



Structure and Morphology Study of Both Un-doped and P-doped ZnO

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Over the past decades, Zinc Oxide (ZnO) semiconductor and its derivatives have been extensively developed because of its optoelectronic properties, such as piezoelectric and photocatalytic properties. Since ZnO is an intrinsic n-type semiconductor; therefore, how to synthesize high-quality p-type ZnO semiconductors with doping and investigate their optoelectronic properties and local chemical structures are important and necessary. In my project, I present two studies of synthesizing both un-doped and phosphorus doped ZnO nano/microstructures by hydrothermal method and chemical vapour deposition (CVD) technique, respectively. Figure 1a) and Figure 1b) are the low magnification SEM images of P-doped and un-doped ZnO prepared by the hydrothermal method, respectively. By comparing the Figure 1a) and Figure 1b), much more products can be found on the substrate in image 1b) than image 1a), which means un-doped ZnO product has more quantity than P-doped ZnO products. This phenomenon may be caused by the phosphorus dopant changing the growing environment of the ZnO crystal and affecting the growth of ZnO crystals. The precursor concentration determines the density of the rod distribution. When the first generation of nanorods appears, further nucleation would be more likely to participate in the growth of existing nanorods instead of forming a new nucleus on the silicon substrate. Since the phosphorus substitute the Zn in P-doping ZnO products; therefore, the concentration of Zn^{2+} is influenced in P-doping ZnO products and affects the value of surface coverage.

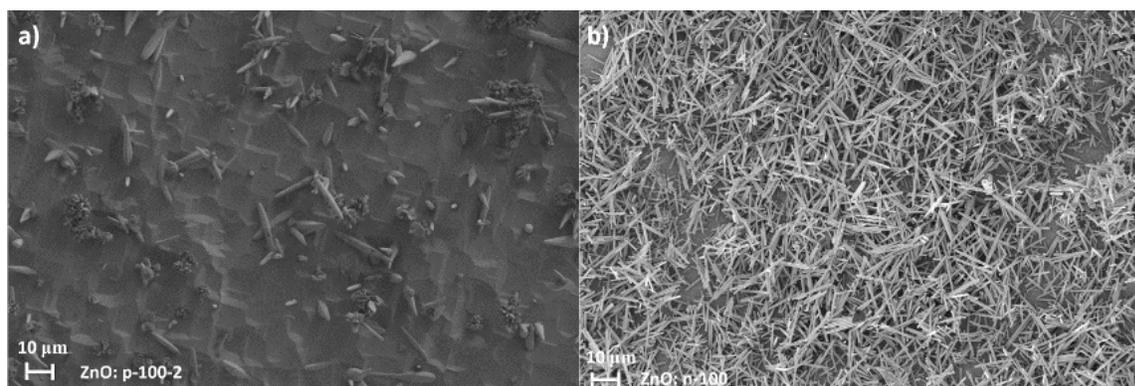


Figure 1. low magnification SEM images of P-doped and undoped ZnO prepared by the hydrothermal method.
a). P-doped ZnO structures. b). undoped ZnO structures.

Figure 2 is the EDX mapping of zinc, oxygen, phosphorus in P-doped ZnO structure prepared by the hydrothermal method. As shown in the Figure 2, the majority elements of P-doped ZnO are Zn and O. There are phosphorus signals can be found in P-doped ZnO structures as well, but signals are very weak as expected, and they are most noticeable in the few scattered particles which are likely unreacted precursors. However, there is a P distribution that matches that of the Zn and O signal. Thus Figure 2 suggests that the phosphorus has been doped into the ZnO crystal structures.

Figure 3a) and Figure 3b) are the low magnification SEM images of un-doped and P-doped ZnO prepared by the CVD method, respectively. By comparing Figure 3a) and Figure 3b), there are more products can be found on the substrate in Figure 3a) than Figure 3b), which means un-doped ZnO product has more quantity than P-doped ZnO products. This phenomenon may be caused by the phosphorus dopant changing the growing environment of the ZnO particles and affecting the growth of ZnO products. The chemical reaction for ZnO synthesis by CVD is $2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$. The mechanism of ZnO synthesis can be mainly divided as two stages: the formation of zinc vapour, and the nucleation and oriented growth of

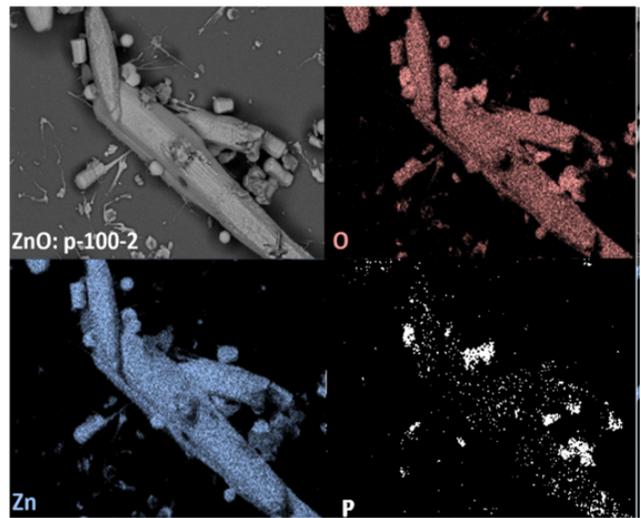


Figure 2. EDX mapping for P-doped ZnO structures prepared by hydrothermal method

ZnO. First, the Zn powder would be heated until the gas phase. Then, the Zn vapour would react with the Au layer and form alloy droplets. When the alloy droplet became supersaturated ZnO particles would be grown on the silicon wafer surface. Therefore, the amount of precursor (Zn) can be predicted as the dominant role during the ZnO synthesis process. Since the phosphorus substitute the Zn in P-doping ZnO products; therefore, the concentration of Zn^{2+} is influenced in P-doping ZnO products and affects the value of surface coverage, and the quantity of P-doped ZnO products is less than un-doped ZnO product.

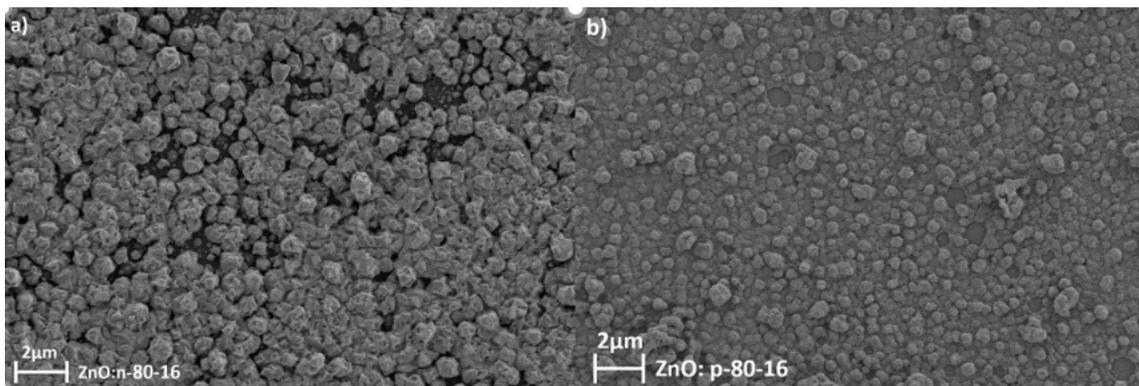


Figure 3. SEM images for un-doped and P-doped ZnO structures prepared by CVD method. a). un-doped ZnO structures. b). P-doped ZnO structures

Figure 4 is the EDX mapping of zinc, oxygen, phosphorus in P-doped ZnO structures prepared by CVD method. As shown in Figure 4, the majority elements of for P-doped ZnO are Zn and O. There are phosphorus signals can be found for P-doped ZnO structures as well, but signals are weak. There is a P distribution that matches that of the Zn and O signal. Thus Figure 4 suggests that the phosphorus has been doped into the ZnO crystal structures.

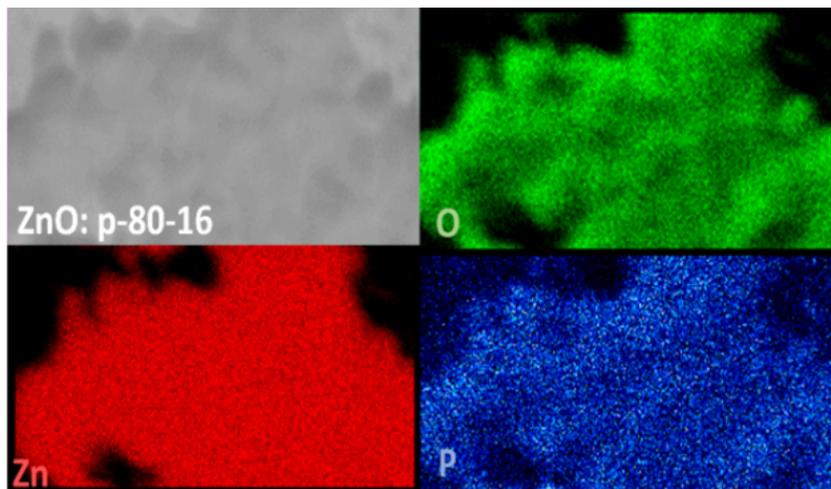


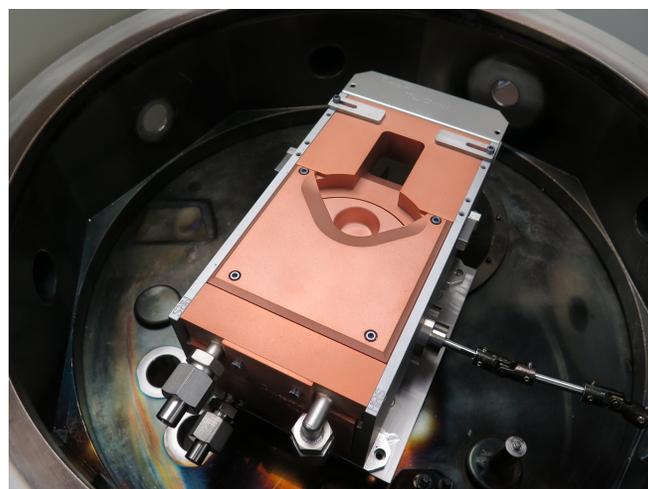
Figure 4. EDX mapping for P-doped ZnO structures prepared by CVD

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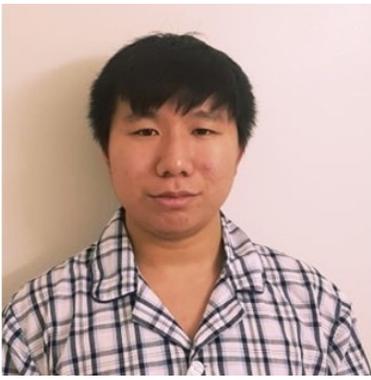
The new Temescal Power Supply and Electron Beam Beam Source for the HOSER evaporator have finally arrived!!! We are currently in the process of installation and once operational, the system will be able to evaporate metals, non-metals as well as experimental materials.



Temescal CV-6SLX 10kV 6 kW Power Supply and Beam Controller



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Calcium Phosphate Coatings on Titanium Synthesized using Electrochemical and Biomimetic Deposition

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In biomaterial research, there is much attention surrounding the use of titanium (Ti) and titanium-based alloys as implants to support pre-existing biological structures because of their low toxicity and desirable mechanical properties. However, due to the metallic nature of Ti, osseointegration has shown to be an obstacle. A suggested approach to this problem is to deposit a thin layer of calcium phosphate onto the metal surface, in hopes of promoting chemical bonding between the implant and bone. Unlike Ti, calcium phosphates have high biocompatibility and exhibits a similarity in chemical composition with natural bone. As a result, the mechanical strength and toughness of Ti is combined with the bioactive properties of calcium phosphate. This deposition process allows for potential growth of bone-like material to form on the substrate surface, improving the osseointegration of the implant.

In my project, calcium phosphate coatings were deposited on Ti metal substrates via two chemical methods: electrochemical deposition (ECD) and biomimetic deposition (BMD), respectively. The deposition efficiencies, coating morphologies and compositions were comparatively studied. To enhance the coating-metal attachment, the surface of the Ti was first anodized to create a layer of TiO₂ nanotubes¹. In ECD, the treated Ti substrate was used as cathode in an electrochemical cell with Pt being the anode. The electrolyte solution contains Ca(NO₃)₂ · 4H₂O as the Ca precursor and (NH₄)H₂PO₄ as the phosphorous source. Past studies have shown that traditional current deposition led to low adhesive coatings, therefore, pulsed current deposition was used instead². BMD was performed by placing the treated Ti substrate in a simulated body fluid, at 69C. Using Scanning Electron Microscopy (SEM) at the Nanofabrication Facility at Western University, it was

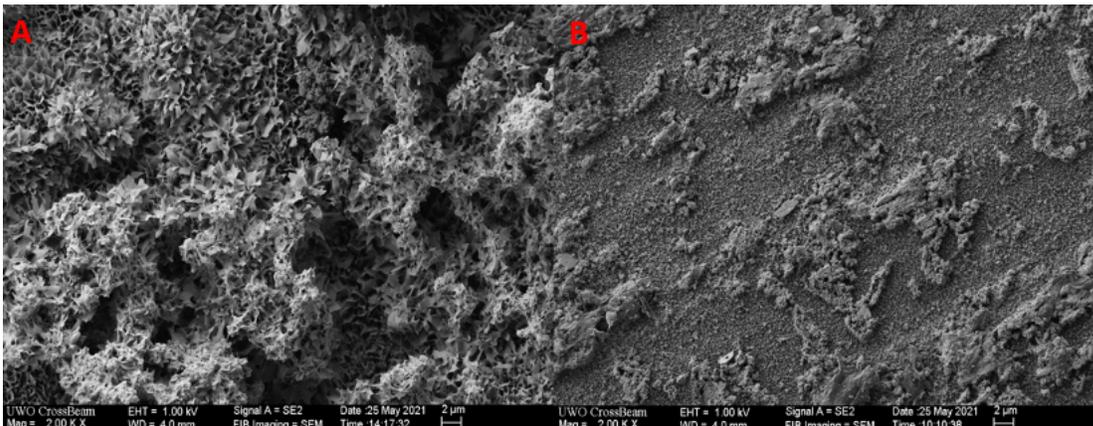


Figure 1: SEM Imaging of Calcium Phosphate (Inorganic Precursor) on Titanium Nanotubes (A: ECD, B: BMD)

found that the coating formed by ECD provides higher uniformity and greater coverage in comparison to the biomimetic method (**Figure 1**). In particular, the coating formed by ECD is only 1 hour, while after 24 hour of BMD, only partial coverage is achieved. The morphology of the crystals shows a resemblance to hydroxyapatite³. Characterizations are underway to confirm the crystal structure of the coatings.

We also attempted to replace the inorganic phosphate with an organic phosphate source, phosphoserine, in the ECD process. Previous studies suggest the phosphoserine can bind strongly with Ca²⁺ and grow into flower-like structures⁴. The SEM image reveals that the coating synthesized with phosphoserine has a unique morphology, which contains both cuboid and stacks of plates (**Figure 2**). Our current hypothesis is that the growth of the crystals is influenced by the linking effect between the phosphoserine molecule and the Ca²⁺. The next step of this project is to optimize the morphology of the coatings prepared by ECD, and examine their bioactivity using osteoblast cells.



Figure 2: SEM Imaging of Calcium Phosphate (Organic Precursor) on Titanium Nanotubes via ECD

References:

- (1) Su, Z.; Zhang, L.; Jiang, F.; Hong, M. Formation of Crystalline TiO₂ by Anodic Oxidation of Titanium. *Progress in Natural Science: Materials International* **2013**, 23 (3), 294–301.
- (2) Mokabber, T.; Lu, L. Q.; van Rijn, P.; Vakis, A. I.; Pei, Y. T. Crystal Growth Mechanism of Calcium Phosphate Coatings on Titanium by Electrochemical Deposition. *Surface and Coatings Technology* **2018**, 334, 526–535.
- (3) Ciobanu, G.; Carja, G.; Ciobanu, O.; Sandu, I.; Sandu, A. SEM and EDX Studies of Bioactive Hydroxyapatite Coatings on Titanium Implants. *Micron* **2009**, 40 (1), 143–146.
- (4) Zhou, H.; Jiang, Y.-Y.; Tan, S.; Liu, L.-J.; Yao, Q.-T.; Xia, Y.-J.; Fan, Y.-S.; Hu, J.-P.; Zhou, Z.-F.; Lu, B.-Q.; He, S.-S.; Chen, F. Flower-like Calcium Phosphoserine Complex as Biomimetic Mineral with High Bioactivity. *Ceramics International* **2020**, 46 (13), 20914–20922.

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