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To cite this version:

U Cvelbar. Towards large-scale plasma-assisted synthesis of nanowires. Journal of Physics D: Applied Physics, 2011, 44 (17), pp.174014. 10.1088/0022-3727/44/17/174014 . hal-00613275

HAL Id: hal-00613275

https://hal.science/hal-00613275v1

Submitted on 4 Aug 2011

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Submitted to J. Phys. D.: Appl. Phys. (Special Issue Plasma Nanoscience)

Towards large-scale plasma-assisted synthesis of nanowires

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Abstract

Large quantities of nanomaterial like nanowires are needed to overcome large market price of nanomaterial and make nanotechnology widely available for general public use and applications to numerous devices. Therefore, there is enormous need for new methods or routes for synthesis of those nanostructures. Here plasma technologies for synthesis of nanowires, nanotubes, nanoparticles or other nanostructures might play a key role in the near future. This paper presents a 3-dimensional problem of large-scale synthesis connected with the time, quantity and quality of nanostructures. Herein 4 different plasma methods for nanowire synthesis are presented in the contrast to other methods e.g. thermal processes, chemical vapor deposition or wet chemical processes. The pros and cons are discussed in detail for the case of two metal oxides: iron oxide and zinc oxide nanowires, which are important for many applications.

(Some figures in this article are in color only in the electronic version)

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1. Intoduction

With the development of new technologies, especially for semiconductor industry, a requirement for smaller size materials grew as fast as the size of applications decreased. The quest for a new material lead to nanosize materials, like nanotubes, nanowires, quantum dots, nanopyramids, nanopowders, etc., which are synthesized by numerous methods. Today we can basically make most types of nanosize material (e.g. oxides, sulfites, alloys, etc.) which can be of different sizes, shapes or even crystal structure. In most cases, synthesis processes cannot be well controlled or even more, they are not always reproducible due to many parameters which can influence synthesis reactions. Repeatability off course depends on the method and the synthesis system. And normally the synthesis is easier to control in small volumes, systems or reactors. Going to larger volumes and scales increases cost, process control problems & reproducibility as well as influences material quality. Therefore, the biggest problem is still large-scale & large-quantity production of nanosize materials.

The easiest shape of nanomaterials to synthesize in large-quantities is nano-sphere like material, e.g. different nanopowders or quantum dots. More exotic and difficult shapes are nanopyramids, nanoflowers, nanocones, etc., but at the same time they don't poses high values for general applications. More desired shape is nano-cylinder-like including nanowires, nanorods or nanotubes, which are alternative nanomaterials by function to nano-spheres, either for solar cells, batteries or other photochemical and electrochemical applications. In this paper we will focus only on nanowires, especially metal (iron and zinc) oxide nanowires, which found wide use as chemical sensors [1], optoelectronic devices [2], dye-solar cells [3], gas sensors [4], etc.

Metal oxide nanowires (NW), e.g. iron oxide can be synthesized on a large-scale thru many routes; either with wet chemical treatments (sol-gel mediated reactions [5-7], hydrothermal [8-9] or solvothermal processes [10]), thermal and/or gas decomposition [11-19], chemical vapor deposition (CVD) [20] and plasma-assisted methods [21]. The so-called wet chemical procedures which include sol-gel mediated reactions, hydrothermal processes or solvothermal processes and their variations are widely spread for synthesis of iron oxide or zinc oxide. However these processes are typically difficult to control on a nanosize level and yield rather small amounts of material as well as have relatively large synthesis time which can be hours long (Figure 1). Additionally, we have problems with impurities, reaction catalysts or surfactants, which need to be separated from synthesized nanowires and this represents in many cases a serious problem. Alternative to wet chemical procedures are thermal procedures which include also a gas decomposition typically on hot surfaces. In this group we can categorize also a flame synthesis [22], resistive heating [18], thermal oxidation [17,19,23] or hot surface gas mixture decomposition (e.g. decomposition of gas mixture CO_2, SO_2, NO_2, H_2O on 504-600°C heated Fe substrates [11] or decomposition of $Fe(CO)_5$ vapors on 300-400°C Si or glass substrates [15]). These thermal procedures yield rather sufficient amounts of NWs on surfaces which are pure without any impurities. Their growth can be well controlled, meaning that their morphology can also be well determinated during growth. Whereas the downturn of thermal processes are intermixed forms of metal oxides (e.g. $Fe_{1-x}O$, α-Fe_2O_3 and Fe_3O_4) and sometimes relatively large synthesis times hours long (Figure 1) [22,12]. However, some faster thermal growth methods have been demonstrated [18,22]. Generally, more time-efficient are normally CVD procedures which yield same amounts of material in much shorter periods, even below hours or tens of minutes. However, downside is a use of templates, NWs are in most cases

polycrystalline, processes are hard to control and tailoring NW shapes is difficult. One of efficient methods for such material productions is mixed method with the thermal/gas synthesis method and is called hot-wire or hot filament CVD [24,25].

Most of these stated methods unfortunately don't produce sufficient amounts of NWs in milligram or gram amounts which would help to overcome a large market value of NWs and consequential a wider use in applications. Here we need to find new ways to produce more NWs in shorter time periods which will take us less than one hour. The answer can be found in plasma-assisted synthesis methods, which can yield in some cases gram amounts [26,27], but there are still some drawbacks to the plasma technology, which need to be addressed. Generally, plasma-assisted methods can be divided into 4 routes for NW synthesis plus mixed routes which employ two or more methods. These methods can be used for synthesis of different NW types on different substrates or NW can be simply collected after the synthesis. To demonstrate applicability of different routes, we will concentrate only on iron oxide and zinc oxide NWs. Synthesis routes for iron oxide NW (e.g. α-Fe_2O_3) can be also compared with the routes for CuO_2, V_2O_5, Nb_2O_5 or ZnO with SnO_2 NW.

2. Fast plasma routes for synthesis

2.1 Plasma-enhanced chemical vapor deposition

Plasma-enhanced chemical vapor deposition (PECVD) is modified version of CVD which incorporates plasma and is used to deposit nanostructures including NWs from gas state (vapor) to solid state on a substrate. Chemical reactions involved in the process occur after creation of

plasma of the reacting gases with vapors. The schematic of the process is presented in Figure 2a, where we can see that the material, in our case metal M (Fe, Zn) or metal oxide, is evaporated or chemically sputtered from a target, interacts with plasma species or carrier gases and then is deposited from plasma to the substrate surface. Here is worth mentioning that when we have a physical sputtering of target material into plasma and deposition, the method should be called Plasma-enhanced physical vapor deposition. Unlike physical sputtering, in chemical sputtering, plasma ions react chemically with the target material and the so formed compound evaporates out thru one of several possible mechanisms.

With PECVD route is relatively easy to prepare ZnO NWs, but it seems much harder for iron oxide NWs. This is due to almost 3-times lower melting temperature of zinc and needed heat for vaporization compared to iron. There are almost no reports on PECVD synthesis of iron oxide nanowires. The only report worth mentioning is synthesis of pyramid-line Fe_3O_4 NWs by Gao [21], where they used CH_4 and N_2 for sputtering of hematite α-Fe_2O_3 into plasma, and consequently deposited onto Fe_2O_3 substrate.

Contrary to iron oxide NW, there are numerous reports on synthesis of ZnO by PECVD route. The PECVD synthesis of ZnO NWs can be performed in a single step thru self-assembly [28-30] or a two-step method [31]. The single step procedure reported by Iizuka *et al.* the zinc is sputtered from a zinc target, reacts with oxygen on the substrate to form ZnO nanostructures in O_2+Ar plasma [32,33]. Authors used a hollow-type magnetron (HTM) RF plasma source at a frequency of 13.56 MHz, where the sputtering rate of Zn is controlled by the biased voltage and the oxygen flow rate. On the other hand, the neutral oxygen atoms in plasma play a key role in oxidation of sputtered Zn and enable deposition of ZnO as NWs on SiO_2 substrate.[32] Experiments revile that the synthesized ZnO NWs are folded and bundled on the substrate.[33]

Whereas the alignment of NW depends on density of sputtered Zn atoms, seen in optical emission spectra (OES) from Zn/Ar spectral line intensity ratio.[33] The best line intensity ratio for NW synthesis is supposed to be Zn/Ar with a ratio 2/1. Then Zn can also be vaporized in air (N_2+O_2) plasma and deposited as ZnO NWs in order to get other shapes, e.g. hexagonal columns [34], or can be synthesized with other carrier gases e.g. H_2 [35].

The two step PECVD method for ZnO NW growth employ evaporation of solid zinc powder thru thermal heating by hollow-cathode discharge to over 1000°C in a protective Ar atmosphere, followed by oxidation with atomic oxygen, and condensation from the gaseous phase on the Si substrates.[36] In this case the surface temperature, oxygen radical flux, quantity of zinc powder and polarity are the most important factors for ZnO NW fabrication on the industrial scale. The two step method can be also separated into the nucleation and the growth step. Typical example of nucleation step is variation of oxygen content in a gas mixture with diethylzinc to create a precursor for zinc and oxygen on c-plane sapphire, Pt film on SiO_2/Si and Si (100) substrates. [31] Within the two step PECVD method, the special cases of ZnO NWs can be found, e.g ZnO/a-C core shell nanowires. [37]

2.2 Plasma-catalyst assisted

Plasma-catalyst assisted synthesis of NWs is performed when substrates are coated with a thin film or a layer of separate catalyst particles, which can lead to a metal oxide NW growth with catalyst particles at their tips or at the bottom (Figure 2b). [38-40] In many cases, the metal containing gas or the liquid with catalyst particles are not readily available for a deposition of

many metal oxides from plasma to the surface. Therefore, it is easier to start with either solid metal or metal oxide nanoparticles deposited in a nanometer layer, using sputtering or evaporation. These particles are then used as a nanometer-sized nuclei which catalyze reactions with plasma species or selectively attach certain building units supplied from plasma gas phase (Fig. 2b). As a result we get various nanostructures including NW. In this process, the size of nuclei (catalyst particles) or a catalyst layer thickness can determine the thickness of synthesized NWs on the sample surface. [38,41,42]

There are no reports on a synthesis of iron oxide nanowires with plasma-catalyst assisted route. Whereas for ZnO NW growth, there are some reports on such synthesis thru vapor-liquid-solid (VLS) mechanism. In this case, the gold (Au) nanoparticles are used as catalysts to grow ZnO nanostructures. However, there are some drawbacks to VLS growth, since it requires a very high temperature up to 925°C, so that Zn vapor can be dissolved into the Au catalyst to form an alloy droplet. After saturation, Zn precipitates out from the droplet and is oxidized as ZnO NWs grow.[43]

2.3 Plasma flight-thru

The plasma flight-thru method encircles various processes that can reshape or/and synthesize new NWs from particles, e.g. solid-liquid-solid (SLS), solid-vapor-solid (SVS), solid-liquid-vapor-solid (SLVS) growth mechanism during their time of flight thru plasma. In this method, particles passing thru gaseous plasma, typically with a free fall, can be either melted or vaporized and then interacted with plasma species for reshaping or tailoring into new types of NWs (Figure

2c). [44-46] This method works very well with non-thermal or even with thermal plasmas created in high-frequency discharges and at high gas pressures.

This method is relatively new for synthesis of NWs and has very high yields. However, there are no reports on synthesis of any iron oxide nanowires thru this route. The main problem could be the time iron or iron oxide particles spend inside the plasma during the flight thru. This time of flight should be much longer, so that we could get reshaping thru SVS phase, since iron or iron oxide need relatively high temperatures for melting or evaporation. Meaning, we need to apply more aggressive plasmas with higher densities of radicals or longer dwell time.

On contrary to the iron oxide, the ZnO NW flight thru synthesis has been reported in 5 papers by 3 different groups, which used either DC, RF or MW discharge. The group from Taiwan used DC plasma discharge operated at 70 kW and atm pressure, where Zn powders were fed into plasma jet thru carrier gas and subsequently underwent vaporization, oxidation and quench process. [44,47] They noticed that the ratio between carrier gases significantly influences the formation of shape and length of NWs. In the case of N_2 carrier gas, the addition of Ar helped reshaping the precursors-zinc powders of average size 10μm from spheres into elongated or NW-like structures, and less N_2 gas in plasma should favor formation of elongated rod/NW-like nanostructures. [44] Therefore different types of plasma gases can affect the nanopowders morphology. The same group has also concluded that the feeding powder impurities, input power and residence time of powder, influence the shape of nanoparticles including synthesis of tetrapot-like elongated structures. The ZnO NWs had higher length vs. diameter (l/d) ratio with increased input energy and longer residence time. [47]

Similar experiment was carried in RF discharge operating at 4 MHz and 30 kW, where also Ar and N_2 were used as forming gas and sheath gas, respectively. [48] The Zn powder

underwent vaporization, oxidation and growth process following the flowing gas in the reactor. In order to get ZnO, oxygen gas was injected into system together with sheath gas which reacted with Zn powder. They also demonstrated that different amount of oxygen, given at different flow rates can tailor the length and diameter of NW at the same conditions. The optimal flow rate for NW synthesis was found between 2.5 and 5 l/min. They concluded that the oxygen partial pressure and supersaturation of zinc vapor, controlled by feedstock rate of starting material, play key roles in a growth of ZnO NWs or nanorods (NR). [48]

The highest NW l/d dimension ratio and yield of ZnO NWs by plasma flight-thru method was achieved by Sunkara *et al*. They used 2.45 GHz MW plasma jet reactor at atm pressure and input power ranging from 300 W to 3 kW. [26,27] In their experiments, the sheath gas was air with flow rate 10-15 slpm. To sheath gas they added also a reforming gas H_2 (100 sccm) and O_2 (500 sccm). This method uses the same mechanism of particle reshaping as stated above, but has higher efficiency of synthesis, since 80-90% of all powders are reformed into NWs already after the first run. Because of this, it presents a large potential for future large scale industrial NW production, taking into account also the lowest energy consumption needed for reshaping Zn powders into ZnO NWs compared to other discharge sources.

2.4 Direct plasma synthesis

Direct plasma synthesis is process where NWs are grown after exposure to gaseous plasma, directly from the substrate with epitaxial growth - bottom up principle. The method is simple and doesn’t use any templates, catalysts or deposition from a vapor phase. In this method, typically metal foils or pieces are exposed to gaseous plasma radicals, which interact with metallic

surfaces, are dissolved into material, and consequentially create nanostructures on the surface. For SLS growth mechanism, the NWs grow on the top of melts. This SLS growth is typically used for a low-melting metals or metal oxides.[49] In this case, plasma or temperature liquefies the solid metal, on top of which at first stage solid metal-oxide nuclei are created, and in second stage NWs are grown.[49-51] The selective growth at the molten metal, sometimes referred as self-catalytic growth on molten phase occurs thru liquid-phase epitaxy. Whereas for the solid-solid (SS) phase, epitaxial NW growth occurs after a similar spontaneous nucleation, when nuclei are created due to the phase transformation of metal to metal oxide (Figure 2d). In this respect it resembles plasma-catalyst assisted growth, but from its own nuclei. With this method, NWs can be raised from the nuclei only when we overcome the initial surface instability created by plasma. At the same time this method enables precise tailoring of NW shapes and lengths by just controlling the plasma radical flux to the surface [52-57], the electrical conditions and the surface temperature [58,59]. And more, NWs grow directly on the metallic surfaces which can be directly employed for various applications without any additional procedure steps, what lowers production costs and problems. [60-62]

This route is rather new, and has been first reported in 2005 for the growth of Nb_2O_5 NWs on niobium foils. [63] Authors used radiofrequency ICP plasma, generated in O_2 gas at low gas pressures (50-200 Pa). Since then, the method was demonstrated also for other metal oxide NWs including hematite α-Fe_2O_3. [51,63,64] Authors found that single crystalline α-Fe_2O_3 NWs array growth can be controlled by the flux and the dose of neutral oxygen atoms and oxygen ions to the surface.[65] Since atoms and ions heat the surface thru recombination processes, the released heat can be used to overcome surface temperature of 570°C for Fe to undergo spontaneous nucleation to hematite phase α-Fe_2O_3. [64] This can be effectively achieved also by

controlling the electrical conditions on iron surfaces exposed to reactive oxygen plasma.[58] After nuclei are created, the surface temperature need to be controlled, since increase in temperature can result in different nanostructures, e.g. α-Fe_2O_3 nanobelt structures, due to increased mobility of atoms, or even absents of any nanostructures.[64] Therefore the growth of NWs can be only done in narrow well defined temperature range. Although the proper surface temperature is required for NW growth, it is not the most important growth parameter. The most important is the flux of neutral atoms and ions, which supports growth "supply and demand" and can tailor the shape, thickness and length of NWs which are erected from nuclei.[58,64,65]

Conversely, there are no reports of such growth for ZnO NW. This is probably due to low heat evaporation energy needed for sublimation of zinc in vacuum, where zinc leaves surface into gaseous plasma during processing before the stable ZnO nuclei can be created. For this case SLS growth mechanism should be applied.

2.5 Mixed plasma routes

Mixed plasma routes are methods which combine two or more of stated NW synthesis routes. The typical example of such method would be synthesis of NWs with catalytic particles mixed together with other metallic particles in plasma flight-thru. Here the catalytic particles would represent the nucleation cores on which the other vaporized metallic particles could recombine into NWs from gaseous phase. Although there are no reports on such synthesis of zinc oxide or iron oxide NWs, this method can be found in reports for synthesis of other NWs or nanotubes, including CNT. [66-69]

As a mixed plasma route we could also classify mixed PECVD and plasma flight-thru route where Zn powders are deposited into quartz tube which is feed with O_2 gas and a swirled gas N_2+O_2 (air) which blows particles into MW plasma torch. These particles are then evaporated, reformed and deposited in colder region of quartz tube as ZnO NWs. [70,71]

3. 3 parameters for large-scale synthesis of nanowires

3.1 Time

The time is important parameter when we look for the large-scale nanomaterial synthesis, but depends on the material that we would like to synthesize. Before we saw that some plasma routes are not useful for synthesis of some nanomaterials or have not yet been developed. And more these synthesis routes predominantly depend on material which is being synthesized.

If we concentrate on synthesis of iron oxide nanowires or nanorods, then we can see that there are no reports on plasma synthesis by flight-thru or by plasma-assisted catalyst support, which is used for many NWs (Figure 3). On the other hand we have some alternative methods such as Pulsed laser deposition (PLD), which takes 60 to 140 minutes to synthesize exotic ε-Fe_2O_3 NW. [72] Better process efficiency can be found in some thermal routes such as rapid flame synthesis, which can take about minimum 20 to 30 minutes [20] or resistive heating with only a couple of minutes [18]. Otherwise thermal processes over different sub-routes can generally take rather long time periods with anything between 20 min to 12 h or a couple of days. [12,13,73,74] The most time-efficient process reported is direct plasma synthesis during the synthesis of α-Fe_2O_3

NWs. This process takes only several minutes, and produces large amounts of NWs (Figure 3). Better efficiency of this plasma process compared to thermal processes is somehow logical, since plasma uses already dissociated molecules into atoms or ions which readily interact with surfaces without any intermediate states like in thermal gas-surface interactions. Result of this is better time-efficiency, since no molecule sticking, adsorption and dissociation due to increased temperature is needed. This better time-efficiency can be found also for plasma-enhanced chemical vapor deposition (PECVD) compared to standard CVD processes. The PECVD can be even 10-times more time-efficient in respect to CVD. Rather large variation of time required for synthesis is seen in the wet chemical processes such as hydrothermal or solvothermal. These processes take a couple of hours or even days, and depend on too many parameters and step-operations. Based on distribution of all reported syntheses for iron oxide NWs seen in Figure 3, the least time-efficient is gas decomposition method, which can take several days. [15,75]

For the zinc oxide NW/NRs, the reports are displayed in Figure 4. The most time-efficient plasma synthesis process is flight-thru method, where Zn or zinc oxide particles are reformed when passing thru plasma. This process normally takes less than a second, and has been reported for the time periods from 1.7×10^{-4} to 5×10^{-3} min.[26,27,44,47,48] Very fast is also combination of PECVD and plasma flight-thru, where NWs are synthesized in only one second (1.7×10^{-2} min). [70,71] This method is followed by direct plasma synthesis with several tens of seconds, but the slowest is PECVD process, which takes more than 10 min. [32-37] And more all shown plasma cases are several orders of magnitude faster then thermal, wet chemical and gas decomposition processes (not shown in Figure 4), and therefore more promising for industrial scale-up.

3.2 Quantity

The time-efficiency is important for a large-scale synthesis, but it needs to be correlated with the quantity of synthesized material. Processes that are time-efficient, but yield small amounts of material are generally not very usefully, except for specific applications. Therefore, we need to look for fast and high-yield routes.

In Figure 3 we can see that plasma processing is superior to gas decomposition, hydrothermal and solvothermal processes as well as to CVD and PLD processes. The highest quantities of iron oxides are reported for direct plasma synthesis with 5×10^{-5} g/min of α-Fe_2O_3 NWs. [64,65] PECVD method doesn't yield high quantities of iron oxide NWs to be adequate for industrial use. The maximum quantity of pyramid-like Fe_3O_4 NWs reported for PECVD was 8.3×10^{-8} g/min.[21] Therefore even PLD and CVD processes yield higher quantities, 6×10^{-6} g/min and 1×10^{-4} g/min, respectively. [72,20] The only competitive process to direct plasma synthesis is thermal, where the highest quantity of synthesized α-Fe_2O_3 NWs reported was about 5×10^{-5} g/min. [18,19,20]

Although iron oxide NW have never been synthesized by plasma flight-thru method, far the best results for the large-quantity of ZnO NWs have been achieved by this method (Figure 4). With plasma flight-thru we can synthesize several tens of grams per minute. More precisely, the best results feature 20 to 50 g/min, which is enough to make NWs widely available for everyday use.[26,27,44,47,48] High plasma flight-thru yields are followed by direct plasma synthesis on foils by maximum 6×10^{-4} g/min. Much smaller amounts of ZnO NWs can be synthesized by mixed methods [70,71] or by large selection of PECVD methods [32-37]. Results are even more discouraging for other methods, such as wet chemical procedures.

3.3 Quality

Additional requirement for a successful large-scale synthesis is nanomaterial quality, which encompasses the dimensions and shape of material, crystallinity, special crystallographic features, surface density, electrical and mechanical properties, purity as well as the process control. In many cases, even when time and quantity are appropriate for a large-scale manufacturing of NWs, it can happen that the quality of synthesized material is not good enough.

One of key points is purity in shape and dimension of synthesized NWs featured by ratio between length and diameter (l/d) of NWs. These two are especially important for plasma flight-thru route, since most of material that passes thru plasma doesn't reform into NWs, but remains in particle shape or starts reforming into tripod or tetrapod NWs at higher temperatures [47,48]. Such NWs are in many cases not desirable and need to be separated from other NWs. Whereas at too low plasma temperatures or higher amounts of feeding powder, the densities of plasma species are not high enough to reform all passing material. The result is mixed product of nanoparticles and NWs which are typically sticked together and inseparable (Figure 5a). The optimal yield vs. quality for ZnO NWs was reported for plasma flight-thru method with 30 kW RF thermal torch operating at atmospheric pressure, which gave 20 g/min with l/d ratio 14. In this case, increase of feeding powder to 37 and 53 g/min, lowered l/d ratio to 8 and 2, respectively. [48] Better reformation of NWs was achieved by Sunkara's group in 1.7 kW MW plasma. Their process yield 20 g/min at l/d ratio of 50, while the reformation of powder to NWs during the first run was already 80-90%. [26]

Better purity of material in single NWs or NW arrays can be achieved in plasmas, compared to other synthesis processes. Thermal routes normally produce different types of metal oxides and not only the desired ones. While the wet chemical routes or gas decomposition contain impurities which are residuals, side products of synthesis or foreign atoms build into NWs. These impurities significantly affect properties of synthesized material. In thermal oxidation of Fe foil the thick basal layer contains also other iron oxide phases e.g. γ-Fe_2O_3 and Fe_3O_4, beside α-Fe_2O_3 NWs. At the same time we get only α-Fe_2O_3 NWs with thin basal layer of α-Fe_2O_3 after direct plasma synthesis (Figure 5b). In application as electrode such thermally prepared sample will not be useful, since a thick iron oxide layer with multiple iron oxide phases will act as a trap for passing electrons. While in the case of plasma synthesized NW array, electrons will easily pass thru the layer without any significant losses. Additional advantage of plasma synthesized NWs is also so-called lattice superstructure, which is in α-Fe_2O_3 NWs featured by periodic oxygen vacancy planes (Figure 6a). [64,76] These planes are probably created due to surface-thermal stress initiated during fast epitaxial growth. And more these structures give nanowires p/n-type properties without any doping, and enable more efficient charge transport along the wires. On contrary there are no such structures observed on thermally prepared samples (Figure 6b), when the NW grow slowly and in thermal equilibrium. On the other hand this doesn't necessary hold for some α-Fe_2O_3 NWs made with fast thermal flame synthesis.

For many applications, single crystallinity of NWs is desirable. Therefore we aim to create only single-crystalline NWs during the large-scale plasma synthesis. This is hard to achieve especially for PECVD and plasma-catalyst assisted processes, where typically long winding wires are composed of polycrystalline particles or catalyst atoms which are incorporated into the

NW structure. The single-crystalline NWs are also very often converted to polycrystalline after subsequent annealing process in various gas mixtures during synthesis process.

Last but not the least the shape control of NWs is important, not only l/d ratio, but the morphology of the wire. Changing plasma parameters during the growth enables us to tailor NW in different ways. The NWs can be thicken or narrowed during the growth or widen at the bottom, etc. Tailoring of NWs can be achieved by controlling the flux of neutral atoms or ions to the treated surface. If the incoming flux of ions and the ion energy is increased during the synthesis, then the basal diameter of NWs widens, making them a tip-like and appropriate for application as AFM tips. However in order to control the shape as well as the surface density of synthesized NW, we need to fully control plasma parameters. This is a ground requirement for transfer of nanotechnology to the industrial scale. Additionally plasma parameter control enables optimization of synthesis, since we can link plasma species such as neutral atoms, ions and metastables and their fluxes to surface to growth dynamics. Nevertheless there is still big gap of accessible measurement techniques to control these plasma species. In recent years many groups have successfully applied the new characterization tools for determination of plasma parameters; e.g. catalytic probes [77-81] or LIF [56,82,83] for measuring neutral atom densities, and Langmuir probes [84,85] for charged species. And more, even simple optical emission spectroscopy is becoming more widely accessible and used for monitoring of plasma processes. [86-88] Therefore, we need use these tools to control plasma parameters in order to optimize plasma synthesis, and control more efficiently processing time, quantity and quality of NWs. Consequently by controlling and optimizing processes we can optimize energy used for synthesis. The process energy efficiency will play important role in future selection of synthesis

route, where we will have to look at input energy per synthesize gram of NWs. And here, plasma routes have certainly advantages over the energy-consuming competitive thermal processes.

4. Concluding remarks and future challenges

Plasma routes represent alternative which will replace the standard processes such as thermal, hydrothermal, solvothermal, CVD or gas decomposition processes used for synthesis of NWs. Not only they are faster, but also yield significant gram per minute quantities of NWs. Today, the best results are obtained by plasma flight-thru method with 20 g/min, where powder is passing thru plasma and is reformed. The NWs are typically collected at the bottom of plasma reactor. When we require NWs on the top of sample, then the fastest large-quantity method to grow them is direct plasma synthesis with approx. 10^{-4} g/min. Additional benefit of NW synthesis is production of single-crystalline, pure NWs without any atomic impurities and with the lattice superstructure. Beside this, in plasma synthesis process is relatively easy to control by monitoring plasma parameters which can determine other NW features e.g. l/d ratio and shape.

For development and optimization of the large-scale NW manufacturing, we need to address 6 future challenges. These challenges are:

1) Understanding better the growth origin of NWs and the role of plasma parameters;
2) Development of the theory that describes NW growth;
3) Further optimization and exploration of plasma flight-thru and direct plasma synthesis process;

4) Exploration of new plasma routes for the synthesis of other NW types (other metallic oxides, sulfites, etc.);
5) Development and implementation of the tools for control and monitoring of plasma parameters during synthesis;
6) Improvement of the process energy efficiency [89] with the maximization of input energy per synthesized quantity of nanowires at better material quality.

Acknowledgement

The author gratefully acknowledges Slovenian Research Agency (ARRS) for financial support thru US-SLO bilateral collaboration grant and national project research grant.

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Figure captions

Fig.1: Schematic representation of methods for the large-scale synthesis of nanowires on the time scale. (Colour online.)

Fig. 2: Schematics representation of NWs plasma synthesis process with a) PECVD, b) plasma-catalyst assisted, c) plasma flight-thru and d) direct plasma synthesis route. (Colour online.)

Fig.3: Time required for synthesis of iron oxide NWs vs. synthesized quantity for all reported plasma-assisted syntheses in comparison with other methods e.g. thermal, gas decomposition, PLD, CVD and hydrothermal/solvothermal. (Marked areas denote synthesis results for specific method, but can always be stretched towards smaller quantities.) (Colour online.)

Fig.4: Time required for synthesis of ZnO NWs vs. synthesized quantity for all reported plasma-assisted syntheses. (Colour online.)

Fig.5: SEM images of a) ZnO NW synthesized from Zn powder by plasma flight-thru method in 1.7kW MW system, and b) α-Fe2O3 NW synthesized by direct plasma synthesis on Fe substrate in 1kW RF ICP low pressure plasma system.

Fig.6: (a) HRTEM image of a typical (direct) plasma-grown α-Fe_2O_3 NW showing an edge-on view of several ordered oxygen vacancy planes (indicated by arrows). (b) FFT of the images shown in (a) with indexing consistent with the [001] zone axis. An array of superlattice spots originating from the order oxygen vacancy planes is visible in addition to the α-Fe_2O_3 spots (indexed spots). The distance between the superlattice spots matches that of the 1/10 (3-30) planes. (c) HRTEM image of a typical thermally-grown α-Fe_2O_3 NW. Its FFT shown in (d) does not reveal any superlattice pattern. (Contributed by J. Jasinski, UofL)

Figures

Fig.1

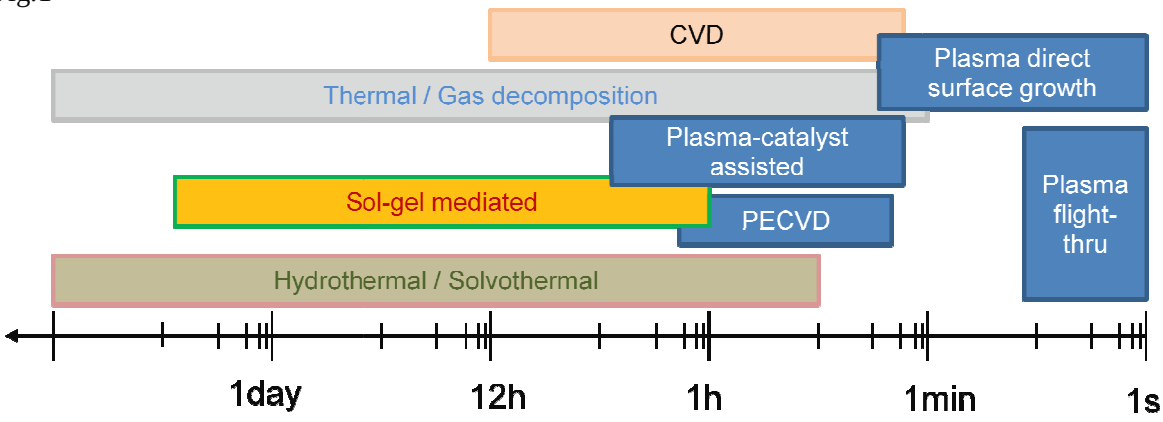


Fig.2

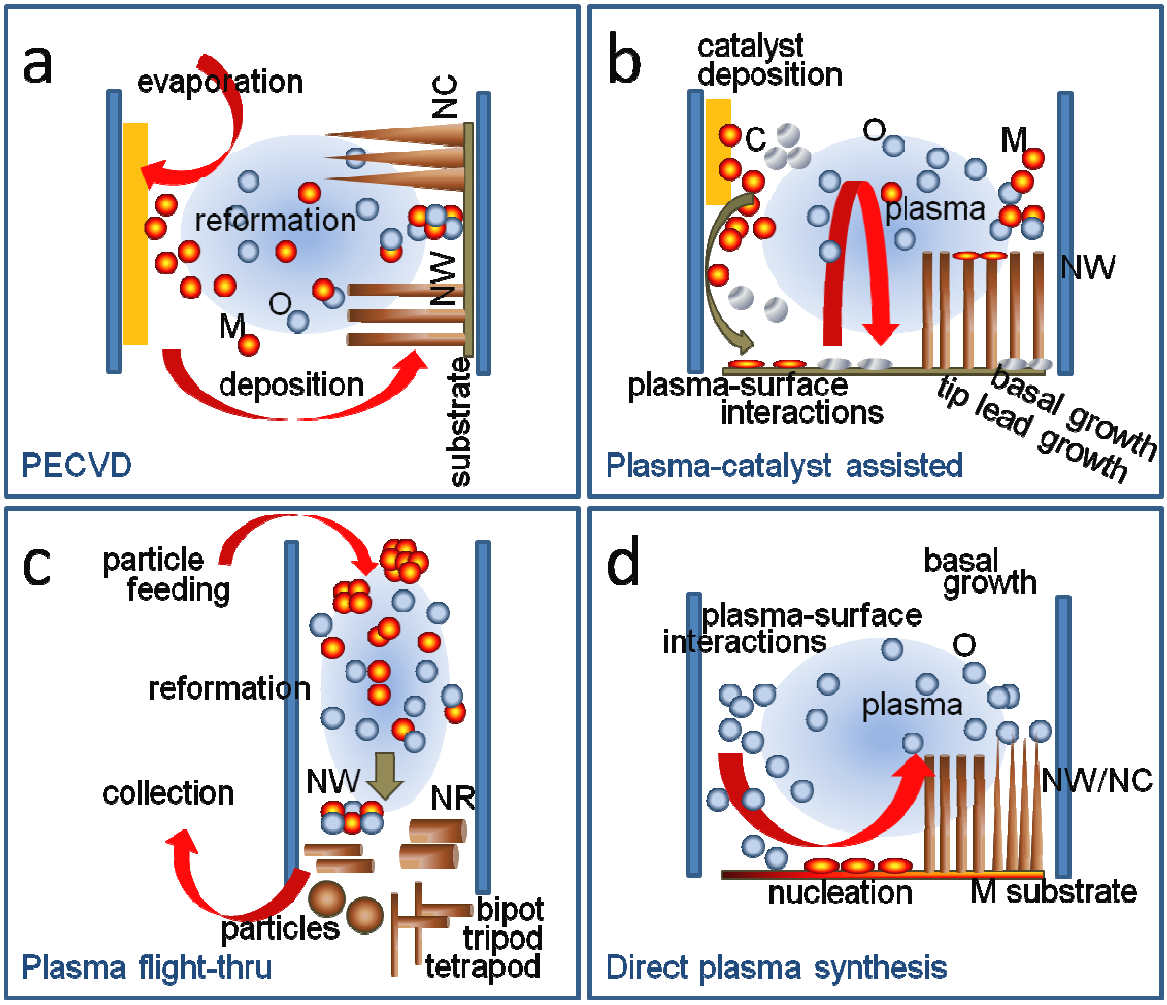


Fig. 3

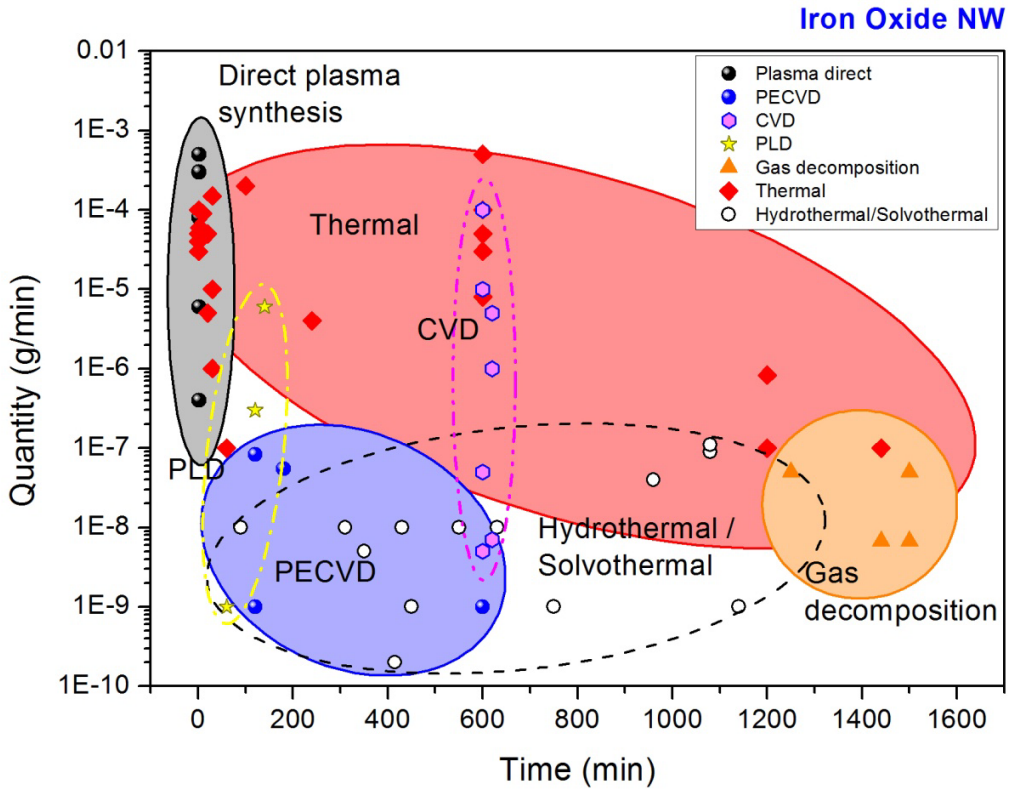

Iron Oxide NW
Direct plasma synthesis
Thermal
CVD
PLD
PECVD
Hydrothermal / Solvothermal
Gas decomposition
Plasma direct
PECVD
CVD
PLD
Gas decomposition
Thermal
Hydrothermal/Solvothermal
Quantity (g/min)
Time (min)
0.01
1E-3
1E-4
1E-5
1E-6
1E-7
1E-8
1E-9
1E-10
0
200
400
600
800
1000
1200
1400
1600

Fig. 4

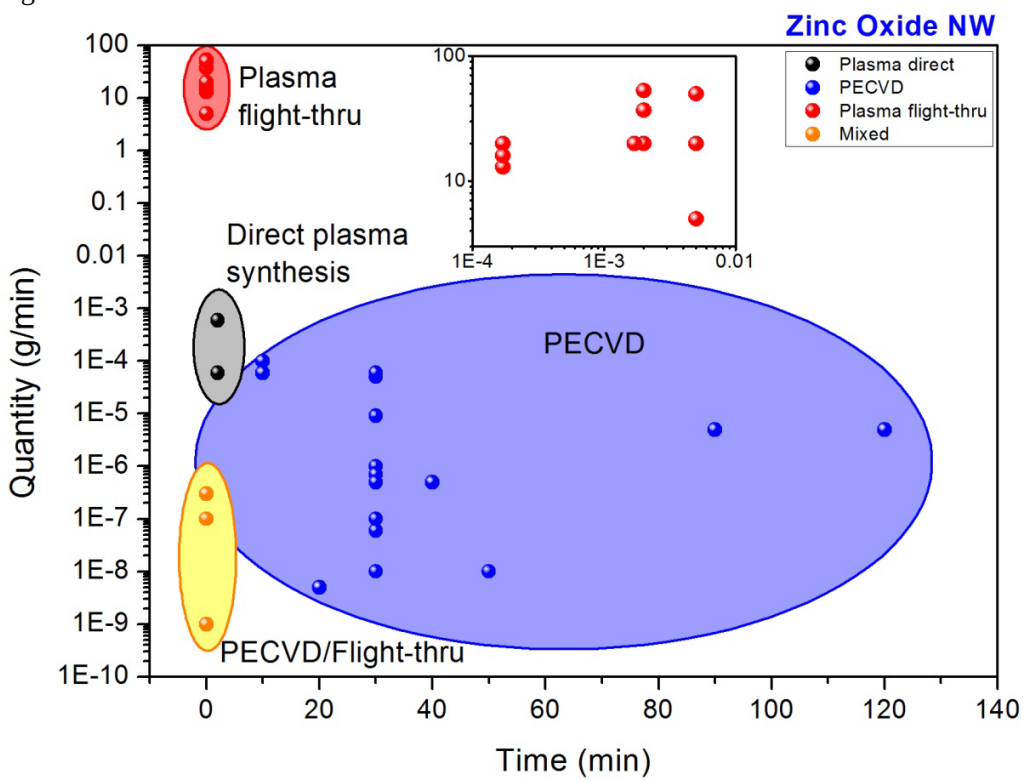

Zinc Oxide NW
Plasma flight-thru
Direct plasma synthesis
PECVD
PECVD/Flight-thru
Plasma direct
PECVD
Plasma flight-thru
Mixed
Quantity (g/min)
Time (min)
100
10
1
0.1
0.01
1E-3
1E-4
1E-5
1E-6
1E-7
1E-8
1E-9
1E-10
0
20
40
60
80
100
120
140
1E-4
1E-3
0.01

Fig.5

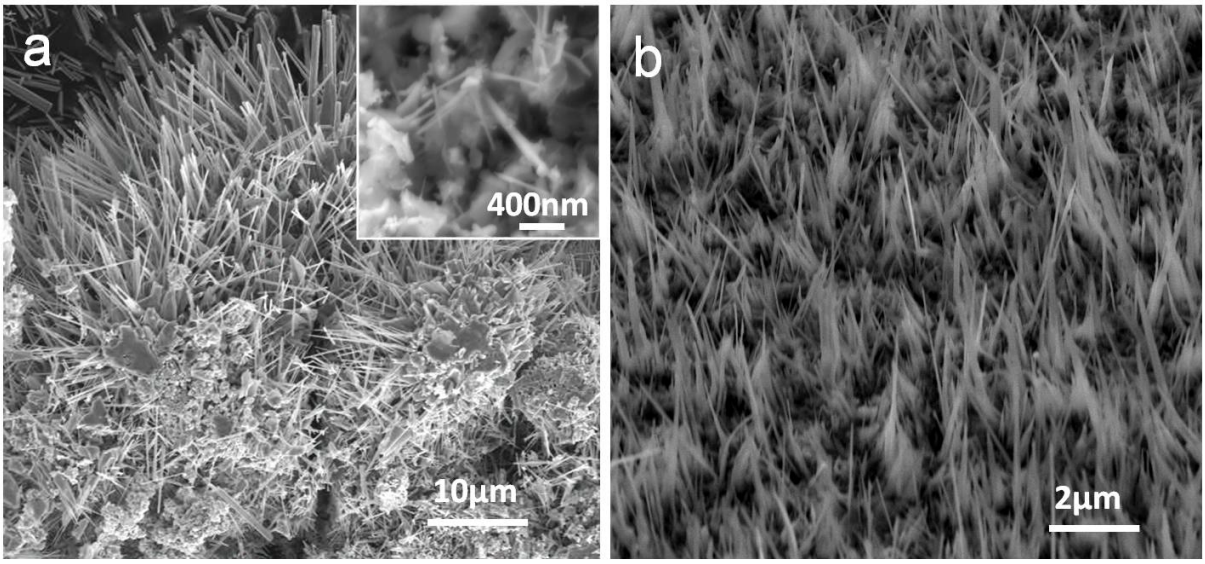
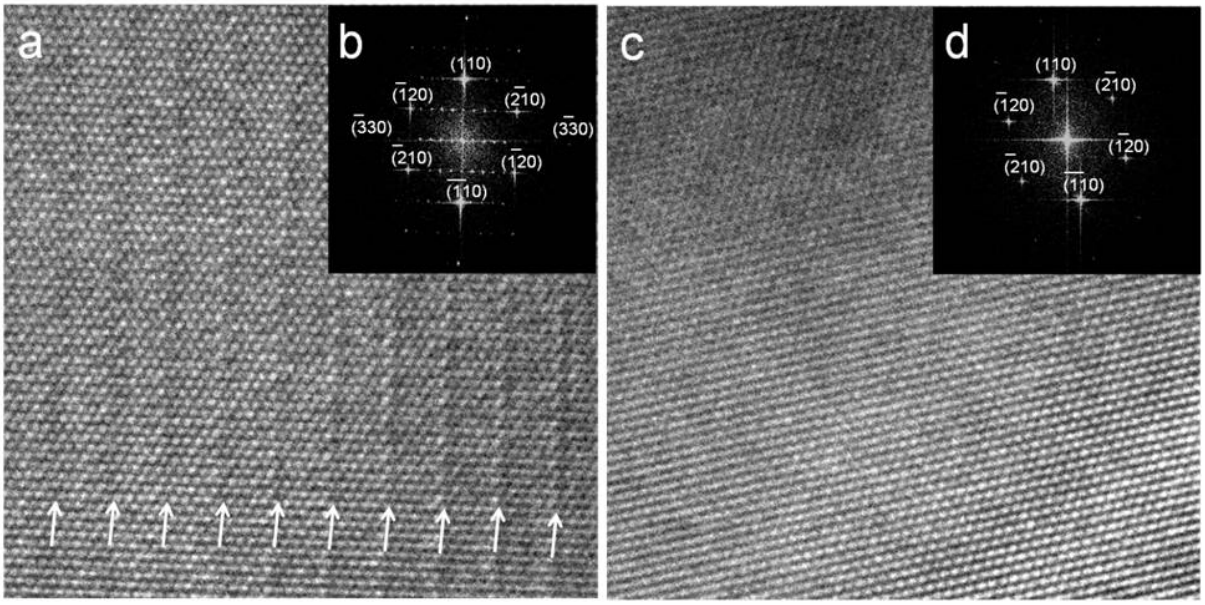

a
400nm
10μm
b
2μm

Fig.6


a
b
(110)
(1̄20)
(2̄10)
(3̄30)
(330)
(2̄10)
(1̄20)
(1̄10)
c
d
(110)
(2̄10)
(1̄20)
(1̄20)
(2̄10)
(1̄10)