# **GOALI:** Nanowire Integration Processes to Gain Control over Location, Dimension, and Orientation

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This research developed processes to integrate nanowires on surfaces. The first part of this paper describes our research on ZnO nanowires. The second part describes our work on Si nanowires.

## Part 1. Work on ZnO

## Abstract:

We report a method to nucleate, grow, and transfer single crystal ZnO with control over location, orientation, size, shape, and final substrate material (sections 2, 3). The process uses an oxygen plasma treatment in combination with a photoresist pattern on Magnesium doped GaN substrates to define a narrow nucleation region and attachment points with desired 100 nm scale dimensions. Nucleation is followed by lateral epitaxial overgrowth producing single crystals of ZnO with desired size (100 nm - 100  $\mu$ m) and shape (rods, wires, walls, disks) over 2 inch wafers. The formation of extended uniform arrays of ZnO/GaN heterojunction micro UV LEDs/Solar Cells (2.3 µm on a side) is demonstrated as a first application with light coupling between faceted areas within the equidistantly pitched devices. The quality of the patterned ZnO is high; the commonly observed defect related emission in the electroluminescence spectra is completely suppressed and a single near-band-edge UV peak is observed.

**1.1 Introduction:** ZnO micro and nanostructures have been produced using a large number of different synthetic routes<sup>[1]</sup> and the applications that utilize the unique properties keep increasing. The 3.3eV direct bandgap and 60meV exciton binding energy is exploited in ultraviolet optoelectronics<sup>[2-4]</sup>, room temperature lasing<sup>[5-8]</sup>, and solar cells applications<sup>[9-11]</sup>; extremely long photocarrier lifetimes have been observed yielding UV photodetectors with 108 internal gain<sup>[12]</sup>; the optical properties in combination with n-type conduction support transparent transistor and display applications<sup>[13,14]</sup> while the piezoelectricity is

utilized in power generation<sup>[15]</sup> and force sensing applications<sup>[16]</sup>. The integration of these device prototypes on a wafer scale will require access to ZnO micro and nanostructures with a variety of dimensions at known locations. A wet chemical approach is desired for reasons of processing cost when compared with gasphase methods and a number of patterned and seeded growth methods have been reported. Patterned selfassembled monolayers with hydrophobic and hydrophilic endgroups have been used on silver<sup>[17]</sup> or silicon substrates<sup>[18]</sup> yielding densely packed 400nm diameter and 2µm long ZnO nanorods in regions that were 2µm wide with empty areas in between. Out-ofplane orientation varied but has been improved by seeding ZnO nanocrystals through thermal oxidation of zinc acetate<sup>[19]</sup>. Perfect vertical orientation, however, requires substrates such as GaN, MgAl<sub>2</sub>O<sub>4</sub><sup>[20]</sup>, or Sapphire<sup>[21]</sup> which can be partially masked with photoresist to achieve patterned growth. Qualitatively all of these methods produce nanorods in the seeded or unmasked areas with limited control over the location and density. Continued growth leads to coalescence into a polycrystalline film as the diameter increases with grain boundaries and defects in between. Continued growth in combination with photoresist has also been reported to lead to a lateral overgrowth; a previously reported concept to produce high quality GaN thin films<sup>[22]</sup>. For ZnO on MgAl<sub>2</sub>O<sub>4</sub>, lateral growth over patterned photoresist improved the dislocation density by a factor of 100 compared to the window region containing coalesced nanorods<sup>[20]</sup>. Subsequent growth using a second window yielded continuous ZnO thin films with reduced dislocations<sup>[21]</sup>.

This paper reports on a new method using oxygen plasma to surface engineer nucleation areas to produce vertical single crystal ZnO nanowire rows, extended walls, and disk type structures on p-type GaN at addressable locations on a surface with tailored >100nm lateral dimensions and sub-100nm lateral positional accuracy. The concept uses a plasma process and photoresist patterns to reveal non-oxidized

magnesium sites that nucleate growth. Nucleation in non-oxidized areas is followed by epitaxial overgrowth producing patterned areas of ZnO over 2 inch wafers. Adjusting pH increased ZnO deposition yield and enabled formation of high quality ZnO crystals. ZnO/GaN micro-LEDs and solar cells were fabricated. The LEDs possessed strong near band edge electroluminescent emission. Deep-level defect emission in the red and yellow is absent which implies that the ZnO microcrystals are of high quality. A hexagonal star like radiation pattern is observed which is explained by light emission through crystallographic facets.



**Figure 1.1** Process steps for producing ZnO crystals through nucleation at the photoresist-GaN interface. (A) Conventionally patterned photoresist on Mg-doped GaN is exposed to an (B) oxygen plasma to deactivate Mg dopands that otherwise act as nucleation sites as well as to produce (B close-up) a transitional region which contains non-oxidized Mg to nucleate growth. (C) Solution growth at different pH and growth time yields individual (left), and merged laterally overgrown ZnO structures (right). The merged structures can fill the photoresist opening which eases LED device fabrication (Fig. 5).

1.2 Patterned ZnO Growth: Figure 1.1 shows the patterned growth process. Photolithography, oxygen plasma treatment, and solution-based growth are the basic process steps to produce ZnO micro and nanocrystals at exact locations on a surface. The oxygen plasma is used to oxidize Mg dopands to inhibit nucleation and growth in the center area while it etches the resist leaving behind a transitional region to nucleate ZnO growth. Subsequent lateral epitaxial overgrowth yields ZnO structures that are larger in diameter than the initial nucleation region. The patterned surface (Fig. 1A) is formed with standard photolithography on a Mg-doped GaN substrate, doping concentration 5x10<sup>18</sup> cm-3, TDI inc., Silver Spring, MD. Following a prebake at 115°C for 60 seconds, Shipley 1805 photoresist was spun at 3000 RPM, softbaked at 105°C for 60 seconds, exposed using a Karl Suss MA-6 Mask Aligner, and developed in Microposit

351 developer for 30 seconds. The patterns can directly be used for growth leading to a polycrystalline ZnO film in the exposed GaN areas which shows that the basic developer containing sodium hydroxide and exposure to photoresist do not adversely affect ZnO nucleation on p-type GaN. However, to produce single crystal structures of high quality a plasma treatment is required (Fig. 1B). The treatment yields a narrow nucleation region where the oxidation state transitions from fully oxygen passivated to partially and nonoxidized while it removes organic residues on the GaN surface which is required to accomplish uniform growth over the entire wafer. We optimized this process and exposure to a 100-watt, 100 mTorr oxygen plasma for 30 seconds worked best to completely prevent nucleation on fully oxygen passivated Mg-doped GaN. The growth of ZnO (Fig. 1.1C) is carried out in a glass vial and based on a previously published procedure<sup>[17]</sup>. In short, growth is initiated by adding zinc acetate, Zn(CH<sub>3</sub>COO)<sub>2</sub>, and hexamine, (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>, to 70 mL of deionized water such that the solution contained 25mM of each compound. To grow the ZnO crystals, the solution was heated in an oven to 90°C for times ranging between 10 minutes to 3 hours. Following the growth, samples were removed from solution and briefly rinsed with DI water. While this is the basic process we found that the initial pH of the growth solution is an important additional parameter to control. The glass vial initially contained deionized water at pH 5.5; the slightly acidic nature is attributed to  $CO_2$ absorption from the ambient environment. It was necessary to increase the initial pH to 7.5 by adding small amounts of ammonium hydroxide, NH4OH, to form continuous extended single crystals.

Figure 1.2 shows representative images of ZnO structures that form at the plasma activated interface; with an increase in pH from 5.5 to 7.5 the crystals transition from individual ZnO nanorods (Fig. 2A.B) to single crystal lines with a rectangular 1 µm wide and 0.8 µm tall crossection (Fig. 2C,D). Independent of the pH no nucleation and growth is observed on either the photoresist or the GaN. The presence of Mg dopants is the key element to accomplish the observed localized nucleation in some areas and passivation in others. A number of control experiments have been carried out which support this claim. First, we were not able to produce single crystals with high dimensional control on undoped and n-doped  $(5 \times 10^{17} \text{ cm}^{-3} \text{ Si})$  GaN samples in concurrent growth experiments (90 minutes, 90°C, 25mM zinc acetate, 25 mM hexamethylenetetramine, initial pH 7.5) with p-doped (5x10<sup>18</sup> cm<sup>-3</sup> Mg) GaN control substrates. The undoped and n-type samples produced ZnO structures with uncontrolled nucleation sites. The effect of the Magnesium can be explained by looking at the electronnegativity. Magnesium is an alkaline earth metal that exhibits greater ionic characteristics and lower electronegativity than the group III element gallium. Mg-O (oxvgen electronegativity: 3.5) is more energetically stable than Mg-N (nitrogen electronegativity: 3.1). The enhanced ionic characteristic of magnesium within the GaN lattice should lead to an enhanced concentration and attachment of precursor ions such as OH<sup>-</sup>, Zn<sup>2+</sup>, and their complexes. The affinity of OH<sup>-</sup> and subsequent localized decomposition of Zn(OH)2 is expected to lead to a preferential nucleation and growth in the Mg-rich region. Second, plasma oxidized Mg sites should block OH<sup>-</sup> attachment and suppress growth in areas towards the center of exposed GaN. This is consistent with the experiment. We observed complete deactivation of the nucleation sites through oxygen plasma treatment and this was only possible on Mg doped substrates. Third, the treatment with photoresist is not the primary cause of the suppressed growth in the center region. ZnO will grow in this area; elimination of growth requires the plasma treatment. Finally, the deactivation of the nucleation sites can be directly confirmed by plasma treatment of a bare p-type GaN chip that was partially covered with a glass slide. Subsequent growth revealed a 1.5µm-thick continuous polycrystalline ZnO film in the non-oxidized areas, and no ZnO in the area that was fully exposed to the plasma. In summary, Mg sites are active and readily oxidized. The formation of an ionic Mg-O bond upon exposure to the energetic oxygen ions leads to the deactivation of the nucleation sites.



**Figure 1.2.** Patterned integration of ZnO structures through nucleation at the GaN(bright)- photoresist(dark) interface. (A, B) Nanorods with an average diameter of 300 nm and (C, D) continuous waveguide-like structures with uniform rectangular cross-section are shown. Selectivity is large and no ZnO nucleation or growth is observed on either photoresist or oxygen passivated p-GaN. Increasing the initial growth condition from pH 5.5 to 7.5 caused the transition from isolated (A,B) to continuous ZnO single crystal structures (C,D). 10  $\mu$ m scale bar in (A,C). 1  $\mu$ m scale bar in (B,D).

Once nucleation has occurred and facets are produced the ZnO growth continues independent of the substrate. In other words the presence of the substrate is no longer relevant and growth does not deviate from conventional ZnO hydrothermal deposition. For example, HMT increases the aspect ratio but does not completely stop lateral growth. With an initial pH of 7.5 and assuming that ZnO growth occurs immediately upon immersion in the growth solution, the growth rate can be estimated at 2.8Å/second along the c-axis and 0.8Å/second along the a- or b-axis crystallographic direction.

The use of a sequence of lithography and oxidation steps did not adversely affect previously passivated nucleation sites. This allows for the formation of more complex nucleation areas. Figure 1.3 shows a set of ZnO wall and interdigitated electrode type structures formed using a two step sequence. The first sequence used photolithography, plasma oxidation, and removal of resist to produce parallel lines of fully oxidized GaN. Next the process was repeated whereby the photoresist pattern crosses the original pattern at controlled angles; the wall structures (Figs. 1.3A,B) had an angle of 90°, and the interdigitated electrode structures (Figs. 1.3C,D) had an angle of roughly 1° between the initial oxidized GaN strips and final photoresist trenches; the resist is not removed during the second step to yield narrow nucleation regions and illustrated structures.

Process parameters including growth time and layout of the nucleation sites can further be modified to form larger crystal domains with well controlled dimensions. Figure 1.4 shows an example, photoresist with 3µm diameter circular openings and 6µm center-to-center spacing were oxygen plasma treated, resulting in ringshaped ZnO nucleation areas along the circumference of each hole. ZnO deposited initially in the ring-shaped regions (inset Fig. 1.4A), then merged by lateral overgrowth over a longer growth time of 3 hours to become the well-faceted hexagonal crystals. The largest interior dimensions of the hexagonal crystals were 4µm, indicating that ZnO laterally overgrew the photoresist hole by ~0.5µm. Lateral overgrowth occurred over the oxidized GaN as well, such that ZnO filled the photoresist holes to completely cover the GaN surface



**Figure 1.3.** ZnO structures fabricated by multiple oxidation steps. Angle between initially oxidized GaN strips and final ZnO nucleation strips was varied from 90° (A,B) to approximately 1° (C,D), resulting in walls and interdigitated electrode type structures, respectively. 10  $\mu$ m scale bar in (A,C,D). 1  $\mu$ m scale bar in (B).

Using the photomasks the structures can be placed with a positional accuracy (40 nm, STD) calculated by measuring the center-to-center distance of the ZnO crystal that have been produced, specifically Figs. 1.2B, 1.3D, 1.4A. The use of higher resolution e-beam patterns could reduce these numbers. Lateral overgrowth leads to merged crystals with a narrow size distribution (15%, STD) calculated by analyzing top down dimensions (Fig. 1.2D and Fig. 1.4A).



Figure 1.4. Images depicting a square array of ZnO hexagons with well controlled dimensions and spacing. The structures are nucleated from (A insets)  $3\mu$ m-diameter rings and (B) merged together into single crystals.  $10\mu$ m scale bar in (A).  $1\mu$ m scale bar in (A insets, B).

3. ZnO/GaN LEDs and Photovoltaic Cells: Figure 1.5 shows an array of ultraviolet heterojunction n-ZnO/p-GaN LEDs produced using the growth process to study the electrooptical properties. There have been a number of reports on n-ZnO/p-GaN heterojunction LEDs. Recent work has replaced the polycrystalline ZnO thin films<sup>[2,23-25]</sup> with ZnO nanowires<sup>[3,26,27]</sup> to take advantage of the nanowire properties - high crystallinity and fewer grain boundaries. The results are interesting: one report showed electroluminescence (EL) under reverse bias while the other reported forward bias emission<sup>[26,27]</sup>. A follow up study in our own group confirmed low efficiency reverse bias emission<sup>[4]</sup> which was attributed to tunneling breakdown where hot carrier injection and recombination predominantly occurred in the GaN film. Most of the previous devices including our own<sup>[4]</sup> suffered from defect related emission around 585 nm. The improved device structure shown in Fig. 1.5A completely eliminates the defect related emission. The fabrication is detailed in the supplemental section. In short, the device was formed using the hexagonal ZnO disks (Fig. 1.4A) that completely filled the openings in the insulating photoresist matrix. This overgrowth method provides an advantage over earlier designs that required deposition of an insulating layer and polishing or etching to expose the top of the ZnO. The new process does not require these process steps and was found to be more effective in eliminating pinholes and shorts between the sputter coated ITO top contact and GaN. Applied forward bias revealed a sixpointed star of violet light under a 10x optical microscope objective (Fig. 1.5B) which cannot be explained by the layout of the array which has a square lattice. Higher resolution analysis using a 50x objective (Fig. 1.5B inset) showed areas of high light intensity to match directions perpendicular to the hexagonal ZnO facets which suggests that some light is transmitted and coupled preferentially along directions perpendicular to ZnO facets. We have not vet changed the dimension and spacing between the ZnO microLEDs to study coupling or lasing. Electroluminescence data (Fig. 1.5C) shows near-band-edge violet and ultraviolet emission from the ZnO-GaN heterojunction, and absence of any peaks in the 500 to 750nm wavelength range, where deep-level ZnO crystal defects commonly radiate light.<sup>[4,28]<sup>1</sup></sup> The absence of deep-level radiative defects indicates that ZnO deposited using plasmadefined nucleation areas is a high quality material. Pinholes are one defect type that are reduced by oxygen plasma treatment as illustrated qualitatively in Figure 1.6.



Figure 1.5. Heterojunction n-ZnO/p-GaN ultraviolet LED. (A) Device structure. (B) Forward bias emission revealing a six-pointed star which is attributed to facet-to-facet (inset) hexagonal propagation. (C) Electroluminescence spectrum showing near-band-edge emission at 3.11eV and absence of defect peaks in the wavelength range 500 to 750nm.

Additionally, illumination with a 6 watt handheld ultraviolet lamp caused the ZnO-GaN hexagonal heterojunctions (again Fig. 1.5A) to function as a photovoltaic cell. The maximum open circuit voltage and short circuit junction current density was found to be 450 mV and 70 mA/cm<sup>2</sup>, respectively. First order estimates yielded 1-9% electrical quantum efficiency. We do not have a precise number since the size of the active junction is presently not known with sufficient accuracy. The ITO formed a successful contact to about 100-300 ZnO/GaN junctions which was determined from the forward bias emission picture. As individual junction area we used 10  $\mu$ m<sup>2</sup> which represented the photoresist opening which assumes that the oxygen passivated and overgrown area does not limit transport. The junction efficiency would be larger if this assumption is incorrect.



Figure 1.6. Effect of oxygen plasma treatment on ZnO deposit morphology. ZnO develops crystalline facets in the case of (A) samples exposed to oxygen plasma treatment, and avoids pinhole defects which are observed in (B) unexposed samples.  $1\mu$ m scale bars.

## Part 2. Work on Si Nanowires

### Abstract:

An in-situ nanowire integration process has been developed where the reactor uses a two step sequence to first seed catalyst particles which are then grown into nanowires without needing to transfer samples from one reactor into another. Step 1: Seed/catalyst particles are selectively assembled at desired locations using a discovered new process (APL 2009) which uses an electrodynamic nanolens to integrate the seed particles at precise locations on a substrate. The precision of this seeding process is better than other self-assembly processes. The standard deviation in placement accuracy is 10 nm. This is possible by a 10x size reduction when compared to the dimension of the guiding patterns. The site specific nanolens seeding process conserves deposited noble metal material. This work has led to three publications. (APL 2009, Small 2010, Nano Lett. 2010). Step 2: The catalyst particles are grown into nanowires using established VLS growth processes.

2.1 Introduction. The synthesis and the integration of inorganic nanomaterials continues to attract considerable growth as it provides a potential solution to the manufacture of low cost printable electronics, optoelectronics, and solar cells with higher performance than their organic counterpart. In addition to low-cost fabrication, devices built on inorganic nanowires could take advantage of their naturally high crystallinity and high flexibility. These properties are particularly desirable for high performance electronics on flexible substrates. However the number of integration techniques that provide control over location, dimension, and orientation are limited and each has its own problems. In many cases the issue is throughput. Typically catalyst deposition is done in one reactor and samples are transported to a second reactor for nanowire growth. To address this problem we have developed an in-situ nanowire growth system that removes the need to extract samples between seed deposition reactor and nanowire growth. After in-situ nanowire growth, post-processing concepts are used to rotate nanowires and ultimately transfer nanowires onto new substrates for potential opportunities in flexible electronics.

**2.2 Seeding Process.** Figure 2.1 illustrates the basic elements and dimensions of the apparatus (A). The apparatus was enclosed in (B) a modified polypropylene desiccator sealed to prevent nanoparticle inhalation. A 10kV, 100mA controlled current power supply (Gamma High Voltage Research Inc., RR5-120R/CPC/M994) was used to ignite and maintain a 10W DC arc discharge between two identical

consumable electrodes. For consumable electrodes we used Au and Zn in wire form (2 to 5 mm diameter). The materials were clamped into slits in copper rods allowing adjustment of the separation. The anode (top electrodes in A,B) was given a high positive potential and the cathode (bottom in A,B) was grounded. Photographs of the arc (B inset) displayed the expected arc luminescence for atmospheric pressure air conditions (20.95% O<sub>2</sub> by mole). Spectroscopy of bluewhite  $O_2$  discharges shows peaks at 419nm<sup>[29]</sup> due to positive ionization of  $O_2$  into  $O_2^+$ , where these ions present in the arc may play a role in nanoparticle charging and formation. The process of nanoparticle formation using atmospheric pressure arcs is established and we refer to  $Smirnov^{[30]}$  for an introduction. In brief high mobility electrons generated by the arc are accelerated by the applied electric field to the anode, producing gas ions as they travel. Incident positive gas ions are brought to the cathode where they impact the cathode tip surface. Erosion is observed only at the cathode because the heavy positive gas ions release more kinetic energy than the electrons when impacting the electrode surface. The eroded material is collected at the sample. During collection an electrometer can be used to measure a positive current,  $I_{SUB}$ ~1nA, indicating that the deposited nanoparticles are positively charged. The erosion process increases with the arc current. To prevent rapid evaporation of the cathodes all experiments were performed at 10W with controlled arc currents <100mA which is guite similar to what is used in atmospheric pressure arc discharge lamps<sup>[31]</sup>.



**Figure 2.1** Schematic and photograph of the basic elements. (A) An atmospheric pressure DC arc discharge is established between two consumable electrodes that are separated by 2 mm. (B and inset) The photograph shows the typical appearance of the arc between Au electrodes. Produced positively charged nanoparticles are collected on a grounded substrate outside the plasma region. Flux and deposition of charged particles is monitored using a Keithley (6517A) electrometer.

Figure 2.2 depicts scanning electron micrographs of gold nanoparticles deposited onto a silicon substrate electrode that was partially shielded using patterned PMMA. After patterning the samples were exposed to 49% HF for 30s before deposition to remove the native SiO<sub>2</sub> layer. Deposition into openings is achieved down to 200nm where electrodynamic focusing allows resolution below 100nm with deposit geometries that depend on resist feature size and time. Nanoparticles are focused into clusters at the center of the resist opening. Throughout the lengthy deposition process it can be seen that particles are absent from the resist, suggesting that nanoparticles are repelled from deposition there. This is quite remarkable and holds for



Figure 2.2. Gold nanoparticle seed collection into features in 80nm thin PMMA ebeam resist. The TEM inset shows these nanoparticles demonstrate diameters below 5nm. Continuous charge-based nanoparticle deposition results in deposition into arrays with 1µm diameter openings.



Figure 2.3. In-situ seeding and nanowire growth system. Sub-10nm seed catalysts are generated and subsequently collected on a substrate. The deposited seeds demonstrate funneled deposition resulting in 8nm standard deviation positional accuracy. Si wires are then grown from the deposited seeds in a high temperature tube furnace with gas phase chemical reactants.

even micron-scale features as shown in the figure. Whether depositing metallic Au over time or semiconducting ZnO the insulating surfaces appear to self-equilibrate to a sufficiently high potential for the nanoparticle flux to be directed to the grounded regions. The focusing effect and small standard deviation in location of the deposits become apparent using Au nanoparticles and 1  $\mu$ m circular openings.

The process is understood to work in the following way: material deposition does not occur on insulators without a conductive substrate, suggesting field directed assembly to be the dominant mechanism. The arc produces a gas medium of high mobility bipolar gas ions and orders of magnitude lower mobility / heavier charged nanoparticles. After introduction of uncharged resist, we expect adsorption of these charged species to be controlled by drift and diffusion favoring high mobility gas ions initially until a steady state is reached where the resist surface is charged. The system equilibrates and establishes whatever necessary fringing field to funnel material to conducting surfaces where they become neutralized. The process is fundamentally different from known xerographic methods where deposition occurs onto the insulating surface instead of the conductor. It is an electrodynamic instead of electrostatic process which means that films of any desired thickness can be formed without depleting the charge differentials that direct the deposition process.

**2.3 Si Nanowire Growth.** Figure 2.3 shows the system for Si nanowire growth. The nanowires were grown from the deposited seeds that were focused into the center of resist openings by the previously mentioned electrodynamic nanolens effect. We utilize a nanowire growth process similar to previously reported methods

where silicon tetrachloride (SiCl<sub>4</sub>) is used as the precursor gas with H<sub>2</sub> as the carrier and our optimal growth occurs at temperatures below 1000 degrees C. The prepared substrate is gently rinsed with isopropyl alcohol and placed into a horizontal tube furnace then the furnace chamber is purged with H<sub>2</sub> at a flow rate of 1900SCCM for 20 minutes. Next, the furnace temperature is ramped from room temperature to temperatures ranging from 800-1000 degrees Celsius, followed by a 10-30 minute annealing step to ensure alloying between the Au catalyst and the silicon substrate. This is followed by a 10-30 minute growth step in which H<sub>2</sub> is flown through liquid SiCl<sub>4</sub> in a bubbler to deliver the silicon precursor gas to the growth substrate. Once the growth process is complete, the furnace is quickly cooled while maintaining the flow of H<sub>2</sub>. The growth substrate is then removed from the furnace.

Preliminary results on nanowire post-processing steps are shown in Figure 2.4. Following in-situ nanowire growth, nanorotation involves the use of a micromanipulator to bring the two surfaces in contact while providing a translational motion. Specifically, we use PDMS which is brought in contact with the tops of the nanowires to apply a shear force to rotate the nanowires into a predefined horizontal direction. The forces between the nanowires and the transfer substrate cause the nanowires to tilt and ultimately break free from the growth substrate. The freed nanowires are then transferred to a flexible substrate. Nanowires grown on <111> crystalline Si substrates were found to grow predominantly in the (111) direction perpendicular to the substrate. However these perpendicular wires were more challenging to free from their initial growth positions since they would often bend instead of fracture at the base as desired. In response <100> Si was used as nanowire substrates. The Si nanowires continued to grow in the (111) direction however in this case the four equivalent [111] growth directions were no longer perpendicular to the substrate. The oblique growth angle allowed nanowires to be more easily freed from the substrate and transferred to a new substrate.

**3. Conclusion:** The reported ZnO nucleation and growth process provides a new route towards the production of ZnO micro and nanostructures at known locations (40nm-STD) with well defined dimensions (15%-STD). The process produces high quality ZnO where deep-level radiative defects are eliminated. In addition to the demonstrated micro LEDs/photovoltaic cells these two features are attractive for a number of applications that aim at integrating devices such as ultraviolet LEDs<sup>[2-4]</sup>, laser cavities<sup>[32]</sup>, waveguides<sup>[5-8]</sup>, high gain photodetectors<sup>[16]</sup> or micro-power generators<sup>[15]</sup> at exact known locations.

The reported in-situ Si nanowire growth process was shown to enable collection Au nanoparticle seeds onto a Si substrate and then epitaxially grow the seeds into Si nanowires. The seed deposition process uses an electrodynamic nanolens to integrate the seed particles at precise locations on the substrate. The precision of this seeding process is better than other self-assembly processes. The standard deviation in placement



Figure 2.4. Schematic of post-processing concepts (top) applied to asgrown Si nanowires (bottom). High density vertical Si nanowires grown epitaxially on <111> substrates as originally proposed (bottom left) were more challenging to delaminate than patterned Si nanowires grown at oblique angles with respect to <100> substrates (bottom right). Si nanowires in the latter case demonstrated the ability to form a cross-bar array after rotation and resulted in a semiconducting mesh following transfer to a flexible substrate.

accuracy is 10 nm. At present we have only varied a few process parameters. Questions of ultimate uniformity and extension to large area deposition using multiple spatially separated discharge regions will require further research.

The nanoparticle seeds were collected on <111> and <100> substrates and then grown into Si nanowires using a VLS process. The postprocessing concepts applied grown wires are still under investigation however preliminary results for the ultimate integration of Si nanowires on flexible substrates are promising.

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