# PLD in Furnace 장비에 의한 Ga-Doped ZnO 나노선 합성 제어

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# Controlled Ga-doped ZnO NWs Synthesized by PLD in Furnace

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**Abstract** - We synthesize ZnO nanowires (NWs) doped with 3 wt% Ga on sapphire substrate using a hot-walled pulsed laser deposition (PLD) system named PLD in Furnace. A proprietary target rotating system is employed in the furnace to ensure the homogeneity of the deposition. The kinetic energy of the laser-ablazed ZnO is controlled for the optimization of NW formation. The physical properties of the resultant NWs are presented.

#### 1. Introduction

For decades, ZnO has attracted wide attention due to its remarkable advantages including wide bandgap, high exciton binding energy at room temperature as well as material stability. So far, ZnO thin films as well as the doping into the films have been intensively researched for lots of applications including transistors and diodes [1,2]. Since we can expect the additional benefits from the materials as their dimension is extremely reduced, nano-scaled structures of ZnO has also been studied extensively. The research has been focused on the preparation of the diversified nano-morphologies including nano-tubes, nano-horns, nano-wires, and nano-rings [3]. In spite of the morphological achievement, doping control into the nanostructures is highly desired for more advanced application of the structures, such as nano-FETs, nano LEDs, as well as nano lasers. However, only limited studies on the doped ZnO nanostructure show the feasibility of controlled doping into the miniaturized structures. Amongst strong doping candidates, Ga is considered as the most effective one for n-type ZnO NWs since the bonding length mismatch induced by the dopant can be minimized [1,4]. On the other hand, for the p-typed ZnO NWs, it is reported that P is the effective dopant when a CVD method is adopted [5].

In this work, we prepare 3% Ga-doped ZnO (GZO) NWs on a sapphire substrate using PLD, one of the powerful tools for the materials synthesis. PLD systems used in this experiment for nanostructure preparation has hot-walled temperature control for the kinetic energy control of the reacting particles, target rotating operation for the uniform material deposition, and off-centered substrate position with respect to the flume from the target in order for the control of the energy and the flow of the particles. Au catalyst guarantees vapor-liquid-solid (VLS) mechanism for NW growth. As a result, bottom grown ZnO NWs with stack-structure are obtained. NWs have the diameter and length of  $\sim\!120$  nm and  $\sim\!1~\mu\text{m}$ , respectively. Excellent crystalinity is confirmed by photoluminescence (PL) spectrum examination.

## 2. Experimental Optimization

The GZO NWs are synthesized with our PLD in Furnace system controlling NW growth kinetics. Especially, for the homogeneous laser ablation of the target, the target is designed to be lotated. Thus, the deleterious corn formation on the surface of the target can be avoid. As can be seen in Fig. 1, the PLD in Furnace system consist of electrical furnace, target and substrate loading system, and laser. The NWs are grown by VLS method with Au layers of  $30{\sim}50$  Å as the catalyst. The NW growth is optimized around 750°C. Since there is temperature gradient along the substrate holder, the sample position with respect to the target should also be considered in order to adjust the density and mobility of the ablazed particles from the target. In this work, the substrate is located 2.5 cm away from the target. Injected inert gas (Ar)

makes the atmosphere not reactive for the reacting particles ensuring stable and controllable synthesis condition. A mass flow controller guarantees the stable Ar flow into the furnace. Excimer laser operated at 248 nm is employed to shot the target. The energy density and repetition rate are 1.5 J/cm² and 5 Hz, respectively. Before the deposition, there should be pre-deposition step in that the laser shots the surface of the target 3000 times to modify the surface condition. The deposition process continues for 30 minutes.

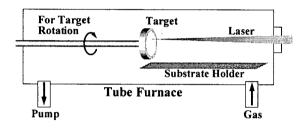


Fig. 1 PLD in furnace system for NW synthesis.

### 3. Result and Discussion

With the Au clusters formed from the Au layer deposited by thermal evaporator, the particles from the target ablazed by the excimer laser is dissolved into the liquid Au particles followed by the precipitation to form the NWs from the bottom of the Au catalysts described by VLS mechanism. SEM photos presented in Fig. 2 depict the optimization of the NW formation. As can be seen in Fig. 2(a), in case the kinetic energy of the particles is too high, GZO thin film is formed since the reacting particles are moving around wide range of substrate surface.

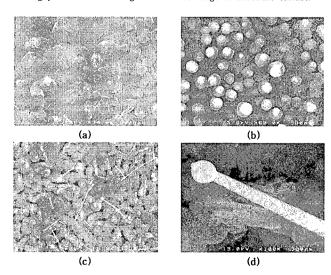


Fig. 2. SEM photos of (a) deposited GZO thin film at 950°C with 30 ÅAu, (b) the initial stage to form GZO post grown at 950°C with 50 ÅAu, and (c),(d) GZO NWs synthesized at 750°C with 30 ÅAu. The magnifications are (a) 30K, (b)60K, (c) 10K, and (d) 100K.

Fig. 2(b) illustrates that the diameter of the GZO 'posts' is as thick as 150 nm when the Au layer is too thick, therefore the gold balls have large diameters. In order to achieve longer posts, longer deposition time is expected. In Fig. 2(c) and (d), we can find the controlled GZO NWs. An Au catalyst ball located on the top end of the NW illustrates the bottom growing mechanism of the NWs. Due to shorter length Ga-O (1.92Å) compared with that of Zn-O (1.97Å), it is considered that the induced lattice mismatch provides the negative strain in the crystals, thereby induces the stack-structured NW (see Fig. 2(d)). Resultant ZnO NWs have the diameter of  $\sim 120$  nm and the length of  $\sim 1~\mu m$ .

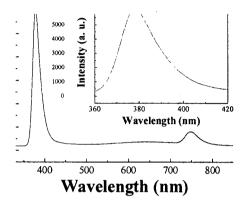


Fig. 3. Photo luminescence of the synthesized GZO NWs. Inset shows the magnified UV peak.

Fig. 3 shows the photoluminescence data of the prepared GZO NWs. The strong UV emission can be found at 378.1 nm (see inset) illustrating the blue shift of optical band to band transition by Ga-doping that is explained by the Burstein-Moss shift. It can be found that there is negligible defect knowing from the suppressed emission in visible range saying that our NWs have an excellent crystalinity.

#### 4. Conclusion

In this work, the controlled synthesis of GZO NW is achieved by PLD in Furnace method. By further researches on the variety of cases, it is expected that the systematic doping mechanism in the nanostructures can be elucidated, thereby more intensive applications of ZnO NWs can be realized.

#### [References]

- [1] J. H. Kim, B. D. Ahn, C. H. Lee, K. A. Jeon, H. S. Kang, S. Y. Lee, *J. Appl. Phys.*, 100, 113515 (2006).
- [2] H. S. Kang, B. D. Ahn, J. H. Kim, G. H. Kim, S. H. Lim, H. W. Chang, S. Y. Lee, Appl. Phys. Lett., 88, 202108 (2006).
- [3] B. P. Zhang, N. T. Binh, K. Wakatsuki, Y. Segawa, Y. Yamada, N. Usami, M. Kawasaki, H. Koinuma, Appl. Phys. Lett., 84, 4098 (2004).
- [4] J. Owen, M.S. Son, K.-H. Yoo, B. D. Ahn, S. Y. Lee, Appl. Phys. Lett., 90, 033512 (2007).
- [5] B. Xiang, P. Wang, X. Zhang, S. A. Dayeh, D. P. R. Aplin, C. Soci, D. Yu, D. Wang, "Rational synthesis of p-type zinc oxide nanowire arrays using simple chemical vapor deposition," *Nano Letters*, 7(2), 323-328 (2007).