Rev. Adv. Mater. Sci. 40 (2015) 177-187

EMERGING STRATEGIES FOR SYNTHESIS AND MANIPULATION OF NANOWIRES: A REVIEW

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Received: November 01, 2014

Abstract. Insulating, semiconducting and metallic nanowires are useful in nanotechnology for building blocks because of their anisotropy and small size. The possible methods to assemble homogenous and heterogenous nanowires with great purity and crystallinity are very useful in fabrication processes. Various approaches have been developed for precise positioning of nanowires on the substrate allowing in the integration of nanoelectronic device. With greater advancement in the field of nanotechnology, ample amount of information is available for fabrication and manipulation of nanowires and their utility in development of functional devices like biosensors has been reported. The current paper focuses on the development of functional device and assembly of nanowires. A number of approaches like Vapour-Liquid-Solid and electrodeposition are described. Nanowires used for the fabrication of functional devices have been studied to diminish the inaccuracy and expand the defect tolerance.

1. INTRODUCTION

Nanowires are considered as nanoparticles with diameter smaller than the length and ranges between 10-100 nm in diameter and 100 nm to tens of microns in its length. The fabrication of nanowires can be achieved from a wide range of materials which includes inorganic, electrical conductors, organic, insulators, and semiconductors [1- 13]. Nanowires are advantageous due to the high anisotropic property which can facilitate in the propogation of light and electricity in spatial directions specifically. Multiple heterogenous segments of nanowires when precisely spaced along its length is considered as a fabrication method. Single crystal or amorphous materials nanowire has been fabricated using various methods [14]. A single nanowire device is a very useful component by itself, this when precisely positioned on substrates, or when the nanowire is integrated with other nanowires can result in the development of an integrated device which is highly functional. The electrical conduction of nanowires differ from their bulk counterpart because of the one unconfined dimension and two quantum confined dimensions that is seen. Electrical conduction takes place by bulk conduction and tunnelling mechanism. Nanowires have a wide range of applications in the fields of sensor devices, thermo electric, electronics, optics, magnetic mediums, etc. due to their interesting properties [15].

2. METHODS FOR THE SYNTHESIS OF NANOWIRES

The various methods that are currently employed in the synthesis of nanowires are shown in Fig. 1. The 1D structure of nanowire is due to crystallization [16], where the evolution of a solid from a vapour, a liquid, or a solid phase involves nucleation and growth of the nanowire. When the concentration of the atom, ions or molecules of the solid becomes considerably high, it aggregates to form small nuclei or clusters by homogenous nucleation. These clusters are the initial seeds for the growth and forma-

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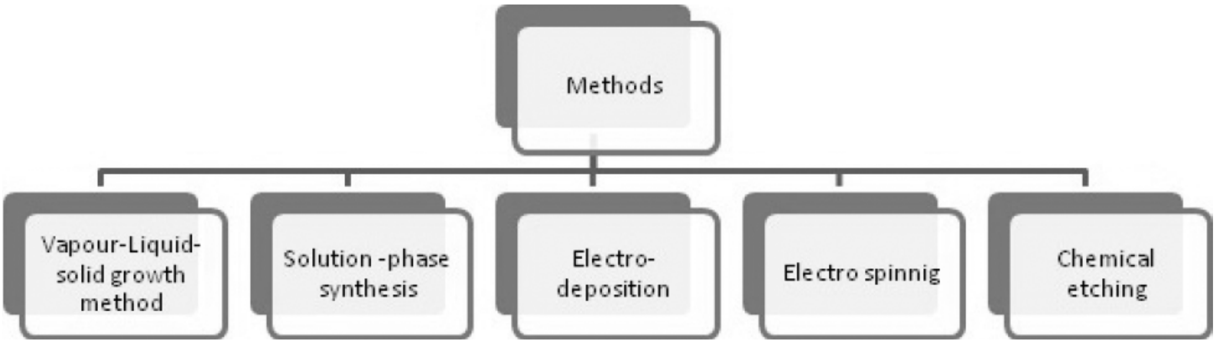

Fig. 1. The various methods that are currently employed in the synthesis of nanowires.

tion of larger clusters. A control over the growth parameters for the synthesis of 1D nanowires can be achieved by employing various chemical strategies, which include: (1) 1D nanowire growth can be facilitated by the use of anisotropic crystallographic structure of the solid; (2) the symmetry of the seed is reduced by the introduction of a solid-liquid interface; (3) the nanowires formation can be directed by the use of 1D morphology templates; (4) the growth habit of the seed can be modified by controlling the level of super saturation; (5) the various facets of a seed during growth can be controlled kinetically using capping agents; (6) 0D nanostructures self assembly [17-23].

2.1. The vapour-liquid-solid growth method

The general synthesis methods for semiconductor nanowires are by utilizing metal nanoclusters as catalysts through vapour-liquid-solid (VLS) process [24]. The metal nanoclusters in this process are heated above the eutectic temperature for the metal semiconductor system of choice; this is done in the presence of a vapour phase semiconductor as source which results in a liquid droplet of the source alloy. The liquid droplets supersaturates due to the continuous feeding of the semiconductor reactant leading to nucleation of the solid semiconductor. The nanowire growth is assisted by the solid-liquid interface which forms the growth interface and in turn acts as a sink leading to the continuous incorporation of the semiconductor into the lattice with the alloy droplet riding on top. The decomposition of precursors by chemical vapour deposition (CVD) or by momentum and energy transfer methods like pulsed laser ablation [25] or molecular beam epitaxy (MBE) of solid materials [19] are used to generate the gaseous semiconductor reactants. CVD was the most popular technique employed. In CVD-VLS method, the growth of the metal nanocluster acts as a catalyst where the gaseous precursor decomposes to provide the semiconductor or reactants in gaseous state.

2.2. Solution phase synthesis

Nanowires formed in the presence of a molecular template or catalyst from a liquid precursor is employed. The gold or silver salts get reduced in presence of polymers such as poly vinyl pyrrolidine (PVP) or cetyl trimethyl ammonium bromide (CTAB). The adsorption of the surfactants are specific to crystalline faces and the growth is enhanced or inhibited along these faces which results in the growth of nanowires spontaneously. The addition of solid crystalline seeds to the solution aids to initiate preferential axial growth along specific crystal faces. The various parameters like concentrations, temperature and surfactants can be modified to control the type of nanowires being formed [26-30].

2.3. Electrodeposition in nanoporous templates

Physical templates are employed within nanoporous membranes to direct the growth of nanowires within these membranes. The fabrication methods for nanoporous membranes include tracketching or anodic electrochemical methods, commercially available membranes with pore sizes ranging from 15 nm to 500 nm and thickness of 60 mm are also used. The process in brief involves the sealing of one face of the membrane using a conductive seed layer. The seed layer can be deposited either by thermal or sputter evaporation onto the membrane. An electrolytic solution containing suitable ions is then used for the deposition of single segment or multi segmented nanowires. The electrolytic cell is formed by the seed layer and the counter electrode immersed in the solution.The current density or voltage, and the duration of electrodeposition process

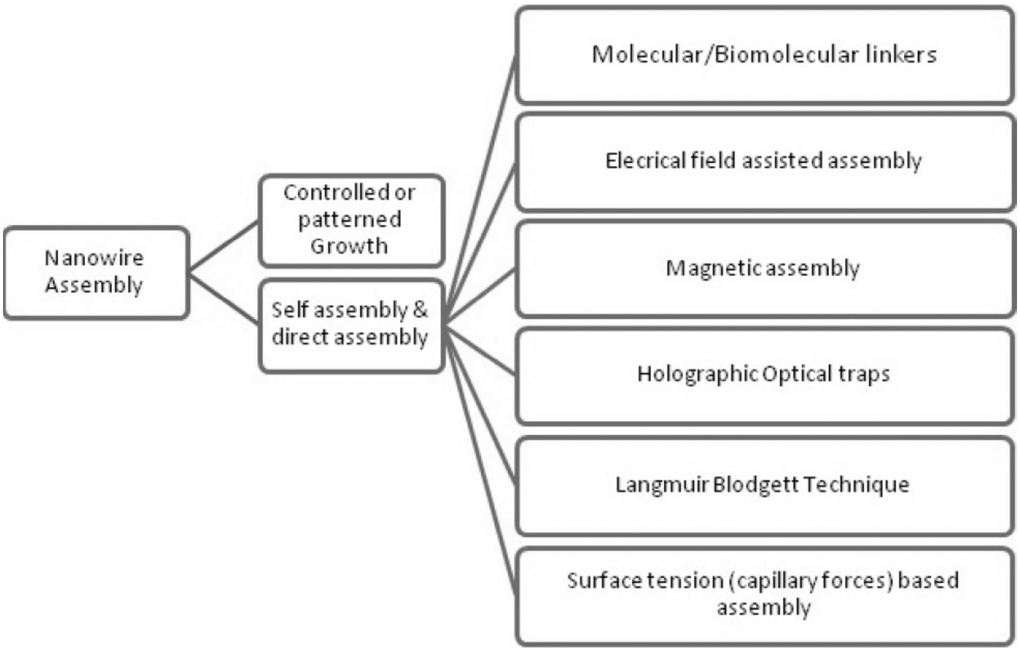

Fig. 2. The assembly of the synthesized nanowires are achieved by the above listed techniques.

can be controlled which in turn restricts the length of the segments within the nanowires [31-38]. The most attractive method to fabricate nanowires is the electrodeposition in templates; theoretically it can be used to make nanowires with any material capable of being electrodeposited.

2.4. Electrospinning

The most efficient and simple way to produce polymeric nanowires is by electrospinning. The method involves a syringe through which the polymer solutions are driven, the surface tension on the tip under high electric field can be overcome resulting in the ejection of a charged jet. The electrical forces present elongates the jet thousands or millions of times until the jet is thin and is scaled to a nanoscale level. The long polymeric nanofibres that are formed can be collected on an electrically grounded metal sheet once the solvent evaporates or the melt solidifies. Electrospinning facilitates in the formation of nanowires that are long with well controlled curvature, when compared to other methods [38-45].

2.5. Chemical etching

Rapid fabrication of large area, highly oriented SiNW arrays on Si wafers by metal induced chemical etching of silicon substrates in HF solution is a convenient method. The parameters such as etching temperature, solution concentration, immersion time in HF solution, space between the metal particles and especially the metal species added into the HF solution strongly affect the morphologies of the obtained microstructures on the surface of the Si substrates [46-48].This method shows little dependence on the orientation or doping type of the Si wafer [47] and also has the advantages of simplicity, large scale production and low cost. It is however hard to control the diameter of the wire and the interspacing because of the random distribution of the metal particles that are formed by electroless deposition or by vaccum thermal evaporation.

3. NANOWIRE (NW) ASSEMBLY AND MANIPULATION.

The manipulation and positioning of nanowires is achieved using scanning probe microscope, but these processes are slow and expensive [49]. Hence, there is a dire need to develop strategies that can either directly integrate the nanowires during growth to form the final device or in the assembly of nanowires to form functional devices. The strategies or processes devised must be highly efficient in its activity with relatively high speed and with reasonable pricing to enable it for large scale production. Fig. 2 presents the assembly of the synthesized nanowires which are achieved by the above listed techniques.

3.1. Controlled or patterned growth

There are a variety of processes employed to grow nanowires involving a catalyst or template, it is possible to aid the growth of nanowires at specific spatial locations which helps in the growth in specific direction by directly patterning the catalyst or template onto the substrate. It is a very attractive method to form vertical or horizontal interconnects. The growth is observed to occur between two patterned microstructures and by this the nanowires electrically connect with the substrates [50-66].

3.2. Self-assembly and directed assembly

A cost effective method of fabrication can generate 3D and integrated systems by directed assembly. A variety of 2D and 3D complex structures which ranges from nanometer to millimetre range can be mass produced by nature, biological self assembly inspired the directed assembly of engineered structures. The method includes tumbling chemically patterned components into fluidic medium where interaction between each other occurs and stable structures with precise functions are formed. The orientation and binding of the components is engineered using various forces that chemically pattern the components. The process is considered as indeterministic and uncontrollable and is unexplored due to the engineering and manufacturing paradigm. Several strategies have been investigated to direct the nanowire assembly with each other or with substrates [67-71]. A few strategies are listed below:

3.2.1. Bio-molecular linkers

The assembly of nanowires can be directed by the use of molecular linkers which forms chemical bonds with each other. The nanowires are exposed to the molecular linkers initially and this is done in the solution or vapour phase. A high degree of specificity can be incorporated to this process due to the availability of a large variety of biological molecules which specifically bind to the particular ligands or receptors. Studies have been reported using biological molecules like DNA, proteins, and virus to link the nanowires in the formation of complex architectures [72-80]. The main advantage of utilizing biological molecules in direct assembly is due to their unique properties of lock-key based recognition, cooperativity and hierarchy in the formation of complex architectures.

3.2.2. Electrical field-assisted assembly

The motion of neutral particles under the influence of an external non-uniform electric field is Dielectrophoresis (DEP) [81]. The polarization of neutral particles and experiencing different forces at the ends of the polarized dipole due to non-uniform electric field at these ends gives rise to DEP. The difference that is formed forces the polarized particles into regions of differing field strength. Voltage is applied across the nanowires that are suspended in a solvent over the contact pads. The nanowires experience a force that causes them to move and orient on the substrates relative to the contact pads. It is possible to direct reversible and irreversible assembly of nanowires into a variety of architectures by changing the solvent, aspect ratio of the nanowires, geometry and spacing between the electrodes frequency and field strength [82-92]. The uniqueness of DEP is that the strategy can be scaled to wafer level, which assists the nanowires to be incorporated in a parallel fashion into devices with control over the placement and alignment.

3.2.3. Magnetic assembly

Another interaction that can be utilized is magnetic force to assemble and integrate nanowires. Magnetic assembly is facilitated by either segments within the nanowire or the entire nanowire is synthesised from ferromagnetic materials like nickel, iron, cobalt or alloys. These segments act like small magnets and orient themselves in an external magnetic field such that the energy is minimized when magnetized. The assembly into bundles and end to end network occurs when the nanowires interact with each other and with the magnetic substrates. Precise positioning of the nanowires on the substrates can also be achieved by applying magnetic forces [93-100].

3.2.4. Holographic optical traps

The nanowires are dispersed in a fluid medium on the stage of a light microscope and the manipulation is done by either a single or multiple diffraction limited optical traps with a holographic optical tweezer. Focussed laser beams are applied to achieve radiation force on the particles in order to manipulate them. The use of optical traps are an attractive method for the assembly of nanowires as they can be done in closed chambers with high spatial accuracy (<1 nm) and is also applicable to a wide range of materials [101-102].

3.2.5. Langmuir-Blodgett technique

The method involves the compression of nanowires that are capped with surfactants at a liquid interface, which is then transferred onto solid substrates.

The dispersion of the nanowires in a fluidic medium causes the wires to float at the fluid-air interface. The solid barriers that surround the nanowires approach each other in a highly well controlled and precise manner; the barriers compress the nanowires at the interface which causes the nanowires to rotate and align themselves in the form of close packed ordered arrays. The main highlight is that it is possible to form arrays of nanowires in an effective manner [103-108].

3.2.6. Capillary forces based assembly

The assembly of nanowires in to 2D and 3D structures have been successful to a certain limit as the integrated structures are not bound permanently to each other. The assemblies generally fall apart when taken from the medium or even under very mild sonication. In addition to this, the strength and extent of the binding is proportional to the overlapping area at the binding sites in case of directed assembly between the rigid nanocomponents. There is a decrease in the strength and extent of binding when there is a presence of any local roughness in the components utilized. It is extremely challenging in large scale integration due to the bonding between the components. In biological self assembly, the components are soft and deformable which enables the mating surfaces to conform to one another resulting in larger contact areas for the optimum binding. Capillary forces based assembly involves (1) hydrophobic organic molecules are employed in the modification of the surface energy of certain segments and thereby the molecules attach themselves to these segments, (2) precipitation of hydrophobic or hydrophilic liquid layers onto the modified segments, and (3) a favourable interaction between the nanowires can be achieved by the agitation of nanowires in hydrophobic or hydrophilic medium, this helps in the direct assembly process. The nanowires that are patterned with a hydrophobic layer collides with a hydrophilic layer, the liquid layers on different nanowires fuse on contact with one another, in order to minimize the surface free energy. The surface tension force between the liquid layers is optimum to hold the nanowires together [109,110]. Large scale integration is possible because the roughness of the nanowires will not interfere with the binding capability. The patterning of various hydrophilic and hydrophobic segments can help in the assembly of nanowires into bundles that are permanently bound.

4. MANIPULATION STRATEGIES FOR NANOWIRE

4.1. Cell manipulation using nanowires

Binding and physical manipulation are the essential mechanics that are involved in cell separation and work well with magnetic nanowires. It is also possible to obtain high purity and yield. The efficiency of the nanowires over the beads may be attributed to the larger magnetic moment, but the large surface area makes them effective in binding to cells. Characterization of the separation efficiency of nanowire size and composition, and also techniques to develop surface functionalization in order to control the nanowire and cell interaction has to be explored to apply this technique [111].

4.2. AFM based manipulation of nanowires

The method involves the bending of the nanowires in a gentle manner and under controlled conditions. Once the nanowire of interest is located and the image is obtained in tapping mode, the point as to where the manipulation force vector to be applied must be determined. The manipulation is invoked in repetitive mode which involves the mode in 'Retrace Lift' where the oscillation of the cantilever is set to zero with a combined effect of negative lift of the tip. This involves the scanning of the material in tapping mode with the cantilever positioned at a certain height above the surface, while the oscillation is halted and manipulation force with the negative lift of the tip is introduced in the retrace scan. The cantilever tip follows an identical method in the retrace mode but with a gradual increase in the manipulation force. Repeated trace-retrace sequence is continued until a movement is observed in the nanowire during the trace scan [112].

4.3. Semiconductor nanowire manipulation using optoelectronic tweezers

Single silicon and CdS nanowires can be trapped using optical tweezers. Due to the optical power density which is quite high and reduced working area (~1 μm x 1 μm), the ability to perform parallel assembly is hindered. Trapping of nanowires between two fixed microelectrodes can be achieved by dielectrophoresis, but it lacks the resolution to manipulate single nanowires and the electrode pattern fixes the trapping sites. A large number of microparticles or cells can be manipulated using optoelectronic tweezers [113].

4.4. Manipulation and assembly of nanowires with holographic optical traps

Semiconductor nanowires can be precisely organized into 2D and 3D structures by use of arrays of optical traps that are holographically projected which manipulates and assembles the nanowires. The use of laser wavelength can be used to enhance the optical trapping force. Advancement in holographic trapping technology will help in making the approach faster and highly parallel. Optical assembly of functional subunits will facilitate hierarchical fabrication of larger systems, through processes that might exploit complementary techniques such as chemically-directed self-organization. The HOT technique also can be extended to bring together diverse nanoscale building blocks such as nanotubes or nanoparticles, to utilize their unique properties in conjunction with those of nanowires. In addition, dynamic systems can be created by exploiting the dynamically configurable nature of optical traps [114].

5. NANOWIRES APPLICATIONS

An overview of the various nanowires applications is demonstrated in Fig. 3.

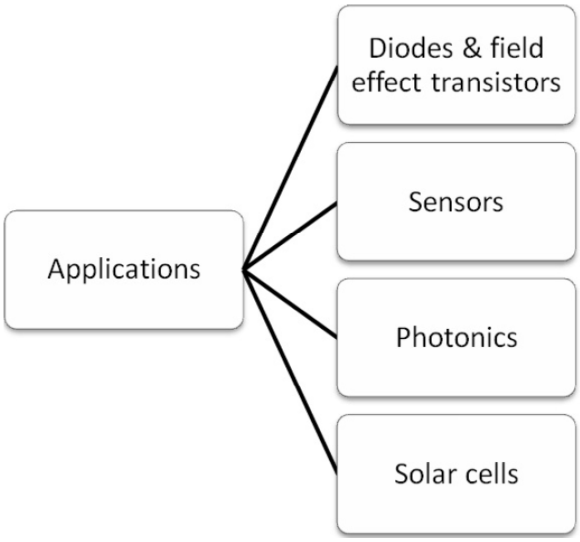

Fig. 3. An overview of the various applications.

5.1. Field effect transistors (FET) and diodes

Field effect transistor stacks have been integrated with homogenous semiconducting nanowires. The semiconducting nanowires are generally thin and hence it is not necessary to pattern the layer of active semiconductor. To integrate the semiconducting nanowires into the devices a certain level of patterning by lithography is necessary. The nanowire heterostructures and its fabrication enable the addition of dielectrics, metals and semiconductors into the nanowire [115].

5.2. Sensors

The adsorption of the analytes on the nanowires has an intense effect on the properties of the chemical or biological species detected, this is related to their size which is comparable to the size of the nanowires [116,117].It is possible to obtain a label-free and direct electronic read out by exploiting the electronically switchable application of semiconductor nanowires. The change in electrical responses offers a fascinating possibility of using sensors in readouts, alarms and LEDs etc. Field effect transistor (FET) mechanism can be incorporated into semiconductor nanowires for sensing applications [118-121]. The source and drain electrodes are bridged by placing the semiconducting nanowire on the gate dielectric. There are observed changes in carrier mobility as the nanowire surface resembles the bulk of the material used, this confirms the adsorption of the analyte onto the nanowire surface. Exploitation of this strategy it is possible to fabricate highly sensitive protein, pH, DNA and virus sensors.

5.3. Photonics

Semiconducting nanowires that have been engineered using III–V and II–VI direct band gap semiconductors can be employed in the construction of multicolour, nanophotonic systems that are electrically driven [122-130]. The anisotropic geometry of flat ended single crystal nanowires has the ability to behave as Fabry-Perot optical cavity by itself. The nanowires can function as proficient structures as light is constrained within the nanowire [126]. The engineering of nanoscale light emitting sources and detectors at different wavelengths can be done by varying the chemical composition of the different materials and junctions used in the synthesis of nanowires.

5.4. Solar cells

Solar cells can be fabricated using oriented arrays of dense, crystalline dye sensitized zinc oxide

Table 1. Methods for synthesis of nanowires and the mechanism involved.

Sr.no.	Synthesis Method	Process involved in synthesis	Ref. no.
1.	Vapour-Liquid Solid Growth method	Metal nanoclusters are employed as catalysts, which on decomposition in the presence of a gaseous precursor yields nanowires.	19,24,25
2.	Solution phase synthesis	A catalyst or molecular templates in the presence of a liquid precursor is employed. Additions of surfactants are required in certain cases.	26-30
3.	Electrodeposition in nanoporous templates	Physical templates are required with nanoporous membrane which aid in the growth of nanowires.	31-38
4.	Electrospinnig	Polymer solutions are driven through a syringe under high electric field to produce extremely long nanowires.	38-45
5.	Chemical etching	HF solution are employed to produce nanowire under vaccum thermal evaporation	46-48

Table 2. The various manipulation techniques employed with the advantages and disadvantages of the respective methods.

No.	Manipulation Methods	Application	Advantage	Disadvantage	Ref. no.
1.	Biomolecular Linkers	Recognition of biological molecules	Facilitates Lock-key recognition	Applicable only for biological molecules	72-80
2.	Electrical field assisted assembly	Assembly of nanowires to construct complex structure	-It can be scaled to wafer level, -Control over both placement & alignment	High control over the manipulating conditions are required.	81-92
3.	Magnetic assembly	Construction of magnetic assembly	-Energy minimization, -Precise positioning	ferromagnetic constituents are required.	93-100
4.	Holographic optical traps	Manipulation of wide range of materials	-Focused manipulation, -High spatial accuracy	Highly controlled environment is required.	101,102
5.	Langmuir Blodgett technique	Compression of nanowires	Ordered array are formed.	Limited to solid barrier to form ordered arrays.	103-108
6.	Surface tension based assembly	-In the patterning of hydrophilic & hydrophobic segment of nanowires, -Assembly of nanowires into permanetly bonded bundles	Modification of hydrophilic & hydrophobic segments are possible	The assembly is stable only in fluidic medium	109,110

nanowires [131]. The advantage of using nanowires are due to the direct electrical connections and the high internal surface enables the efficient and prompt carrier collection in the device, as opposed to thick films of zinc oxide. The charge transfer at the interfaces also had a considerable increase due to the use of single crystal planes, which accounts for 95% of the surface areas.

6. CONCLUSION

Nanowires are considered as attractive tools for various fabricating methods. There are numerous methods available for the synthesis and manipulation of the nanowires. The attractive strategies to assemble nanowires include controlled growth and directed assembly which are considered as bottom-up approaches. The uniqueness of nanowires are their physical and chemical properties which differ from their bulk counterparts. Hence, they are probable candidates for various optical, thermoelectrical, magnetic, electrical,sensors and biomedical devices. Implementing these techniques for the development of functional devices with higher variability, yield and tolerance is the challenge.

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