

Atomic Layer Deposition/Molecular Layer Deposition for Packaging and Interconnect of N/MEMS

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ABSTRACT

Atomic layer deposition (ALD)/molecular layer deposition (MLD) processes are able to fabricate nano-scaled inorganic/organic multilayers. Such multilayers are essential to novel packaging and interconnect technologies for NEMS/MEMS. ALD/MLD coatings could reduce water vapor transmission rate down to 5×10^{-5} g/m²/day or lower for excellent hermetic/vacuum sealing. ALD/MLD coatings can also modify nanowire/nanomesh structures critical to flexible thermal ground planes that can reach an effective thermal conductivity of 30,000 W/mK and heat flux removal of 200 W/cm². ALD/MLD coatings can enhance the stability while reducing thickness of an embedded Li-ion battery. In addition, the ALD/MLD-based inorganic/organic multilayer can be used for interconnecting nanowire-based photonics.

Keywords: Atomic layer deposition, molecular layer deposition, ALD, MLD, packaging, MEMS, NEMS

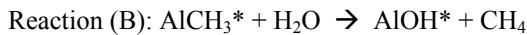
1. INTRODUCTION

Microelectromechanical systems (MEMS) technology is known to be critical to the advancement of optoelectronics. With the length scale reduced by another 1000 times, nanoelectromechanical systems (NEMS) technology is expected to be more important than MEMS. For a device example, GaN nanowires grown on a silicon substrate can be defect-free if they are grown along c-axis. Such a defect-free structure may enable us to develop future optoelectronic devices with very high efficiency and reliability. For another device example, graphene, a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, can be used for nano-scaled sensors and actuators. Graphene possesses superior electrical, thermal and mechanical properties; it may be the best NEMS materials for sensing and actuating. For a packaging example, copper nanowires can increase heat transfer coefficients by 10 to 100 times due to their extremely large surface area available for evaporation. As a result, we may remove high heat fluxes, e.g. 200 Watt/cm², from active devices through simple immersion cooling. For an energy example, silicon nanowires can increase anode's storage density for a Li-ion battery by 10 times. Their nano-scaled configuration reduces the gradients of Li-ions during charging/discharging processes. The substantially reduced gradients decrease stresses induced by the 400% volume change and will enhance the cycle life of silicon-based Li-ion batteries.

NEMS devices are expected to be integrated with MEMS devices for N/MEMS systems with significantly enhanced performance and reliability. However, NEMS' surface-to-volume ratios would be about 1000 times larger than those of MEMS, which is already known to be strongly affected by surfaces and surface contacts. In order to achieve the performance and reliability enhancement, we must develop nano-scaled coating technologies for precise surface manipulation. Atomic layer deposition (ALD) and molecular layer deposition (MLD) processes are expected to be the surface coating technologies required. This paper will illustrate these two processes with an emphasis on their applications for packaging and interconnect of N/MEMS. ALD/MLD will be briefly reviewed, followed by their applications for moisture barrier coatings, flexible thermal ground planes, Li-ion batteries and packaging and interconnect of GaN nanowires. More information on ALD/MLD fundamentals and applications is posted at <http://imintcenter.org/>.

2. ATOMIC LAYER DEPOSITION/MOLECULAR LAYER DEPOSITION

Atomic layer deposition (ALD) is illustrated in Figure 1 with sequential, self-limiting surface reactions. Surface species deposited by the first reactant in the (A) reaction are reactive with the second reactant in the (B) reaction. Each reaction can deposit only a monolayer. The (B) reaction returns the surface to the initial surface species. Consequently, the two reactions can be repeated in an ABAB... sequence for atomic layer controlled film growth. For example, Al_2O_3 ALD is deposited using the following AB reaction sequence:



where the asterisks designate the surface species. During deposition, the initial OH terminated surface is first exposed to trimethylaluminum ($\text{Al}(\text{CH}_3)_3$, TMA) as shown in reaction (A). This reaction deposits a monolayer of Al and will stop after all of the surface OH groups are converted to CH_3 groups. Once this reaction is complete, the products and remaining reactants are removed from the system. Next, the surface is exposed to water, which reacts with the CH_3 groups to regenerate OH sites. After the products and remaining reactants are purged, the surface is ready for another (A) reaction. This AB reaction sequence is repeated until the desired thickness is obtained. The Al_2O_3 ALD film growth is linear with the number of AB cycles performed and the growth rate is about 1.2 Å per AB cycle. Figure 2 shows a polysilicon MEMS device encapsulated by Al_2O_3 ALD.

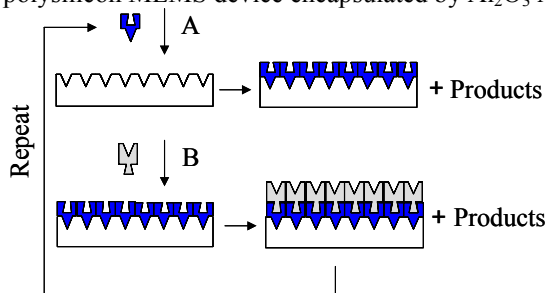


Figure 1: The AB reaction sequence for ALD

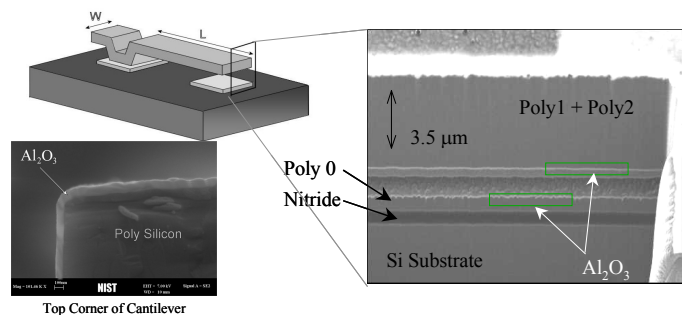


Figure 2: Poly-Si MEMS cantilever beam coated with 60 nm of protective alumina (Al_2O_3) using ALD.

ALD is a manufacturable process for depositing alumina (Al_2O_3), tungsten (W), platinum (Pt), ruthenium (Ru), aluminum nitride (AlN), tantalum nitride (TaN), silicon dioxide (SiO_2), hafnium oxide (HfO_2), zinc oxide (ZnO), titanium oxide (TiO_2), magnesium oxide (MgO), manganese oxide (MnO_2), lead zirconate titanate (PZT) and lithium aluminosilicate (LASO) and many other inorganic materials. The ALD films and processes possess the following appealing features:

1. ALD film thicknesses can be precisely deposited from a few Å to hundreds of nm.
2. ALD films can be deposited at temperatures ranging from 33°C to over 200°C.
3. ALD films are pinhole-free, dense, smooth and highly conformal.
4. ALD films can be deposited on polysilicon, silicon nitride, metals, polymers, and ceramics.
5. ALD films can be deposited on any size or shape device.
6. ALD films can coat high surface area to volume ratio structures with complex geometries.
7. ALD films can deposit insulating or conductive layers.
8. ALD can deposit hydrophobic or hydrophilic layers covalently bonded to the surface.
9. ALD can deposit on selective areas defined by photoresist or other protective materials.
10. ALD coating process' deposition rate is high enough for semiconductor manufacturing of microprocessors and memory chips; its rate is to be increased by another order of magnitude when the roll-to-roll ALD is developed.

During the past, ALD coatings have proven to be effective to protect MEMS devices from electrical short¹, charge accumulation², moisture-induced adhesion³, wear⁴, creep⁵ and other failures protected using self-assembled monolayer (SAM)⁶. ALD coatings are good for MEMS devices; however, they are not enabling processes since most of MEMS devices can tolerate the variations achieved by existing surface coating processes. On the other hand, ALD coatings are essential to NEMS devices that demand sub-nm variations in surface coatings. More importantly, ALD coatings can be integrated with newly developed molecular layer deposition (MLD) coatings for a nano-scaled, inorganic/organic multilayer.

An example of MLD is illustrated by a three-step reaction sequence as shown in Figure 3. The three-step ABC reaction is the sequential reaction of TMA, ethanolamine (EA) and maleic anhydride (MA). This reaction sequence incorporates a metal alkyl reactant, a heterobifunctional reactant and a ring-opening reactant. This three-step ABC reaction sequence avoids the possibility of double reactions and leads to very robust and linear MLD growth. Other possible three-step ABC reaction sequences using heterobifunctional reactants, ring-opening reactants and reactants with masked or protected functionalities offer a wide range of possibilities for the MLD of organic and hybrid organic-inorganic MLD films⁷. These new combinations, together with previous ALD processes, will significantly increase the range of thin film materials that can be deposited conformally with precise thickness control. Figure 4 illustrates a configuration representing inorganic/organic multilayers with the following appealing features:

1. ALD/MLD inorganic/organic layers are covalently bonded.
2. ALD/MLD layers can enhance the mechanical toughness of brittle functional ALD layers by inserting compliant organic layers.
3. ALD/MLD layers can be accomplished in the same reaction chamber with unlimited number of combinations of inorganic and organic materials.
4. ALD/MLD layers can be designed to meet specific electrical, optical, thermal and mechanical properties by varying inorganic combinations and/or organic combinations.
5. ALD/MLD layers can be functionalized to meet specific chemical or biological requirements.

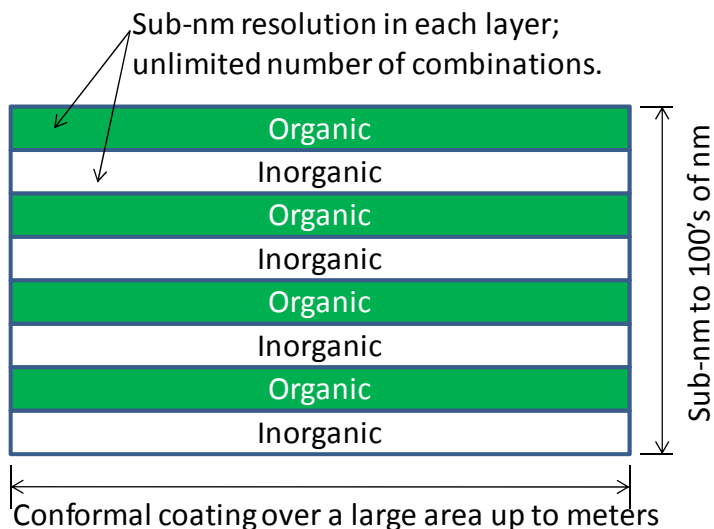
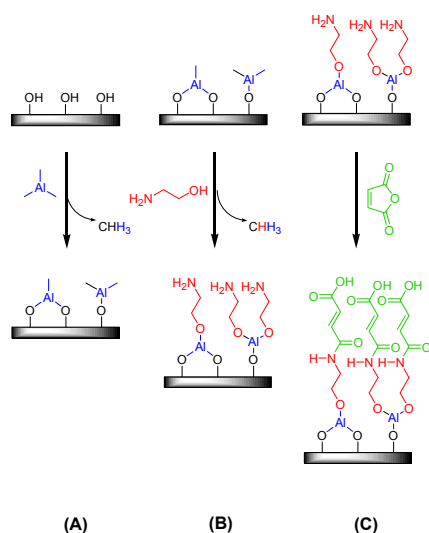


Figure 3: A schematic of the three-step ABC reaction

Figure 4: Inorganic/organic multilayers fabricated by ALD and MLD.

We expect to see a large number of application-specific ALD/MLD multilayers to be designed and fabricated on different N/MEMS devices and packages to meet different requirements. In the following sections, we will illustrate this potential with a few novel packaging solutions.

3. ALD/MLD FOR MOISTURE BARRIER COATINGS

Moisture and oxygen barrier coatings are important to protect organic LEDs, organic electronics, organic solar cells and other flexible electronic/optoelectronic components from performance degradation. These coatings are also critical to provide hermetic and vacuum sealing for wafer-scale N/MEMS packages. Recently, atomic layer deposition (ALD) has been demonstrated as an ideal technique to produce high quality moisture/gas diffusion barriers. As shown in Figure 5, the moisture permeation rate of typical polymers can be reduced by more than 10^3 times using a single-layer Al_2O_3 ALD coating with a thickness of 25nm^{8,9} and to 10^5 times using $\text{Al}_2\text{O}_3/\text{SiO}_2$ bi-layers consisted of Al_2O_3 ALD and rapid SiO_2 ALD¹⁰. With nano-scaled inorganic Al_2O_3 , the barrier coating would not crack until it reaches a critical strain around 1% under mechanical loadings, e.g. bending or tensile loads¹¹. Roughly speaking, the critical strain increases with decreasing thickness of the inorganic layer. Therefore, the 1% critical strain is already much higher than those achieved by CVD-based barrier coatings with the layer thickness larger than 20 μm . The ALD coating would enable the device/package substrate encapsulated to reach some flexibility required for high throughput manufacturing or functionality. However, such a critical strain needs to be increased.

As shown in Figure 6 for a hermeticity vehicle covered by Al_2O_3 ALD seal¹². This vehicle was developed for the flexible thermal ground plane to be discussed in the next section. The ALD seal cracks due to stress concentration around the corner between the Kapton film and the copper cavity. The crack patterns are consistent with those reported in the previous study¹¹. This problem can be solved by a design for stress reduction or increased critical strain.

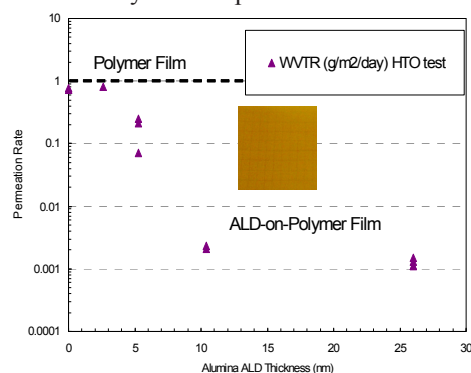


Figure 5: Al_2O_3 ALD moisture barrier coating over a polymer film

The best approach to increase the critical strain is to create an ALD/MLD barrier coating as shown in Figure 4. With the organic buffer layers added, we may decrease the thickness of the inorganic layer to 5 or even 2nm¹³. For the same total thickness, we can increase the mechanical toughness substantially while reducing moisture permeation rates. The results of the new barrier coatings with ALD/MLD multilayer will be reported in the near future.

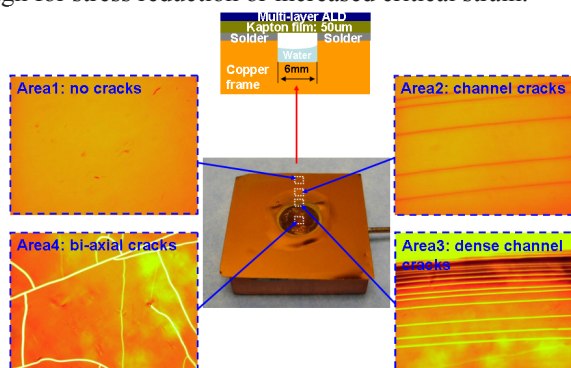


Figure 6: Cracking of Al_2O_3 ALD moisture barrier coating initiated by undesirable mechanical loadings

4. ALD/MLD FOR FLEXIBLE THERMAL GROUND PLANES

Flexible thermal ground plane (FTGP) is a new approach to improve the commonly used heat pipes by increasing its effective thermal conductivity substantially while creating a two-dimensional instead of one-dimensional thermal transport¹⁴. Figure 7 illustrates a FTGP configuration. Flexible circuit boards with interconnect circuits and thermal vias are assembled to form an enclosure, e.g. 40 cm long and 1mm thick. Inside the enclosure, there is a nano-mesh membrane separating liquid water from water vapor. The chips attached to the bonding pads would vaporize water with heat dissipated. The vapor would be transported to the condenser attached to the next cooling level. This evaporation/condensation process achieves very effective heat transfer; it is why heat pipes are commonly used in laptop computers, desktop computers and other thermal systems. Using nanowires/nanomeshes, we expect to be able to remove heat flux as high as 200 W/cm^2 and reach effective thermal conductivities as high as $30,000 \text{ W/mK}$ (note: copper's thermal conductivity is around 400 W/mK). One of the main reasons for such enhanced heat transfer is due to substantially increase surface area by using nanowires and/or nanomeshes. For effective evaporation heat transfer, ALD hydrophilic coatings are important to assure strong capillary-induced fluid flow to feed liquid water to the evaporator. For effective condensation heat transfer, ALD hydrophobic coatings are important to assure dropwise condensation. Such coatings do exist. The main challenge is to assure their reliability after long-term immersion in hot liquid water (near 100°C). Figure 8 shows a hydrophobic organic coating degrades significantly after only 15 hours in 75°C water.

This ALD reliability problem is relatively new. It is essential to design and fabricate optimum ALD/MLD multilayers for reliable hydrophilic and hydrophobic coatings immersed in water or other transport media required for different FTGPs.

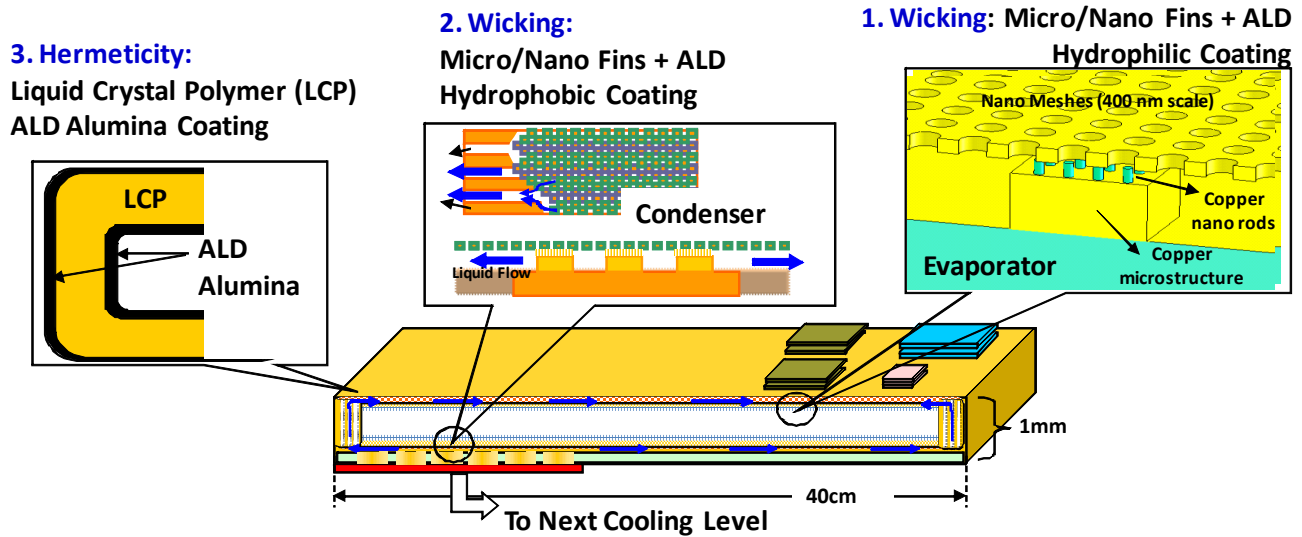


Figure 7: Flexible thermal ground planes enabled by ALD/MLD coatings

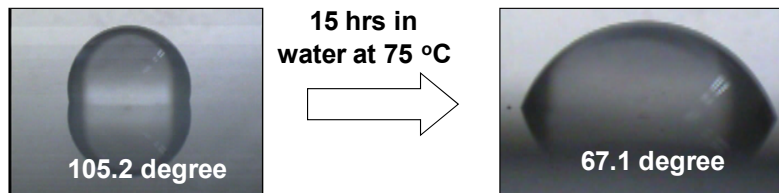


Figure 8: ALD hydrophobic coating degraded quickly without an appropriate treatment

5. ALD/MLD FOR LI-ION BATTERIES

Embedded Li-ion battery is important to the advancement of N/MEMS systems since the battery is always the largest and the heaviest component in the system. Figure 9 presents the roadmap of iMINT short-term and long-term research activities to improve battery's storage density, cycle life and charging/discharging rates. Without changing active electrode materials, we expect to increase the volumetric storage density by two times in the near future. With a new silicon-based anode, we expect to increase the density by another two times. With a new cathode material, we may increase it further by another two times.

ALD is one of the main technologies to be used for the short-term and long-term improvements. Figure 10 presents an exciting result¹⁵. Micro/nano-particles with high surface-to-volume ratios are essential to increase battery storage and enhance its stability even at a high charging/discharging rate. However, these particles can also be damaged quickly due to large surface exposed to electrolyte. SEI (solid electrolyte interface) can be formed quickly after a few charging/discharging cycles. As shown in Figure 10, the LiCoO₂ cathode's specific capacity drops quickly after 10's of cycles. With only 2 Al₂O₃ ALD layers, however, the cathode becomes very stable even after 100 cycles. On the other hand, with 10 Al₂O₃ ALD layers, the cathode's capacity drops substantially because it is blocked by the Al₂O₃ insulating layer. These results demonstrate a unique ALD surface coating optimized to protect electrodes from damage during high charging/discharging rates. With sub-nm resolution, we are able to identify the optimum ALD coating for stable performance without blocking ions transport. This exciting protection mechanism achieved by ALD coatings can be applied to graphite (anode) and other electrode materials. When nanoparticles are used to form electrodes, the ALD coating would become more critical due to its self-limiting growth of uniform film even down to sub-nm thickness

range. With ALD coatings today and ALD/MLD coatings in the future, we expect to reach the short-term and long-term goals defined in Figure 9.

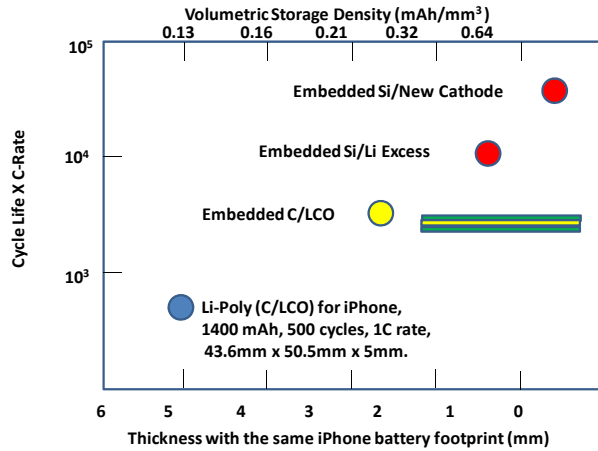


Figure 9: iMINT research roadmap for embedded Li-ion batteries

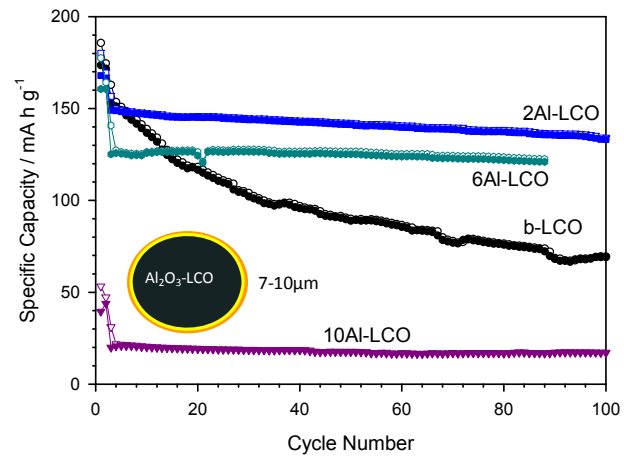


Figure 10: iMINT research roadmap for embedded Li-ion batteries

6. ALD/MLD FOR INTERCONNECT OF AS-GROWN NANOWIRES

When the characteristic length scale of semiconductor materials is reduced to the nm range, we may be able to grow materials with outstanding properties beyond what we could achieve in micro-scale. A good example is the *c*-axis GaN NWs, as shown in Figure 11, grown on Si(111) using nitrogen plasma enhanced molecular beam epitaxy (MBE)^{16,17}. These wires are defect-free with a great potential to fabricate photonic devices with the high efficiency and reliability. For LEDs, they would also provide excellent surface-to-volume ratio for the maximum possible extraction efficiency. However, there is no known packaging and interconnect technology for such as-grown nanowires.

Figure 12 illustrates a novel ALD-enabled multilayer technology for a packaging and interconnect solution^{18,19}. ALD- Al_2O_3 (30 nm) and ALD-W (40 nm) sequentially deposited on the surface of NWs functioned as a dielectric layer and an electrical interconnection layer, respectively. Conformal ALD- Al_2O_3 coating was verified by field emission scanning electron microscopy (FESEM) as shown in Figure 13. Figure 14 shows the FESEM images of tungsten layers (deposited variously by ALD and sputtering) covering the first ALD- Al_2O_3 layer. ALD deposition provides a high-quality, conformal coating (Figure 14a) compared to the sputter deposited tungsten coating (Figure 14b). With such a multilayer interconnect technology, we are able to interconnect every as-grown GaN nanowire on the silicon substrate. More importantly, as shown in Figure 12, electroplating copper can encapsulate all these nanowires and conduct heat effectively from each one (LED or transistor) of them to the silicon substrate through copper. If needed, CVD diamond can be used for more effective heat spreading.

The thickness of the ALD multilayer is nano-scaled thin; as a result, its thermal resistance is negligible. Table below summarizes the thermal resistances estimated for: 1) a current transistor configuration with heat source embedded in a GaN substrate; 2) a nanowire cooled by conducting through nanowire itself; 3) a nanowire encapsulated by polymer, e.g. BCB; 4) a nanowire encapsulated by copper; and 5) a nanowire encapsulated by copper with different ALD layers considered¹⁹. The ALD-enabled copper heat spreading reduces the thermal resistance of as-grown nanowires by 600 times. In addition, this resistance of 0.09 K/W is only 50% of that of the current transistor embedded in the substrate. The ALD multilayer can be replaced by ALD/MLD multilayer in order to enhance its mechanical compliance and toughness (see Figure 4). Such a novel nano-scaled packaging and interconnect technology will be essential to all nanowire-enabled photonic devices. Their thermal performance may even be better than those of embedded devices manufactured today.

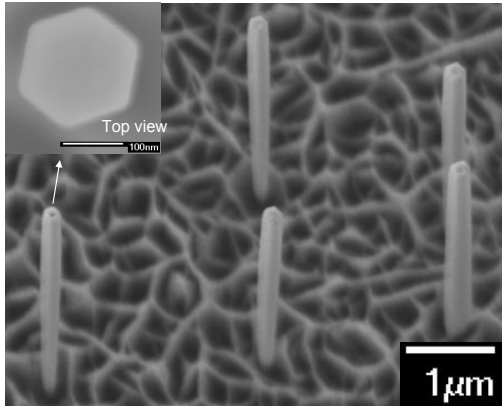


Figure 11: c-axis-oriented GaN nanowires grown by catalyst-free MBE on Si(111), inset: top view of single NW.

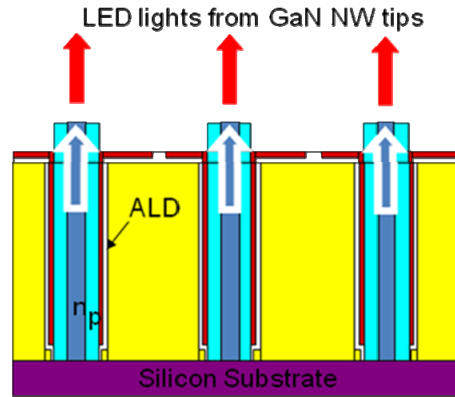


Figure 12: Schematic GaN nanowire LED device interconnected by ALD on core-sleeve p-n junction on a Si substrate.

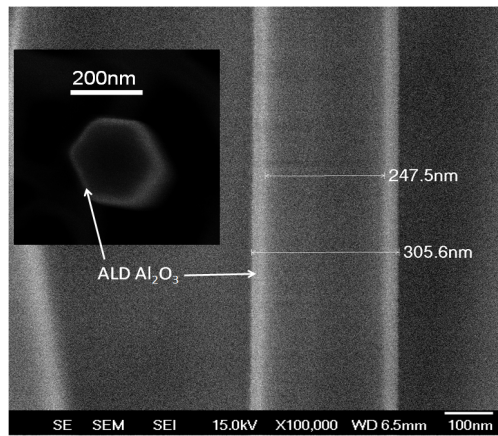
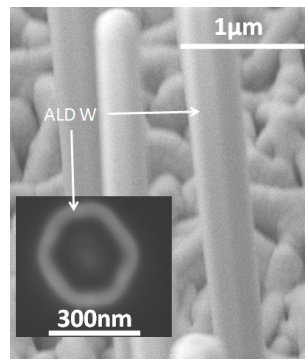
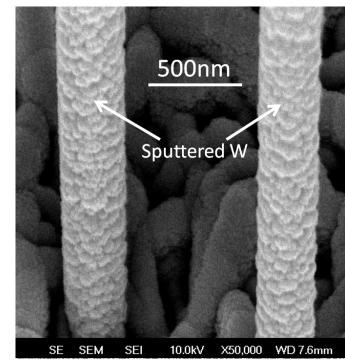


Figure 13: ALD- Al_2O_3 layer (30 nm, shell) on GaN NW(core), inset: top view.



(a)



(b)

Figure 14: Tungsten layers deposited on GaN NWs by different coating methods (a) ALD-W(inset: white outer layer) (b) Sputtered.

Table 1: Numerical simulation results to study heat spreading performance of planar/NW configurations

Simulation case	Cross-sectional schematic drawing (not to scale)	Thermal resistance ($\times 10^4$, K/W)		Temperature difference ($^{\circ}\text{C}$) Power: 50mW
A. Heat source on GaN substrate ($K_{\text{GaN}}=130$ W/mK)	Heat flux source GaN	0.18		90
B. GaN NW on silicon substrate ($K_{\text{GaN NW}}=K_{\text{Silicon}}=130$ W/mK)	GaN NW heat source Si	62		31000
C. BCB-encapsulated NW ($K_{\text{BCB}}=0.29$ W/mK)	BCB Si	29		14500
D. Cu-encapsulated NW without ALDs ($K_{\text{Cu}}=400$ W/mK)	Cu Si	0.068		34
E. Cu-encapsulated NW with ALDs (one Al_2O_3 and one W) ($K_{\text{Al}_2\text{O}_3}=25$, $K_{\text{W}}=174$ W/mK)	ALDs Cu Si	10nm each	0.08	40
		20nm each	0.09	45
F. Diamond-encapsulated NW with ALDs (one Al_2O_3 and one W) ($K_{\text{Diamond}}=1000$ W/mK)	ALDs Diamond Si	10nm each	0.05	25
		20nm each	0.065	32.5

7. ACKNOWLEDGMENTS

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8. CONCLUSION

Atomic layer deposition (ALD)/molecular layer deposition (MLD) processes are able to fabricate nano-scaled inorganic/organic multilayers. Such multilayers are essential to novel packaging and interconnect technologies for Nano-Electromechanical Systems (NEMS) and Micro-Electromechanical Systems (MEMS). ALD/MLD processes was introduced, followed by a few examples associated with packaging and interconnect technologies. ALD/MLD-based moisture barrier coatings could reduce water vapor transmission rate down to 5×10^{-5} g/m²/day or lower, which is good for hermetic/vacuum sealing of polymer packages and organic LEDs and other photonic and electronic devices. ALD/MLD hydrophilic/hydrophobic/protective coatings are also enabling technologies for nanowire/nanomesh structures critical to a flexible thermal ground plane that can reach an effective thermal conductivity of 30,000 W/mK and heat flux removal of 200 W/cm². ALD/MLD coatings over anodes/cathodes can enhance the stability of an embedded Li-ion battery during a substantially increased charging/discharging rate. They can also reduce the battery thickness significantly through the use of micro/nanoparticles. In addition, the ALD/MLD-based inorganic/organic multilayer can be used for the electrical, thermal and mechanical interconnect for GaN nanowire-based photonics. With these nano-scaled multilayers, we are well equipped to develop novel packaging and interconnect technologies for future N/MEMS.

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