for ZnO epitaxy from the viewpoint of achieving large size and high quality at a relatively low cost. Furthermore, ZnO epitaxial growth on Si will facilitate the integration of microelectronics and optoelectronics [17,18]. If ZnO films and nanostructures with high quality can be grown on Si which is capable of mass production, this will be a great advantage, due to potential applications. Research work dealing with fabrication of quasi-one-dimensional ZnO nanostructures (such as nanorods, nanoneedles, etc.) on Si substrates by MOCVD without employing any metal catalysts has been reported [19, 20]. However, systematic investigation on the formation mechanism of ZnO thin films and nanostructures on Si substrates as a function of MOCVD growth conditions has so far been insufficient. Here, we report growth of ZnO thin films and nanostructures on Si substrates in a MOCVD process via morphology control as a function of growth conditions.

II. EXPERIMENTS AND DISCUSSION

Before the growth of ZnO by MOCVD, conventional wafer cleaning and a wet chemical treatment for removing the native oxide from Si(111) substrates by immersion in HF solution were carried out. Diethylzinc (DEZn) and NO$_2$ were used for ZnO growth on Si(111). Typical flow rates of DEZn and NO$_2$ for ZnO growth on Si(111) were 2 – 5 and 100 µmol/min, respectively. Growth for
ZnO thin films and nanostructures was carried out for 60 and 30 min, respectively. Total pressure of the reactor was kept at 8 Torr, and substrate temperatures were varied from 500 to 800 °C. For the growth, electronic-grade (6N) N₂ gas was used instead of H₂ as the carrier gas, to avoid surface etching of the ZnO layer. Photoluminescence (PL), atomic force microscopy (AFM), X-ray diffraction (XRD), and field-emission scanning electron microscopy (FE-SEM) measurements were carried out to evaluate the quality of the grown ZnO thin films, in addition with ZnO nanostructures, on Si substrates.

Effects of the DEZn flow rate on the crystal quality and surface morphology of ZnO thin films were investigated. When the DEZn flow rate was increased from 2 to 4 μmol/min, the c-axis-oriented crystallinity of samples grown at 500 °C was improved, as shown in Figure 1, while their surface smoothness investigated by AFM deteriorated (Figure 2). This fact shows that the growth of ZnO follows a combination mode of two-dimensional (2D) and three-dimensional (3D) growth, rather than a stable 2D layer-by-layer growth mode, on considering the increase of the value of root-mean-square (RMS) roughness with the increment of the DEZn flow rate. Generally, stable 2D layer-by-layer growth of high-quality ZnO on Si substrates is very difficult, due to the larger formation enthalpy of SiO₂ compared to that of ZnO, which is indicative of easy formation of SiO₂ on Si substrates. Although an HF treatment for removing native oxide on Si is carried out, it is very hard to remove the native oxide layer on Si perfectly. This fact means that ZnO growth on Si (strictly speaking, SiO₂) follows a stable 2D growth mode only with difficulty, resulting in the formation of ZnO thin films with rough surface morphology on Si.

PL spectra shown in Figure 3 were measured at 9 K. Figure 3 compares the spectra for the ZnO samples with DEZn flow rates of 2 – 4 μmol/min and growth temperature of 500 °C.
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Fig. 4. AFM images of ZnO thin films grown at 500 °C (a) and 700 °C (b) with DEZn flow rate of 3 μmol/min.

Fig. 5. PL properties (9 K) of ZnO thin films grown at 500, 600 and 700 °C, with a typical DEZn flow rate of 3 μmol/min.

grown at different flow rates of DEZn at 500 °C. With DEZn flow rates of 2 and 3 mol/min, the spectra are dominated by a neutral donor-bound exciton (DX) emission band. On the other hand, in the ZnO thin film grown with a DEZn flow rate of 4 μmol/min, a bound exciton transition (IX) and its LO phonon replicas (IX-LOs) are predominant. The emission band at about 3.312 eV, which is denoted as IX emission, might also originate from a donor-acceptor pair into the ZnO thin-film. However, the thin film samples are undoped. In addition, no shift of the emission band at 3.312 eV was observed as a function of PL excitation power. Thus, we can conclude that the IX emission band is attributed to a structural-defects-bound exciton transition and its LO-phonon replicas [21] or a rotation-domain-structure-induced localized-state-bound exciton transition and its LO-phonon replicas, which is a special feature of ZnO on Si [22].

The surface morphologies of two samples grown at 500 and 700 °C with the same DEZn flow rate of 3 μmol/min are shown in Figure 4. The higher growth temperature resulted in the formation of a ZnO thin film with flat surface morphology, which can be interpreted as enhanced migration of precursors and reactants at the growing surface. The AFM images [Figure 2(a) and Figure 4] showing the surface morphology of ZnO thin films grown on Si indicate the overall tendency of the growth modes of ZnO on Si at different growth conditions, i.e., the 3D growth mode resulting in rough surface morphology is dominant at lower growth temperatures and higher DEZn flow rates, while 2D nucleation contributing to lateral growth and flat surface morphology is promoted at higher growth temperatures and lower DEZn flow rates.

In order to investigate the effect of growth temperature on optical properties, we also carried out PL measurements of the samples with different growth temperatures from 500 to 700 °C. Free-exciton (EX) emission becomes stronger and the full-width-half-maximum (FWHM) value of the DX emission band is reduced in the samples with higher growth temperature, as shown in Figure 5. On considering these facts, it could be suggested that high-temperature growth suppressed generation of structural defects in ZnO.

Growth of ZnO was carried out in growth conditions with a higher DEZn flow rate of 5 μmol/min, compared to the preceding experiments, and growth temperature of 500 °C. First of all, a growth time of 30 s was employed, in order to clearly observe the initial phenomena in the formation of ZnO on Si. Figure 6(a) shows a plan-view FE-SEM image of ZnO nanoislands nucleated on Si. ZnO nanoislands with diameters of about 10 – 60 nm are clearly shown in the FE-SEM image, indicating typical
3D nucleation of ZnO on Si in this growth condition.

In order to study the evolution properties of ZnO nanoislands as a function of MOCVD growth time, we varied the growth time up to 30 min. In the initial stage of growth (growth time in the range of 30 – 180 s) the average diameter of nanoislands increased and the concentration of nanoislands decreased with increasing growth time. This phenomenon may be due to coalescence of a nanoisland with neighbor nanoislands. However, the average height of ZnO nanoislands dramatically increased according to the increase of growth time (growth time more than 180 s), leading to the nanoislands being converted to rod structures with high aspect ratios. Figure 6(b) shows an image of a sample consisting of close-packed nanorods with preferred c-axis orientation.

However, randomly oriented ZnO nanotower and nanocactus structures were formed at 700 °C and 800 °C, respectively, as shown in Figure 6(c) and (d). This is controversial, as considering the previous investigation on the formation of the thin film with smooth surface morphology at high growth temperature as shown in Figure 4. At high growth temperature, the growth behavior of ZnO on the surface of substrates depends strongly on the II-VI flow rate ratio. Recently, Liu et al. have reported that ZnO is of high nucleation density and forms continuous thin films on sapphire substrates at around 700 °C by plasma-enhanced chemical vapor deposition when grown in high oxygen content [23]. On the other hand, when oxygen content in the gas mixture is reduced, it is difficult to nucleate ZnO on the substrates. On taking over their results, the formation of nanotowers and nanocactuses with lower density compared to nanorods grown at 500 °C in this study might be attributed to the fact that ineffective ZnO nucleation on Si by a low NO$_2$/DEZn ratio, namely high zinc concentration, at the high growth temperatures of 700 and 800 °C results in the 3D growth mode of ZnO forming nanostructures with low density on the Si substrates. A more detailed investigation on the formation mechanism of nanotower and nanocactus structures, as well as their optical and structural properties, will be reported in the near future.

### III. CONCLUSION

The formation of ZnO thin films and nanostructures on Si(111) substrates in a MOCVD process was effectively controlled by altering the growth conditions, including source flow rate and growth temperature. ZnO thin films grown with lower DEZn flow rate and higher growth temperature showed smooth surface morphology as well as good optical properties, with a strong and sharp excitonic emission band resulting from suppression of defect generation into ZnO. On increasing the DEZn flow rate, the surface morphology of the thin films becomes dramatically rough, resulting in the formation of various kinds of nanostructures such as nanorods, nanotowers, and nanocactuses, in the growth condition with a DEZn flow rate of 5 μmol/min, depending on the MOCVD growth temperature. From these results, it is concluded that ZnO growth with a higher DEZn flow rate on Si strongly follows a 3D growth mode in a MOCVD process, indicating that a route from thin films to nanostructures relies on the 3D growth behavior of ZnO.

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### REFERENCES

