# Integration and Characterization of Functional Nano-Technology Materials on a Single Chip.

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**Abstract**

New materials demonstrating feasibility for the integration of nano-dimensional devices with multifunctional characteristics on a single chip are being developed. This paper focuses in particular on development of vertical nucleating layer stacks, and growth and characterization of ZnO nanowires/nanorods from the edge of a thin film/heterostructure fabricated on suitable substrate by PLD. The main objective is to identify the best thin film material and its thickness for nucleating ZnO nanowires, and develop growth mechanisms that could yield controlled nanostructure type/shape/size on nanoscaled nucleation layers. The synthesis of ZnO nanowires is done using vapor phase transport process. Dry etching of thin film is done using ICP etched tool to produce anisotropic and smooth sidewalls to test for directed growth of ZnO nanowires.

## I.  Introduction

Recent advances in nanotechnology have demonstrated potential promise for the integration of nanoelectronics, nanophotonics, and other sensor components into single monolithic devices.  The ability to incorporate multiple nanostructures on a single chip shows possibility for the development of advanced nanoelectronic devices with multifunctional characteristics.  A single chip can, for example, incorporate the superior electrical and thermal properties of carbon nanotubes for field effect transistors and thermal management, while also providing the excellent sensing properties of ZnO nanostructures useful for high speed photonics and gas sensing applications.  Such integration, however, will be only possible through the development of a process scheme and thin film architecture that can combine the growth of nearly all types of nanostructures with controlled organization in terms of alignment, orientation, and density.

In this study, the integration methodology of the different nanomaterials is based on vertically stacked thin films grown on silicon for selective lateral growth of nanostructures.  The thin film multistacks comprise of two alternating layers: nucleation layers and masking layers.  The catalytic nucleation layers act as the preferred growth site of a specific nanostructure, while the masking layers act to prohibit the growth of that nanostructure.  The sidewalls of vertically stacked catalytic and masking materials are exposed to lateral growth of nanostructures that can result in one-dimensional arrays of nanowires.
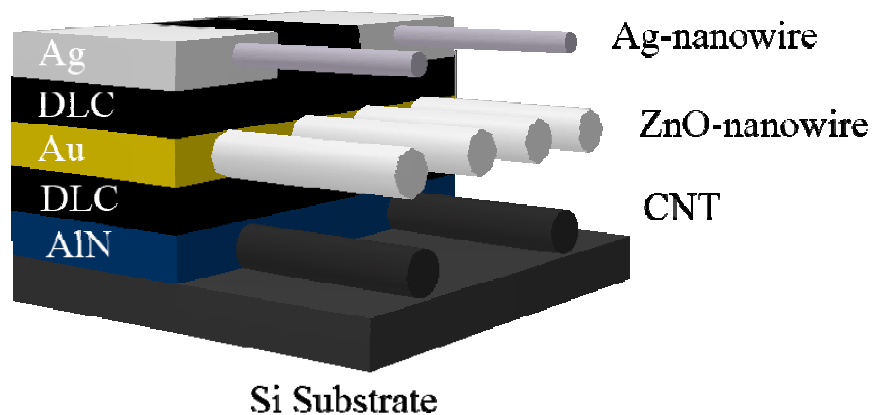


***Figure 1:*** *Schematic of thin film architecture with aluminum nitride (AlN) as the catalytic layer of carbon nanotubes (CNT) and diamond-like carbon as the masking layer.*

This research initiates the development of the proposed architecture by investigating, in particular, on the synthesis, characterization, and integration of one of the most promising nanomaterials: ZnO nanowires/nanorods.  The main objective is to identify the best thin film material and its thickness for nucleating ZnO nanowires, and develop growth mechanisms that could yield controlled nanostructure on nanoscaled nucleation layers.  To achieve this goal different thin films are deposited using pulse laser deposition (PLD)

technique, and tested for growth of ZnO nanostructures by solid vapor transport synthesis at the University of Maryland laboratory.  Different synthesis parameters such as furnace temperature, $Ar:O_2$ gas ratio, and gas flow rate are also tested to examine the optimal growth condition of directed ZnO nanowires.  Efforts to create smooth thin film sidewalls as nucleating sites for lateral and directed growth of ZnO nanowires is done using inductively coupled plasma (ICP) etch tool at the Army Research Lab.

## II.  Experimental

### *Thin Film Fabrication*

Thin films are deposited on silicon substrate by PLD using a KrF excimer pulsed laser ($\lambda$ =248nm) operating at a chosen fixed repetition rate.  Different ceramic targets composed of desired material (AlN, Au, BN, graphite for DLC, and Zn) are placed in the vacuum chamber.  Silicon substrate with approximate size of 2x2 cm is mounted on the substrate heater facing opposite to the target as shown in Figure 2.  The vacuum chamber is pumped down to a base pressure of $10^{-6}$ to $10^{-7}$ torr.  And depending on the desired thin film structural properties needed for nanomaterial growth, the substrate is heated and/or reactive gases such as $O_2$ or $NH_3$ are introduced during the deposition of thin films to achieve desirable stoichiometric characteristics.  The laser beam then irradiates the target at a 45° angle, generating vaporized material known as laser-produced plasma plume that expands rapidly from the target and recondenses on the substrate surface to form thin films.  The targets are rotated during deposition to avoid non-uniform erosion of the target.

Laser

Quartz window

Focusing Lens

Substrate

Target Carrousel

Plasma Plume

Targets
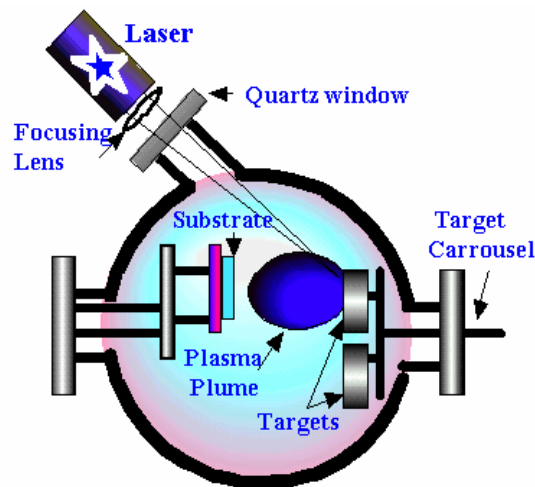
*Figure 2: Schematic of PLD*

DLC thin films with thickness of 2500Å were deposited on five Si substrate samples following the above procedure in a vacuum chamber of $10^{-6}$ torr and at room temperature. The DLC on Si substrate samples were used as a masking layer on Si for later deposition of experimental thin films as shown in Figure 3.  Amorphous DLC is known to prevent

ZnO nanowire growth.  Their chemical stability, hardness, electrical insulation, smoothness, and resistance to wear make them an ideal candidate for the masking layer.
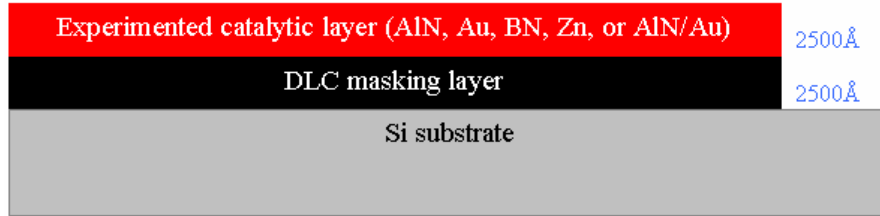


*Figure 3: Cross section of experimented thin film samples*

Each of the five DLC on Si samples is reloaded into the PLD chamber for deposition of experimental catalytic thin film layers.  Au and Zn thin films, being soft metal, are deposited in a chamber pressure of $10^{-6}$ torr and at room temperature.  AlN and BN on the other hand are ceramic thin films and are deposited in a chamber pressure of $10^{-4}$ torr with $NH_3$ gas and at temperature of 700°C to produce smoother surfaces.  The laser energy, frequency, and time used for the thickness achieved are outlined in Table 1.  The AlN/Au bi-layer is a sample with AlN deposited on the DLC thin film, followed by deposition of Au.  Each of the five thin film deposited samples is to be loaded into the nano-furnace for synthesis of ZnO nanowires.

|  | Thin film (target ) | Laser Energy (mJ) | Frequency (Hz) | Time (min.) | Thickness Achieved |
|---|---|---|---|---|---|
| mask | DLC (graphite target) | 1000 | 10 | 30 | 2500Å |
| samples |  |  |  |  |  |
| 1 | AlN | 500 | 5 | 30 | 2500Å |
| 2 | AlN/Au bi-layer | 500/500 | 5/10 | 30/15 | 5000Å |
| 3 | Au | 500 | 10 | 15 | 2500Å |
| 4 | BN | 500 | 10 | 30 | 2500Å |
| 5 | Zn | 500 | 10 | 20 | 2500Å |

*Table 1: Condition for achieved thin film thickness*

### *ZnO Nanostructure Synthesis*

Though ZnO nanostructures can be synthesized using techniques such as metal-organic chemical vapour deposition (MOCVD) or via chemical route, the most extensively explored approach and the one used for this research is vapor transport synthesis.  The vapor phase route is preferred for its simplicity and ability to fabricate ZnO nanostructures in large quantities.  Vapor transport synthesis is further categorized into two processes: catalyst free vapor-solid (VS) process and catalyst assisted vapor-liquid-solid (VLS) process [1].

In the VLS process nanosized liquid droplets of a catalyst metal such as Au, Co, and Sn, etc. are deposited onto the substrate.  The droplets act as catalyst sites for the nucleation and growth of nanowires.  This technique is excellent for growth of nanowire structures since incremental growth that occurs at the droplet/substrate boundary will push the

catalyst upward off the substrate to promote the formation of nanowire structures. Although this process provides site-specific growth at each droplet location, the presence of catalyst particles on the nanowires add impediment by introducing impurities to the nanostructures itself (shown in Figure 4) [2]. For this reason a catalyst free VS method utilizing Zn as an auto-catalyst is being developed at the University of Maryland and used for this research.
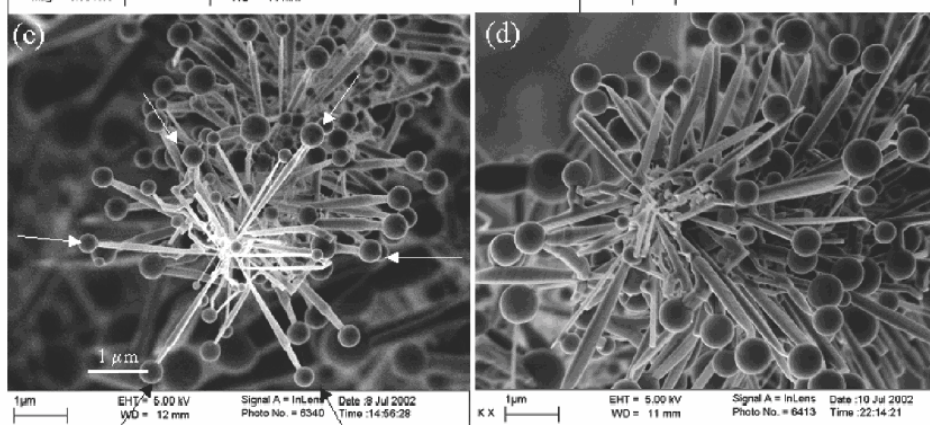


***Figure 4:*** *ZnO nanowires growth using Sn catalysts introduces impurities. P. Gao et.al. J. Phys. Chem. B 106,12654 2002*

In this catalyst free method exposed sidewalls of catalytic nucleating layers act as the preferred growth site of nanowires. The mechanism for synthesis is identical to conventional vapor transport and is outlined in Figure 5. Approximately 2.0 grams of 99.5% purity Zn powder is placed on the alumina boat and inserted into a cylindrical quartz tube from the left side. Substrate samples are mounted onto the substrate holder and inserted into the quartz tube from the right side, placed approximately 1 cm apart from the alumina boat. Then a constant flow of carrier argon gas is introduced through the quartz tube as the furnace temperature rises at the rate of 20°C per minute to the set synthesis temperature. Once the set temperature is reached, a constant flow of $O_2$ gas is supplied through the furnace and the growth of nanostructures takes place for a duration time of 90 minutes. Upon completion, the gas flow of both Ar and $O_2$ is terminated and the furnace is passively cooled down to room temperature.
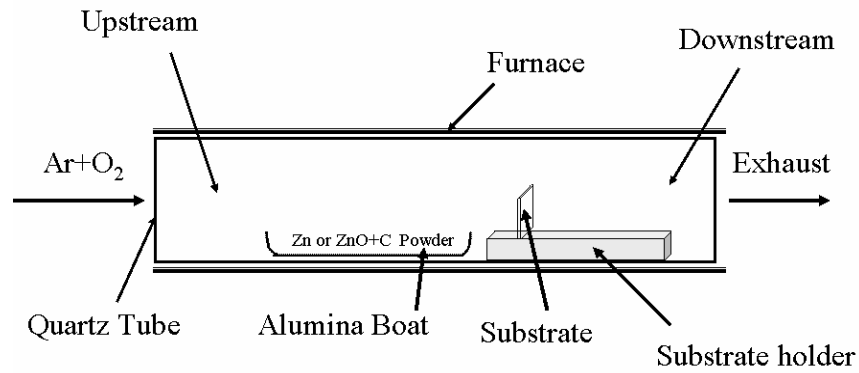


***Figure 5:*** *Schematic of vapor transport synthesis*
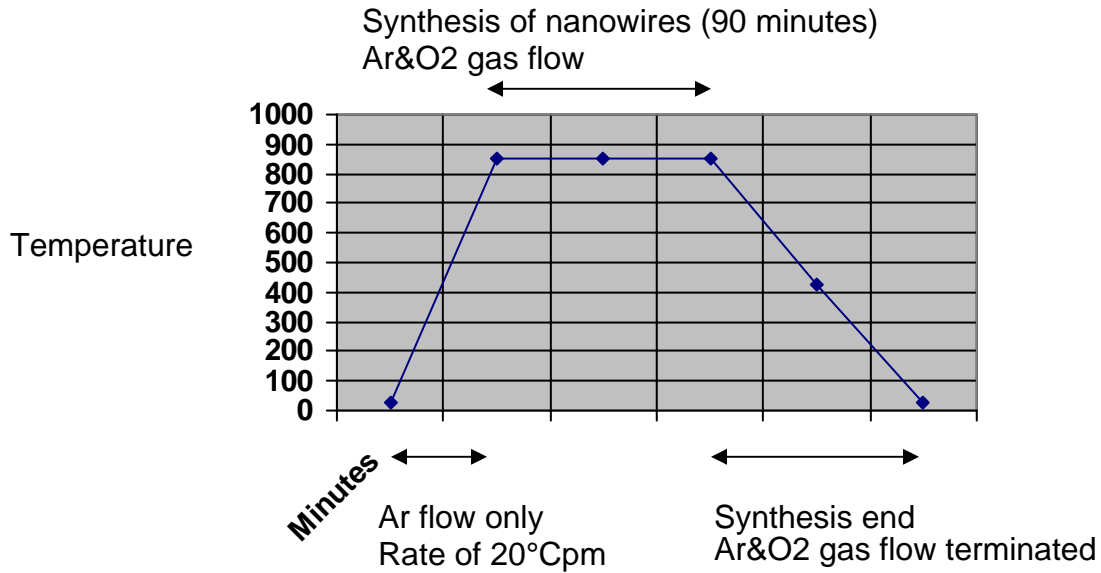
**Figure 6:** *Schematic of synthesis time frame*

Synthesis parameters outlined in Table 2 (temperature, gas ratio, and gas flow rate) are examined to identify the optimal growth conditions for lateral growth of aligned nanowires. The conditions in middle column represent the default synthesis condition. Parameter values for this column have been experimented with before and are used as the base point for the experiment. When one parameter such as temperature is used as the independent variable, tested at either 1000°C or 600°C, the default conditions are used for the other two parameters, gas ratio of 4:1 and flow rate of 60 bubbles per minute (bpm).

| Synthesis parameters experimented | | | |
|---|---|---|---|
| Temperature (°C) | 1000 | *850* | 600 |
| Gas ratio (Ar:O$_2$) | 9:1 | *4:1* | 9:0 |
| Gas flow rate (bubbles per minute) | 90 | *60* | 30 |

**Table 2:** *Varied synthesis parameters*

A total of eleven synthesis runs is conducted. The six runs required to complete the matrix in Table 2 is loaded with Si substrates samples to test for the optimal synthesis condition. While five other synthesis run is conducted under the default condition (850°C, Ar:O$_2$ of 4:1, and gas flow of 60 bpm) and loaded with one of the five thin film samples to test for catalytic nucleation layers.
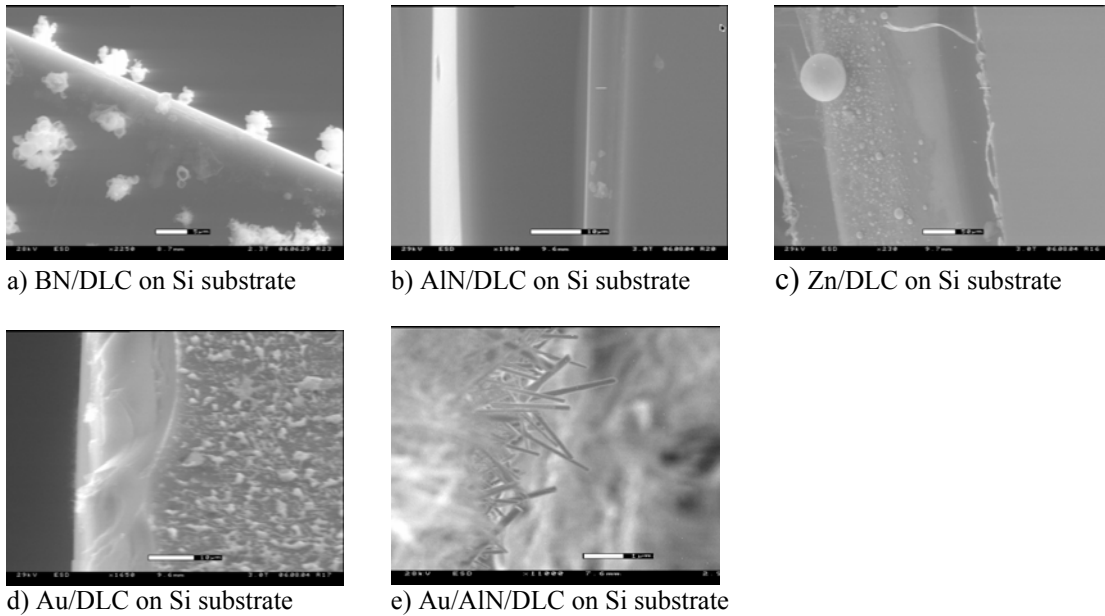
## III.  Results and Discussion

*Catalytic Nucleation Layers*
Figure 7 summarizes the results of the different thin films tested for nucleation of ZnO nanowires. As shown, nucleation of nanowires occurred only from the AlN/Au bi-layers. The other thin film layers displayed no formation of ZnO nanowires. Deposits of

different ZnO particles on the other layers showing no growth demonstrates selectivity of ZnO nanostructure formation on material surfaces.

The reason for growth of ZnO nanowires from AlN/Au bi-layers, and not from AlN or Au layers is yet to be known. One possible explanation for this phenomenon is the possible reaction between AlN/Au layers under the high temperature growth condition of ZnO nanowires. Additional testing and analysis needs to be conducted in order to find out for sure.



a) BN/DLC on Si substrate     b) AlN/DLC on Si substrate     c) Zn/DLC on Si substrate

d) Au/DLC on Si substrate     e) Au/AlN/DLC on Si substrate

*Figure 7: Characterization of ZnO nanowires on tested catalytic nucleation layers using the SEM. All images are taken from the top view looking down on the substrate at the cleaved side walls.*

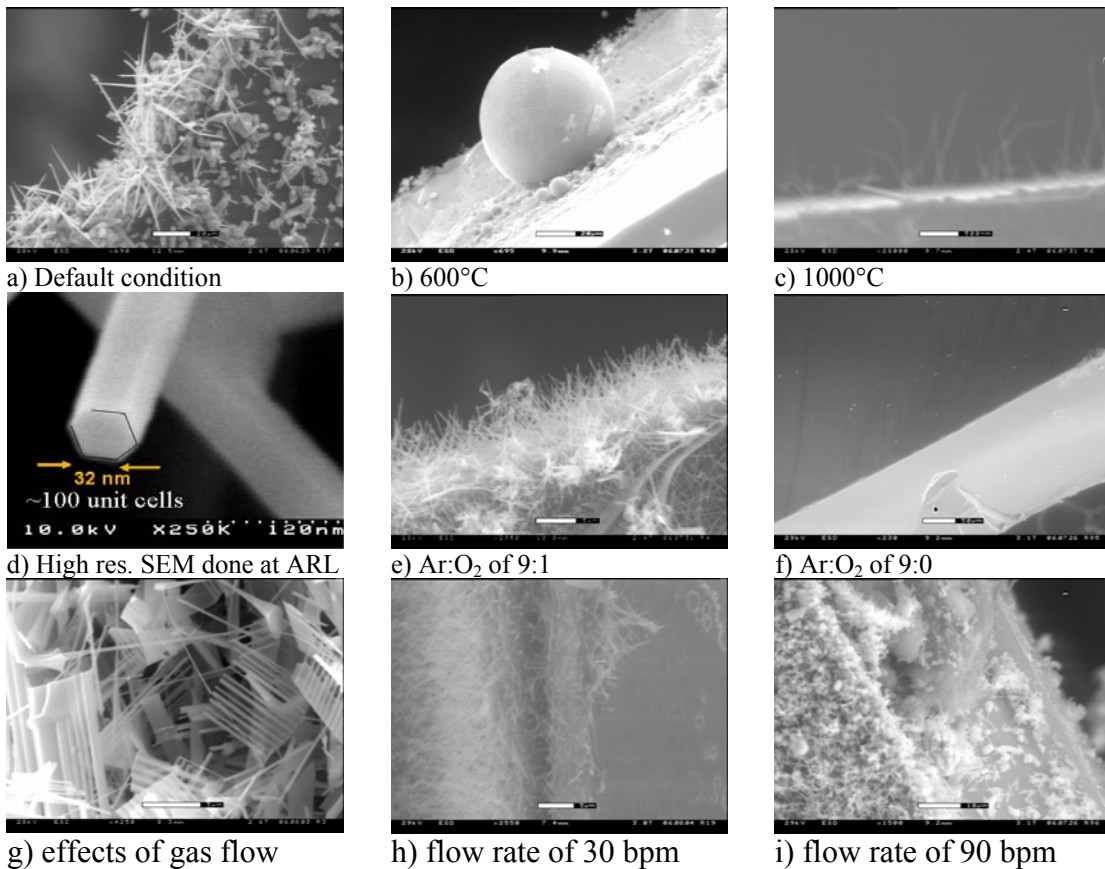### *Optimal Synthesis Condition for ZnO Nanowires*

Figure 8 illustrates the growth of ZnO nanowires under different synthesis conditions. The growth of ZnO nanowires in image (a) is done under the default condition outlined in Table 2. The image reveals large amounts of unwanted ZnO residue on the top surface and sidewalls. The diameters of the nanowires under this growth condition are mostly in the micron scale ranges with nanowires orientation that are totally random.

Image (b) of Figure 8 shows ZnO nanospheres formation under synthesis temperature of 600°C. Sparse nanowires grown at 1000°C are shown in image c. Diameters of the nanowires here are smaller and in the range of 30 to 100 nanometers, with lengths below a few um long. The high resolution image (d), done using the SEM at ARL, shows nanowires of 32 nm in diameter with approximately 100 unit cells. When the Ar:$O_2$ gas ratio is increased to 9:1, unwanted ZnO residue on the substrate surface is largely reduced, as shown in image (e). But further increasing this ratio to 9:0 reveals no growth

of ZnO nanowires.  This demonstrates the critical need for high but precisely controlled Ar:$O_2$ ratio when synthesizing ZnO nanowires.

The flow rate of Ar and $O_2$ is also found to be critical to the synthesis of ZnO nanowires. Nanowires grown under gas flow rate of 30 bpm have smaller diameter sizes and are more directed and aligned as shown in image (h).  When the flow rate is increased to 90 bpm, mixed formation of ZnO nanowires and clusters of ZnO residue are densely settled on substrate surface.  Structures formed in image (g) are found on one specific site on the Si substrate.  Though the synthesis condition is the same as the substrate in image (h), the unique formation of this nanostructure demonstrates the importance of gas flow dynamics on the growth of ZnO nanowires.



a) Default condition    b) 600°C    c) 1000°C

d) High res. SEM done at ARL    e) Ar:$O_2$ of 9:1    f) Ar:$O_2$ of 9:0

g) effects of gas flow    h) flow rate of 30 bpm    i) flow rate of 90 bpm

*Figure 8: SEM images of ZnO nanowires grown on Si substrate under different conditions.*

## IV. Paterning of Thin Films

Results of the experiments conducted provide an enormous leap to producing ZnO nanowires with smaller diameter sizes, and less unwanted ZnO deposits using catalyst free VS process.  The orientation of the nanowires, however, is still undirected and random with only slight improvements through the variation of synthesis parameters. Using cleaved samples for growth of ZnO nanowires from the sidewall still shows

randomly directed nanowires nucleating from the surface. One possible explanation for this phenomenon is the granular and non-uniformed features on cleaved surfaces as shown in Figure 9. To resolve this issue, the thin film structures are dry etched using inductively coupled plasma (ICP) etch tool to produce anisotropic and more uniform sidewalls. It is believed that ICP etching of the thin films will encourage a more controlled and directed growth of ZnO nanowires from the sidewalls.
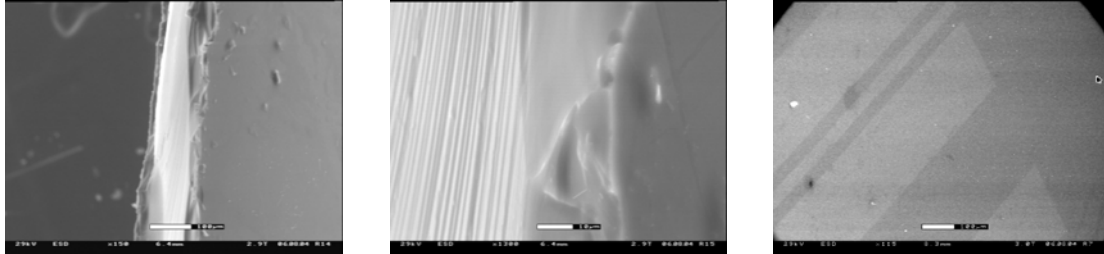


a) Resolution at 100um          b) Resolution at 10um          c) Etched thin film

***Figure 9:*** *Features on cleaved sidewalls of Si are granular and non-uniform, whereas features on the etched thin film are smooth and uniform.*

To etch the thin film stacks, an etch recipe and rate must be determined for each of the thin film material. Since it was shown that growth of ZnO nanowires only nucleated from AlN/Au bi-layers, the etch recipe and rate for AlN, Au, and DLC is determined.

| Material | Gas mixture (sccm) | Rates (ÅPM) |
|----------|--------------------|-------------|
| AlN | $Ar:BCl_3:Cl_2$ (5:20:20) | 800 |
| Au | $Ar:Cl_2$ (5:20) | 1100 |
| DLC | $Ar:O_2$ (5:30) | 1000 |

***Table X:*** *Successful etched recipe and rates for AlN, Au, and DLC*

Though individual etch rates were successfully identified, etching of the multistacks prove to be more difficult. Etching of thin film multistacks require precise etching times of each layer and will require additional dummy samples and experimentation.

## IV. The Next Step: Integration of CNT

Continuing improvements are being discovered for the integration of nanoscaled ZnO nanowires with directed orientation and alignment. Now special consideration needs to be shifted to developing a process scheme for integrating CNT onto the thin film architecture. Lateral growth of CNT between two electrodes during chemical vapor deposition (CVD) has been reported (6). High density nucleation of CNT growth on pulsed laser deposited AlN thin film has also been demonstrated by researchers at the University of Maryland and ARL. The next step is to develop an optimized CVD process that will encourage lateral and controlled growth of CNT from AlN layers. The challenge will be to develop growth conditions that will not disrupt the structures of existing ZnO nanowires. Successfully completing this proposal will demonstrate the feasibility of producing monolithic devices with multifunctional characteristics.

## V. Conclusion

Vapor transport synthesis of ZnO nanowires on different pulse laser deposited thin films shows that directed nucleation of ZnO nanowires are highly selective to surface composition and structure. Of the thin films tested, growth of nanowires only occurred from AlN/Au bi-layers. Future study on nucleation of ZnO from AlN/Au bi-layers may provide valuable information on surface nucleation of ZnO nanowires when using Zn as an auto-catalyst. It is also found that formation of ZnO nanostructures are critically dependent on synthesis parameters such as temperature, and Ar:O2 ratio and flow rates. It is observed that synthesis at higher temperature encourages growth of nanowires with smaller diameters, while high Ar:O2 ratio and low flow rates reduces unwanted ZnO residues on substrate.

It has been demonstrated here that nanowires with smaller diameters and less unwanted ZnO residues can be achieved under the proper synthesis conditions. The feasibility for lateral growth of ZnO nanowires from nucleating thin films is also illustrated. Ongoing research will focus on applying the synthesis conditions identified to thin film multstacks with smooth sidewall patterns create by ICP etching.

## VI. Acknowledgement

## VII. References

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