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Pulsed laser deposition of ZnO nanostructures for hybrid inorganic/organic solar cells

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Abstract

Although today's solar cell market is entirely dominated by wafer-based silicon technologies, nanostructured solar cells have already attracted much attention in order to improve efficiency, reduce cost, or ideally both. Hybrid inorganic/organic solar cells are promising candidates for achieving low-cost solar cell devices. Nanostructural control of the morphology of the inorganic acceptor bears potential for improving charge transfer and conversion efficiencies in such devices by creating direct charge carrier pathways and increasing surface area, respectively[1)].

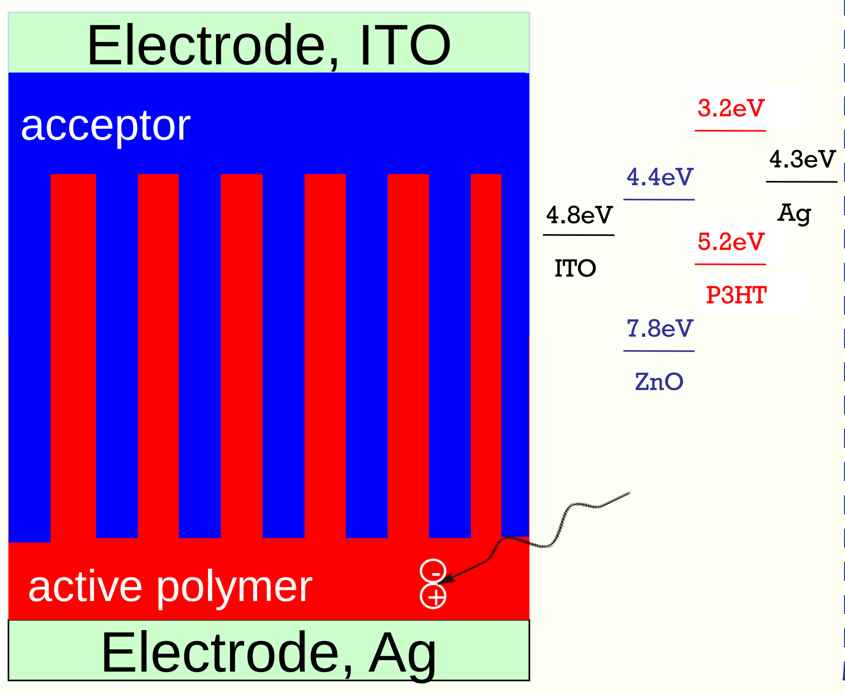
In this work, ZnO nanorods have been grown by pulsed laser deposition (PLD) using Au-catalyst. The nanorods were grown on pre-annealed c-plane and a-plane sapphire substrates, and as-grown samples were examined by scanning electron microscopy (SEM). The influence of sapphire substrate roughness on the ZnO nanorod morphology was investigated.

Principle of the Solar Cell

The principle of hybrid organic/inorganic PV cells is based on the creation of an exciton (tightly bound electron-hole pair) by light absorption in the active polymer. This exciton is dissociated at the interface between the polymer and the inorganic material and gives rise to the photocurrent. The diffusion length of the exciton is very short (typically 10-20 nm) and prevents the exciton from reaching the interface before it recombines. To overcome this problem, the interface area is greatly increased by creating an interdigital structure of inorganic and organic material.

In order to increase the interface area and to avoid the recombination of the exciton, the introduction of nanorods is proposed. ZnO, as the inorganic acceptor, has a wide band gap (3.37eV) and a large exciton binding energy (60meV) and is seen as a good material for ultra-fast photoinduced charge transfer. In practice, the photovoltaic devices are limited by charge transport (insertion of polymer between nanorods) and charge generation (large pores). The low lifetime of the active polymer has also been an issue.

The objectives are to grow vertically-aligned and high area density of ZnO nanorods using PLD, and to investigate properties of the interface between ZnO nanorods and the active polymer and surface modifications. As an active polymer the poly(3-hexylthiophene) (P3HT) have been investigated.

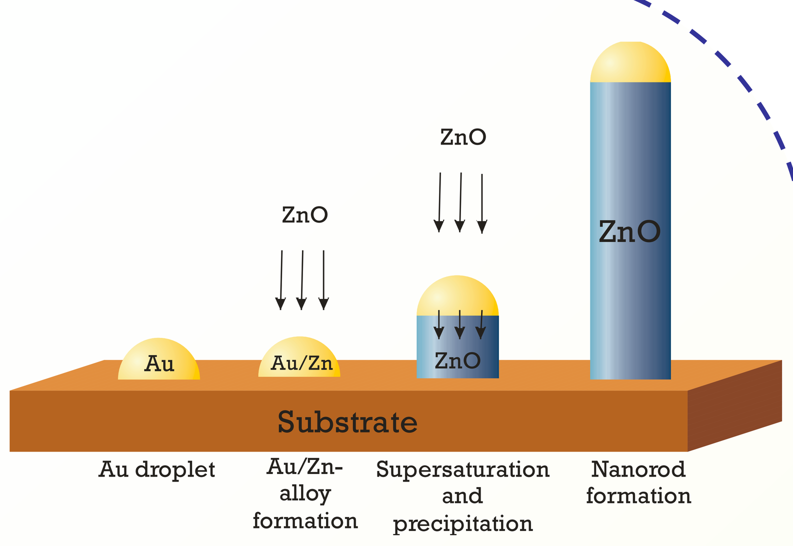


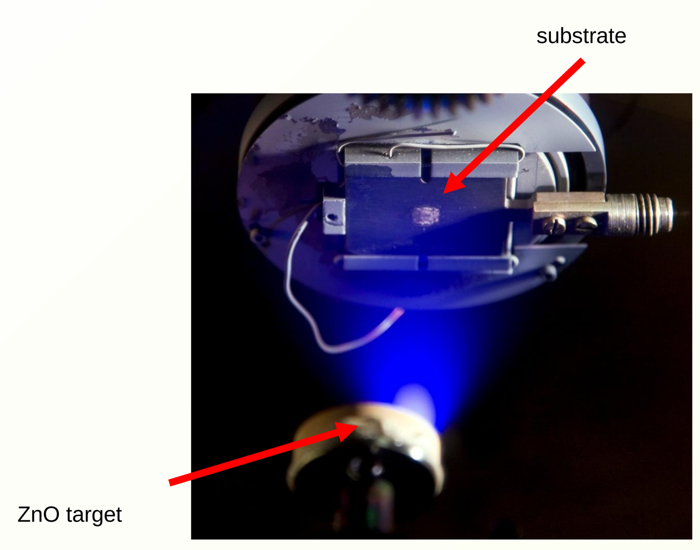
VLS mechanism and PLD growth

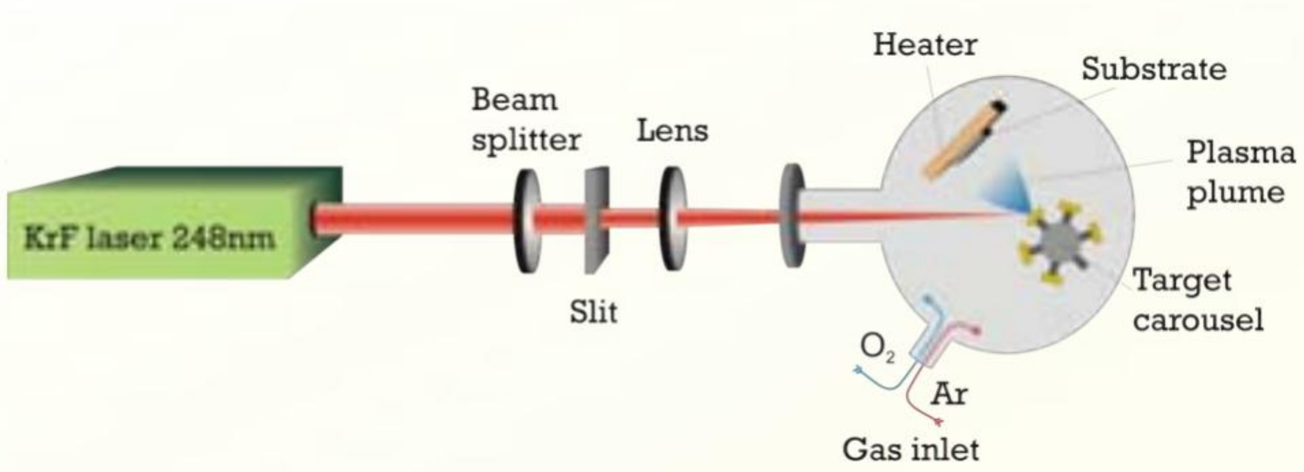
Most of today's nanowires are synthesized using the vapor-liquid-solid (VLS)[2)] growth mechanism, as illustrated here. When the temperature is above the eutectic point of the seed catalyst (Au) and Zn, droplets are formed. The Zn diffuses into the Au/Zn-alloy particle where it becomes supersaturated and ZnO precipitates underneath the catalyst droplet. The Au–Zn binary phase diagram is much more complex than the Au–Si or Ge–Si diagrams and not very well understood.

In PLD, a KrF excimer laser at 248 nm is focused on a scanning target of ZnO, evaporating and depositing material onto a substrate 45mm away from the target. Samples were heated to a temperature of 700°C and background gas pressures were kept at 0.5mbar with gas compositions of 100% O_2 or 95% Ar/5% O_2. Substrates used were a-plane sapphire(11-20) and c-plane sapphire(0001), and the laser fluence on the target was estimated at 1 J/cm^{-2}.

For catalytic growth, a Au layer of about 1.4nm nominal thickness was deposited by e-beam evaporation prior to PLD.







References

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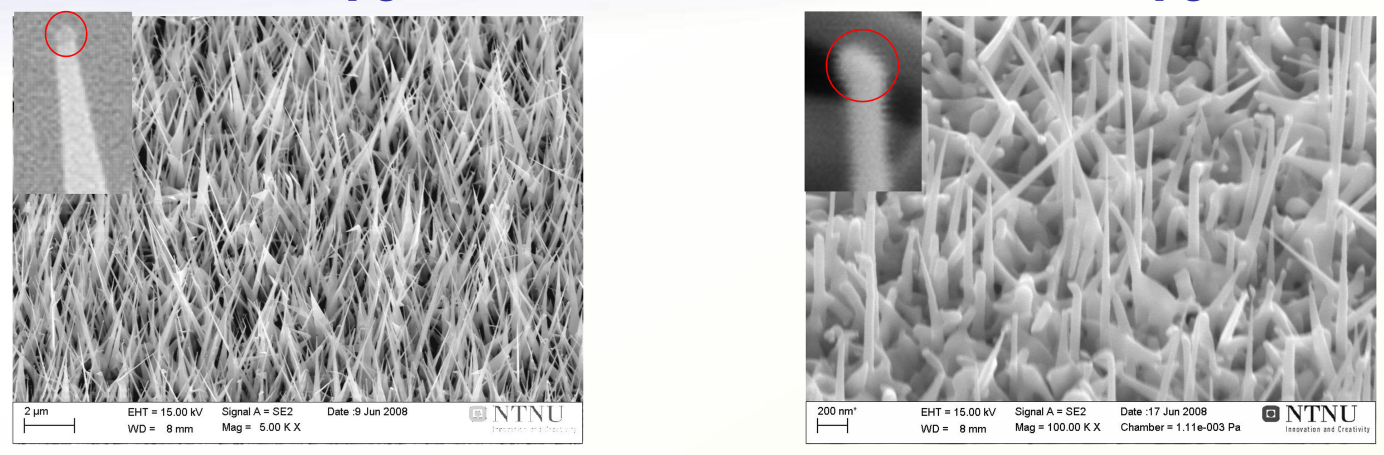
Nanosheets vs. Nanorods

SEM images of samples grown on sapphire for 60 min. at 800°C and 0.5 mbar gas pressure for different oxygen gas content in the PLD chamber:

100% Oxygen | 5% Oxygen

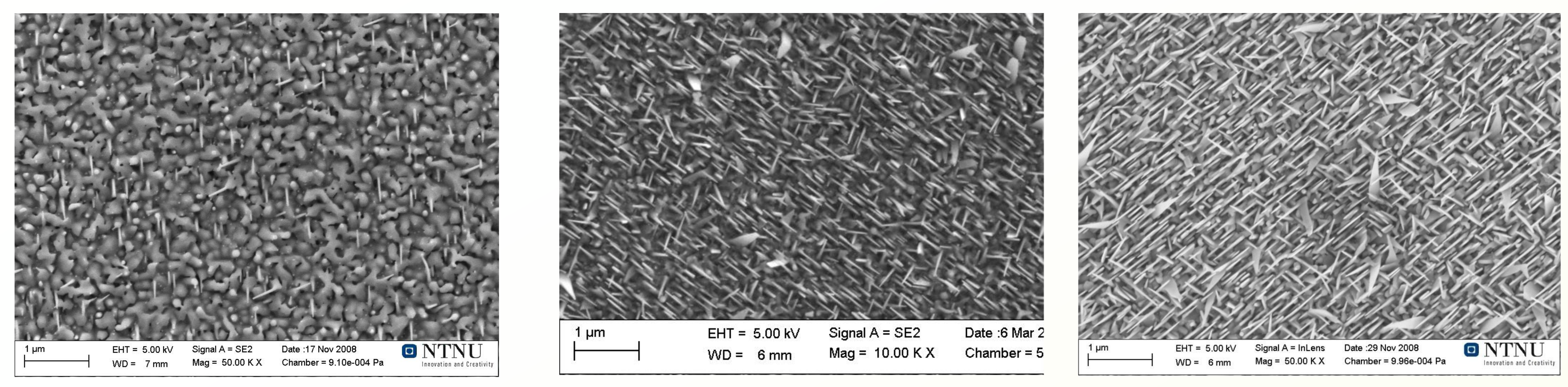


Nanosheet | Nanorods

- Changing the deposition parameters to a pure oxygen background led to preferred formation of ZnO nanosheets.
- Nanorods and nanosheets grew by the VLS mechanism as indicated by Au droplets present on top of the nanostructures

ZnO nanorods

Growth of ZnO on a-plane sapphire after different annealing treatments:

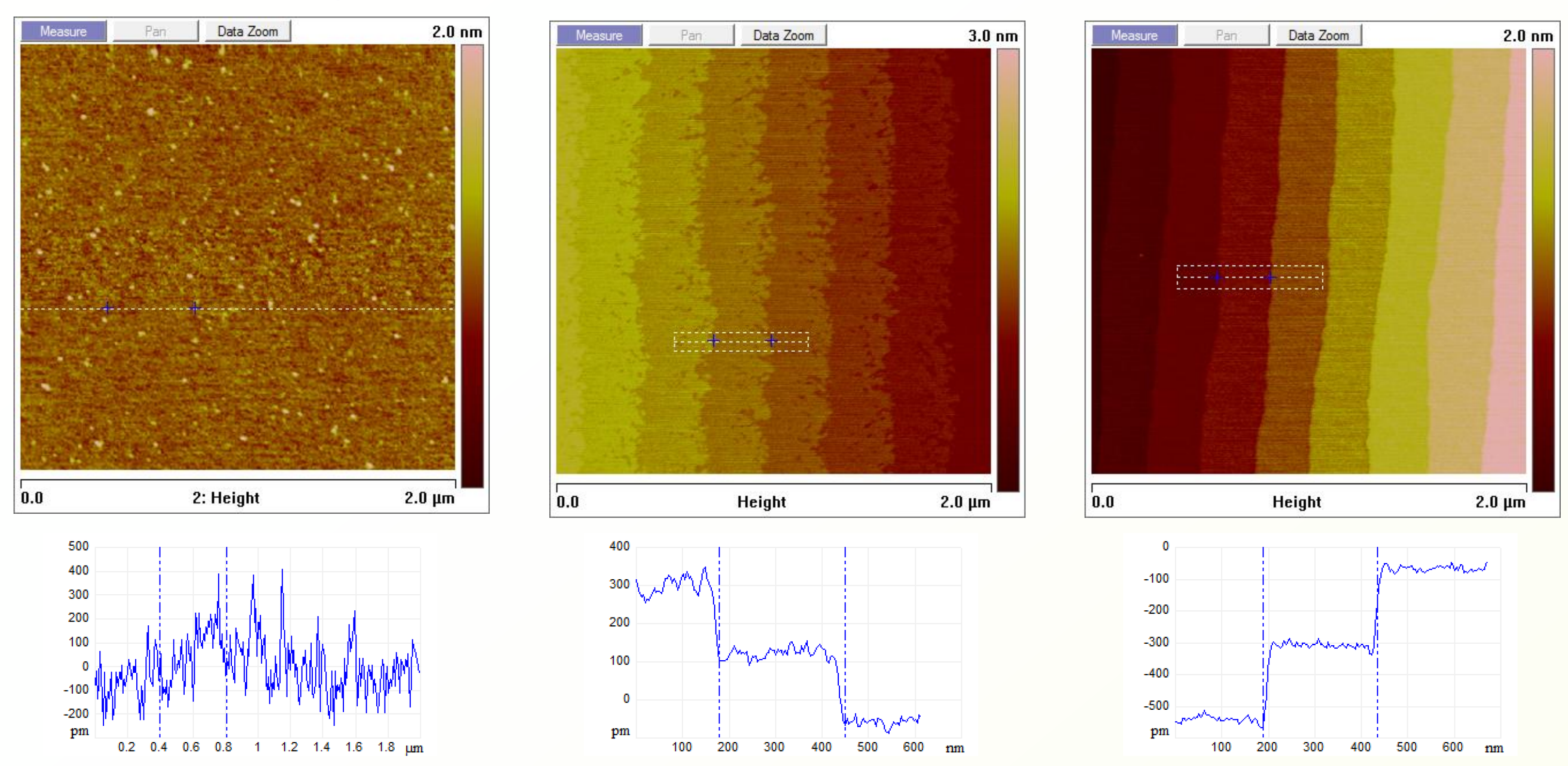


Not annealed | Annealed at 1000°C | Annealed at 1200°C

- Annealing of the substrate can improve the control of the ZnO nanorod growth.
- In case of annealed a-plane sapphire: above an annealing temperature of about 1000°C, the ZnO nanosheets grow in a preferential orientation which is most likely following the underlying sapphire atomic lattice
- In case of annealed c-plane sapphire: no difference observed between annealed and non annealed substrates

Sapphire annealed

Annealing of the a-plane(11-20) sapphire substrate for different temperatures



Not annealed roughness: 0.12nm | Annealed at 1000°C roughness: 0.07nm | Annealed at 1200°C roughness: 0.05nm

- The terrace heights are around 0.21nm which is the distance between two oxygen atoms in sapphire, as previously found in litterature[3)]
- The width of the terraces is believed to be formed due to the off-cut angle
- The a-plane has smoother surface and terraces are observed as early as at 1000°C.
- AFM images of annealed c-plane sapphire (not shown) indicate that a-plane sapphire forms terraces at lower annealing temperatures

Conclusions

In summary, ZnO nanostructure growth via catalytic PLD has been demonstrated, and effects of PLD parameters and substrates have been investigated:

- oxygen-rich background gas led to preferred formation of ZnO nanosheets, oxygen-poor environment to ZnO nanorods.
- in order to get better control of the ZnO growth, the substrate should be atomically flat by annealing the substrates prior to the PLD growth.
- A-plane sapphire substrates show a better terrace formation at a lower annealing temperature than c-plane
- Terrace height is the same as the distance between closed packed oxygen planes in the sapphire structure (0.21nm) while the width of the terraces is due to the off-cut angle[4)]

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