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# 奈米結構氧化物光子晶體材料製程與光電特性研究(1/3)

## Low-temperature Growth of Zn-ZnO Polygon Prismatic Nanocrystals by Thermal Vapor Transport for Photonic Crystals

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### 中文摘要

本研究利用熱蒸發與沉積的製程，成功地在矽基板上生長出六方結構的氧化鋅特殊多面體奈米結構。一般而言，結晶相與成核的種子的控制，對於奈米晶體在成長開始時的本質形狀是很重要的，將含有金屬鋅離子的有機溶液先塗佈在基板上，並以此作為成核的種子。再利用熱蒸氣傳輸製程以氧化鋅粉末為成長源，並通入純氬氣，而在基板溫度為 250°C 下即可成長。結果發現，未作任何後段處理的氧化鋅多面體奈米結構其實是由，六方結構的金屬鋅與外層氧化後的氧化鋅薄膜所組成。我們也設計了許多不同的熱處理來觀察此氧化鋅多面體奈米結構的形貌與結晶性。並可以確定其成長機制應該是由金屬鋅與氧化鋅間無機的架橋機制而來。而這些六方結構的金屬鋅與氧化後的氧化鋅將進一步作為後續光子晶體結構的研究。

關鍵詞：氧化鋅、奈米晶體、光子晶體、螢光、熱蒸發與沉積

### Abstract

A novel hierarchical polygon prismatic nano-structure of hexagonal ZnO and Zn has been successfully grown on silicon by thermal vapor transport and condensation method. Thus, in this work, the organic solvent with zinc chemical compound was first coated and used as seeds on the silicon substrate. Subsequently, it was grown by thermal vapor transport with ZnO powder at 250°C (substrate) in Ar atmosphere. The samples were characterized using X-ray diffraction, scanning and transmission electron microscopy, photoluminescence spectroscopy. The as-synthesized ZnO polygon prismatic nano-structure consisted of hexagonal metallic nuclei (Zn) covered with an oxidation outer thin

film (ZnO). Depending on the different annealing temperature and reaction atmosphere, Zn polygon prismatic structure having various morphologies can be developed. The dimension and crystal phase can be controlled by temperature, time, kinetic surface energy, and capping molecules. The possible formation mechanism for the Zn-ZnO polygon prismatic crystal structure is identified and proposed as the Zn-ZnO mineral bridge mechanism. Although the present nonperfect Zn-ZnO polygon prismatic structure shows weakly UV emission and strongly deep-level emission, the PL properties and crystallization of Zn-ZnO prismatic nanocrystals could be improved by suitable post-treatment. **Keywords:** ZnO、nanocrystals、photonic crystal、photoluminescence、thermal vapor transport and condensation

### I. Introduction

Zinc oxide possesses unique optical, electrical and structural properties that make it useful for a wide range of technological applications such as photo-detector [1], solar cells [2,3], nanolasers [4], and other highly functional devices [5]. Recently, much effort has been invested in fabricating quasi-one-dimensional ZnO nanostructures, because the size and shape of nanocrystal represent key elements that determine their electrical and optical properties [6]. Currently, both gas and liquid phase methods are used to synthesize and control the nanocrystal. The vapor-liquid-solid (VLS) method is the common approach to grow the nanostructure and many researchers have tried to control the process parameter to produce various shape nanocrystal, such as nanorod [7], nanonail [8], nanoblets [9], etc. On the other hand, the liquid phase synthesis of anisotropic nanocrystals has been far more limited, and only the based system has been studied in depth. The liquid phase growth mechanism can sketchy divide into two steps. In the first step, spherical seed nanocrystals

are homogeneously nucleated Precursors with materials for the desired one-dimensional structures are chemically reduced in the presence of capping molecules and seed nanocrystals that serve as nucleation sites. The gas phase process has been explored to produce 1D nanostructure of different cross sections as well as some other exotic shape [10]. However, the gas phase and liquid phase syntheses seem to be hard to reach uniform morphologies at comparatively mild synthesizing conditions.

The photonic band gap crystal is simply a spatially periodic structure consisting of high and low dielectric regions. A promising technique to fabricate 3D photonic crystals with a photonic band gap in optical wavelengths is self-assembling growth of one-dimensional inorganic nano-crystals. In contrast to conventional process we present both gas and liquid method toward the growth of well-proportional and crystallized Zn and ZnO polygon prismatic nanocrystals. In order to recognize the growth mechanism of Zn polygon prismatic structure, different heat treatment and heating profiles were designed to observe the morphology and crystallization of Zn polygon prismatic structure. The crystal size from micrometer to nanometer and phase control of the ZnO polygon prismatic nanocrystals can be achieved by varying the growth time and temperature.

## II. Experimental

ZnO and Zn polygon prismatic nanocrystals were synthesized using a colloidal Zn particles and physical vapor transport system. An alumina tube was mounted inside a high temperature tube furnace. Preparation of colloidal Zn in methanol: 50 ml of a  $1 \times 10^{-2}$  M Zn (ClO)<sub>2</sub> solution is added to 442 ml methanol plus 8 ml 5M NaOH. The solution is vigorously shaken for 10 min and left overnight. After about 24 hours a transparent solution of stable colloidal is obtained. ZnO powder and graphite mixture were used as Zn source. The source material was placed on an alumina boat. After placing the boat at the center of the tube and the substrate locating downstream of the carrier gas flow, the tube was sealed and evacuated by mechanical rotary pump to a pressure of 80 mTorr. As carrier gas of 100% Ar was used, with a flow rate of 10 sccm, reaction was carried out at 1100°C and kept at that temperature for 0.55 hour to form Zn-ZnO polygon prismatic nanocrystals at 250°C (substrate temperature). The Zn polygon prismatic nanocrystals were annealed at 260 in pure oxygen atmosphere (5N) for 30 minutes to form the ZnO layer on the Zn crystals. After that, the Zn-ZnO polygon prismatic nanocrystals were

thermally annealed at 550°C for over 3 hours to study the changes of morphology and crystallization.

The deposited product was characterized and analyzed by scanning electron microscopy (FE-SEM, S4100), and the crystal structure was analyzed using XRD (Siemens D5000). TEM studies of the crystal were carried out a Philips CM20 and Hitachi-600 operated at 200 KeV and 100 KeV, and energy-dispersive X-ray spectroscopy (EDS) attached to SEM and TEM, respectively.

## III. Results and discussion

Figure 1 shows typical scanning electron microscopy (SEM) and TEM image of the Zn polygon prismatic crystals. The diameter of the crystals can be tuned from 30 nm to  $\mu\text{m}$  by increasing the concentration of the Zn(ClO) solution. As the concentration of the Zn(ClO) solution increases, the amount of Zn particles would increase. The Zn particles behave as the nucleus sites of the larger Zn crystals. The amount of Zn nucleus sites would be proportional to the concentration of the Zn(ClO) solution. In the highly concentration solution, the large and sharp Zn polygon prismatic crystals ( $\sim 2$   $\mu\text{m}$ ) were synthesized on the substrate by thermal vapor process (Fig. 1A). On the contrary, as the amount of nucleus sites decreases, the crystal size of Zn polygon prismatic structure shrinks to  $\sim 30$  nm scale (Fig. 1C). Figure 2A illustrates the schematic mechanism of such a process. In this case, the initial nucleus sites were prepared by Zn(ClO) solution. When Zn sources were transported by thermal evaporation process, these nucleus sites would cap these Zn molecules to develop the nanocrystals. In the following step, some of the fine Zn nanocrystals would get together to form the large crystals. According to above statement, it was found that the concentration of the Zn(ClO) solution could determine the nucleus sites. Therefore, the amount of nucleus sites would determine the size of the Zn polygon prismatic crystals. It was found that the initial nuclei of Zn polygon prismatic crystals were emerged into the small Zn polygon prismatic crystals by themselves and its diameter is less than 10 nm, as seen in Fig. 2B. Figure 2C shows the special distribution pattern of Zn polygon prismatic nanocrystals ( $\sim 30$  nm) formed in the initial stage of crystal growth. The spreading region of these distributed Zn nanocrystals has diameter around 150 nm that is close to the composition crystals obtained in our experiments (Fig. 2D). It suggests that the spatial distribution region of Zn nanocrystals would develop the base for the larger size crystals. After the suitable growth time, the Zn polygon prismatic

crystals will be formed on that base (Fig. 2E).

The shape of the Zn polygon prismatic nanocrystals would vary with the growth time. Figure 3 presents the growth of the Zn polygon prismatic nanocrystals as a function of time. The perfect Zn nanocrystals are observed for the growth time of 2 hours. When the growth time exceeds 2 hours, the shape of the Zn polygon prismatic nanocrystals would begin to disintegrate (Fig. 3B). It is well known that metal state will become unstable when the temperature reaches around its melting point. The apparent melting point (Zn: mp 410°C) would be reduced for nanocrystal with size small enough. The balance between the thermodynamic and kinetics would be influenced by the growth time. It implies that if the growth time exceeds the critical time, the equilibrium status would be destroyed. It could be due to the unstable lattice-site of zinc atom in the Zn polygon prismatic crystals, long time thermal heating will make the crystal structure destructible. To keep the stability of grown crystals, the oxidation treatment to modify the surface status of Zn polygon prismatic crystal is applied. Both Zn and ZnO have the hexagonal (hcp) structure. From the growth kinetics point of view, when ZnO is formed, the rearrangement of the sublattices of zinc from hcp (Zn) to hcp (ZnO) has to occur only at Zn reaction front. Therefore, the nucleating ZnO grain has a template to follow the orientation of Zn exactly. Figure 4 shows the surface morphology of Zn polygon prismatic nanocrystal after thermal treatment at 550°C for 3 hours. It is obvious that Zn polygon prismatic crystals with surface treatment could retain the complete crystals structure (Figure 4B). It is due to the ZnO layer formed by surface treatment that prohibits the zinc atoms leaving away lattice and prevents the crystals from being destroyed.

Figure 5 shows the X-ray diffraction (XRD) spectrum of the nanostructures, where the intensity of zinc crystalline phase is different for different treatment. In contrast with crystallization of Zn polygon prismatic nanocrystals, the sample that undergoes the oxidation treatment presents the stronger XRD peak intensity than the other. For the Zn polygon prismatic nanocrystal subjected to oxidation treatment on Zn surface, the crystalline phase can be developed and identified from the XRD (Fig. 5B). Chemical composition microanalysis by energy dispersive spectrometry (EDS) reveals that the Zn polygon prismatic nanocrystals with surface oxidation are composed of more content of zinc compared to those without surface treatment (with an atomic ratio of = 15). This is in a good agreement with the XRD analysis result.

The photoluminescence (PL) measurements of the synthesized Zn polygon prismatic nanocrystals are performed at room temperature, using a He-Cd laser line of 325 nm as the excitation source. As shown in Figure 6, UV and green emission peaks at 380 nm and 530 nm are observed for the Zn polygon prismatic nanocrystals with surface treatment. The PL spectrum is different from that of Zn. Zn polygon prismatic nanocrystal without oxidation treatment. No emission peaks are found because the Zn polygon prismatic nanocrystal is only composed by pure zinc metal in this case. On the contrary, as the Zn nanocrystals have undergone oxidation treatment, the surface will form a thin oxide layer. According to the XRD analysis, the oxide layer is basic zinc oxide. ZnO usually displays two major PL peaks, UV (near-band-edge) emission peak and green (or red) emission peak (deep-level). The deep-level emissions are generally associated with defects in ZnO lattice. Besides, the near-band-edge transition could not effectively exist in the polycrystalline ZnO. Although the developed Zn polygon prismatic nanocrystals are well crystalline, the interface between Zn and ZnO surface layer usually results in large lattice mismatch (17%). The kind of interface becomes the defect generator to support the deep-level emissions. In addition to lattice mismatch, the incomplete oxidation of zinc produces the defects inside surface layer and gives deep-level emission too.

#### IV. Conclusion

Single-crystalline Zn polygon prismatic nanocrystals are synthesized by liquid solution seed nucleation and vapor growth method. The cation concentration of liquid solution determines the dimension of Zn crystals from the nanometer (30 nm) to micrometer scale (2 μm). The Zn polygon prismatic nanocrystals are grown up through a thermal evaporation process. The Zn nanocrystals undergone surface treatment will form the ZnO surface layer. The ZnO surface layer could maintain the polygon prismatic structure and prevent the zinc crystal from being destroyed at higher temperature. In addition, the ZnO surface layer improves the photoluminescence property. Considering their shape, crystal dimension and oxidation behavior, as expected, the crystals having good optical property could be formed within different microcavities. These nano and microcrystals can be further used as building blocks to assemble two- or three-dimensional assemblies.

#### Acknowledgments

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Fig. 1. SEM images of the Zn polygon prismatic crystals synthesized by liquid solution and vapor transport method. A) Zn polygon prismatic crystals of 2- $\mu$ m diameter. B) Zn polygon prismatic crystals of 300-nm diameter. C) TEM images of the Zn polygon prismatic nanocrystals of 30-nm diameter.

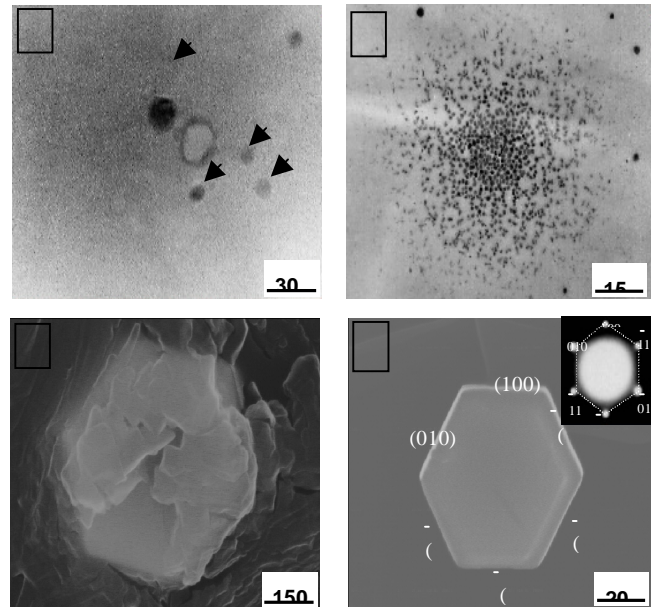
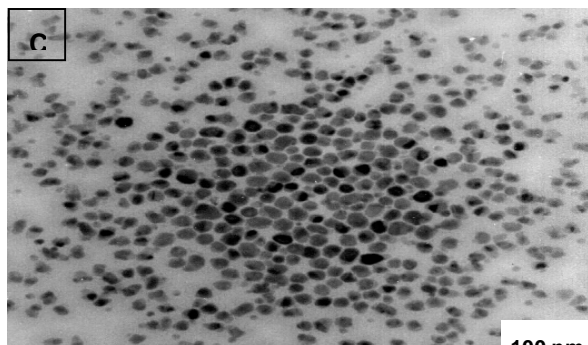
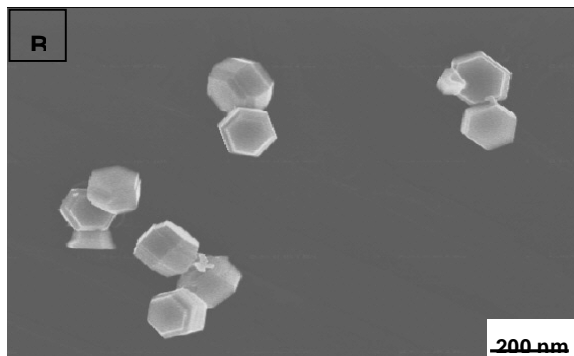
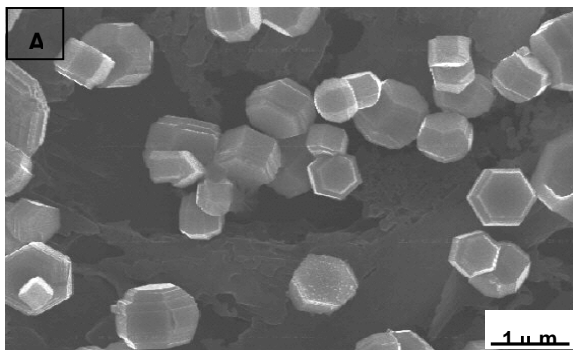
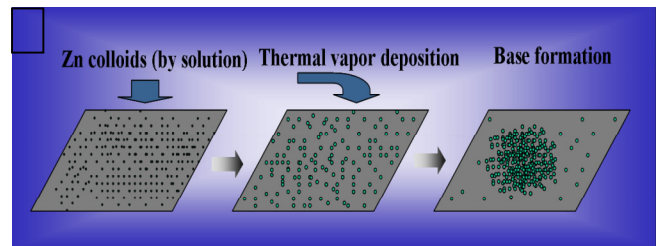
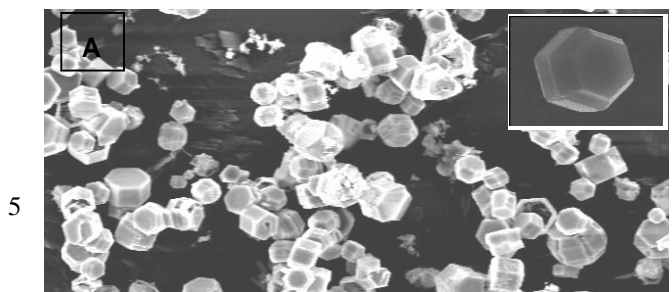


Fig.2. (A) Schematic illustration of growth mechanism of Zn polygon prismatic nanocrystals. (B) TEM image of nuclei of Zn polygon prismatic nanocrystals (~7 nm) (C) TEM image of Zn polygon prismatic nanocrystals (30 nm) formed by thermal vapor process. (D) Growing Zn polygon prismatic nanocrystals (0.6  $\mu$ m). (E) SEM image of Zn polygon prismatic crystals (0.7  $\mu$ m) formed by the collection of the ultra-fine Zn nanocrystals.



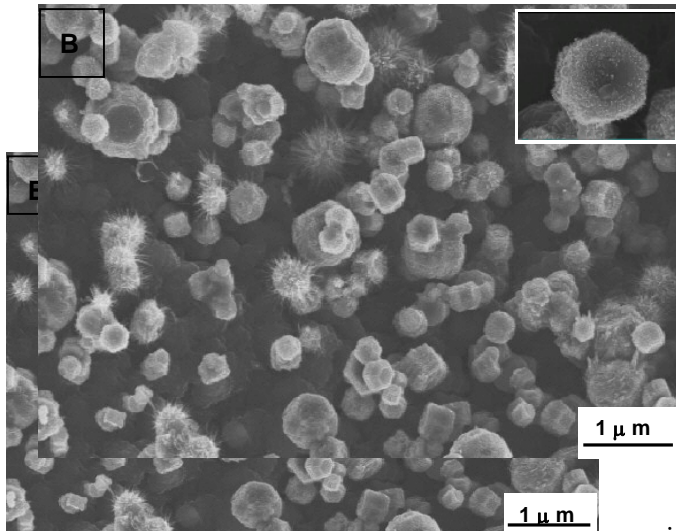


Fig. 3. SEM images of Zn polygon prismatic nanocrystals growing as a function of time. (A) 2 hours. (B) more than 3 hours.

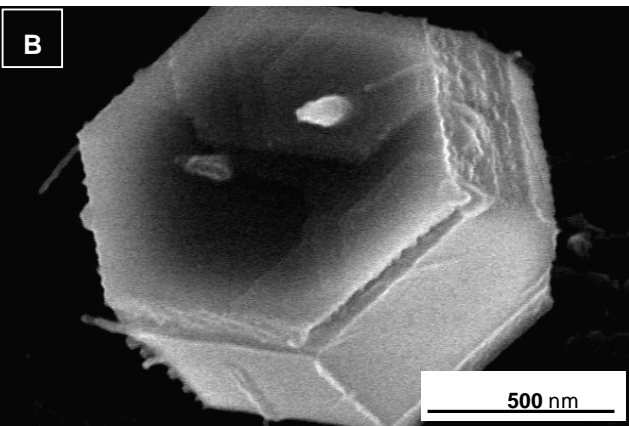
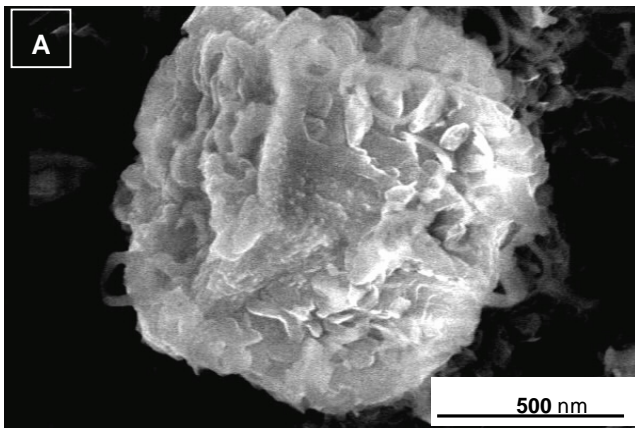


Fig. 4. SEM images of Zn polygon prismatic nanocrystals were thermally heated at 550°C and kept for 3 hours (A) without and (B) with oxidation treatment.

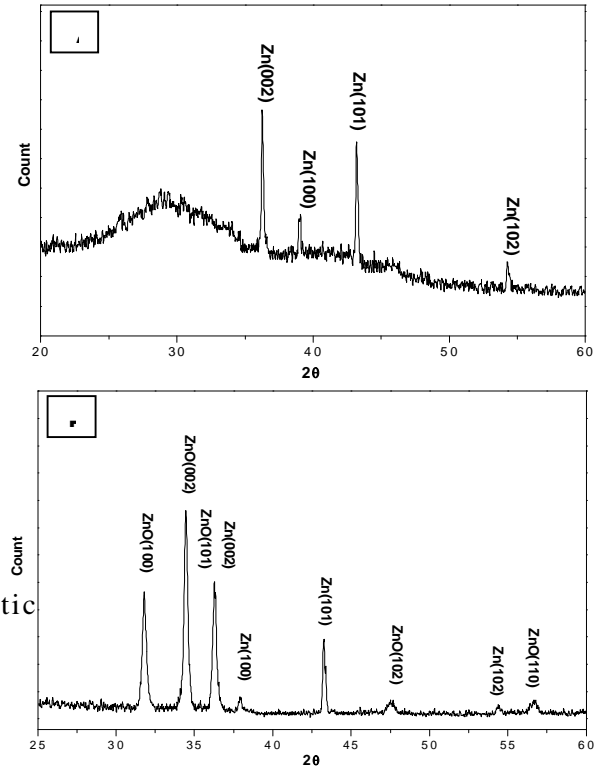


Fig. 5. X-ray diffraction (XRD) spectrum of Zn polygon prismatic nanocrystals were thermally heated at 550°C and kept for 3 hours (A) without and (B) with oxidation treatment.

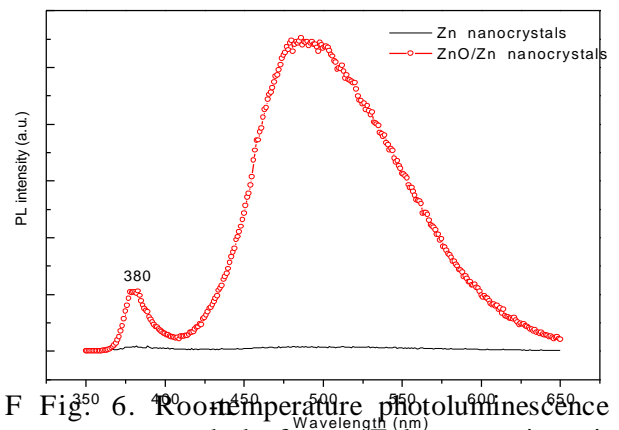


Fig. 6. Room temperature photoluminescence spectra recorded from Zn polygon prismatic nanocrystals with and without oxidation

treatment.