Laser Processing

and

Chemical Vapor Deposition

(CVD)

Laboratories

Laser Processing

Laser Floating Zone (LFZ)

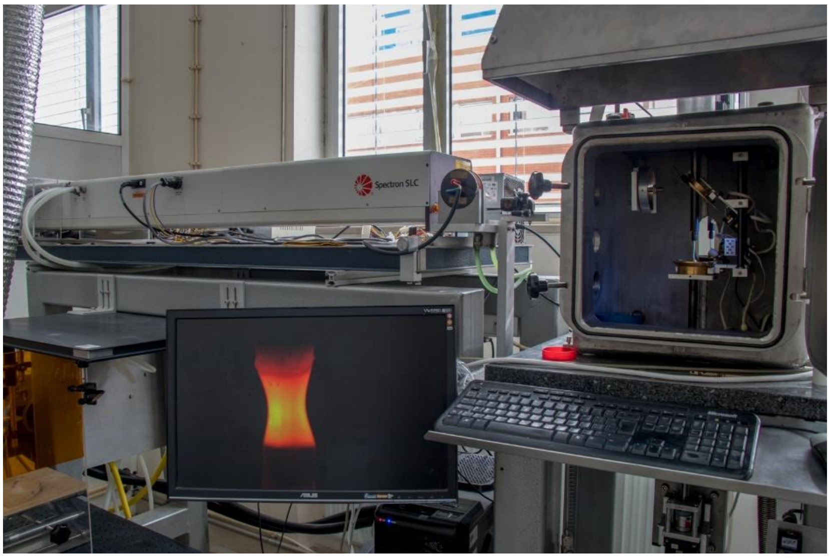
The LFZ technique allows growing materials with very high melting temperature, due to the narrow focus that the laser beam provides. It enables the growth of single-crystals, highly textured polycrystalline materials and amorphous materials. The absence of crucible in LFZ avoids the usual contaminations due to reactions of the molten materials with the crucible walls. The as-grown materials exhibit a rod-like (fibre) shape.

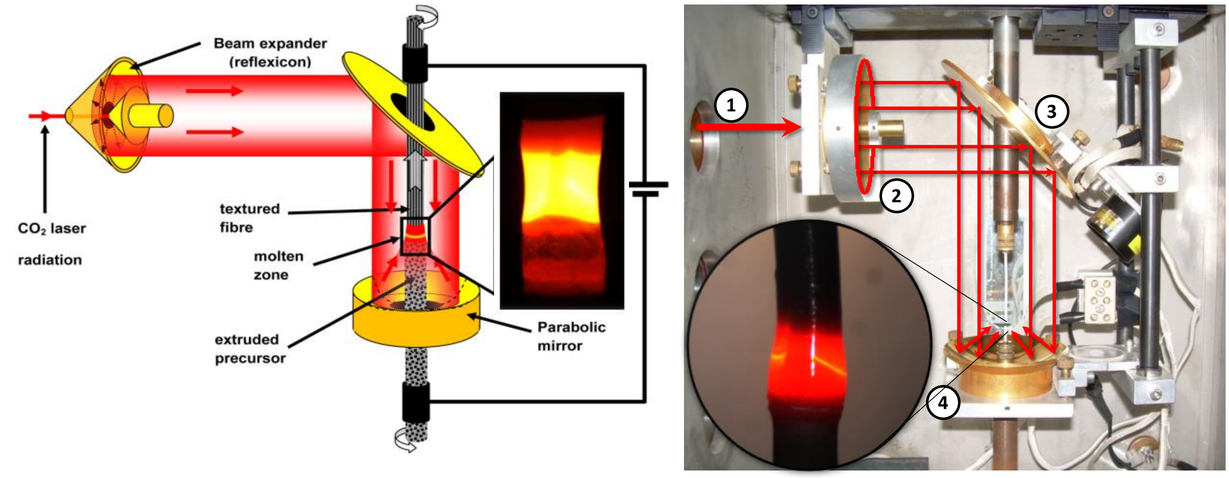
The LFZ equipment includes a laser set-up; a growth chamber; a homemade monitoring system (laser parameters, pulling rate and rotation speed) assisted by real time image acquisition.

The laser set-up comprises a continuous DC pumped 200 W CO_2 laser (Spectron SLC, λ = 10.6 µm) with a gaussian profile featuring a Reflaxicon optical arrangement. A homemade program based in a commercial software (Labview®, National Instruments®) is used to monitor and control the LFZ growth system.

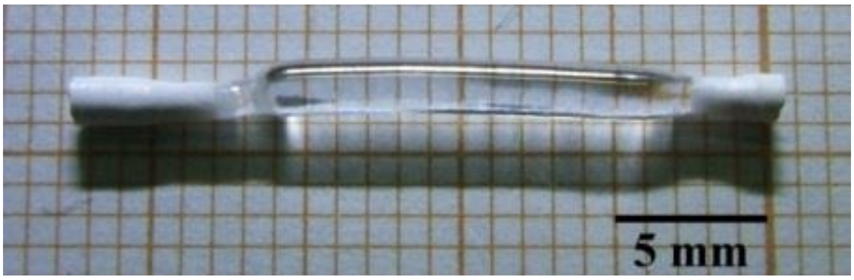
The growth chamber is sealed, enabling atmosphere controlled processing. Apart from air, typical processing gases are Argon, Nitrogen, forming gas (H2/N2), allowing to vary the oxygen partial pressure.

New developments include the growth with an external electrical field, termed Electrically Assisted Laser Floating Zone (EALFZ), while the growth using an external magnetic field it is under patent request.

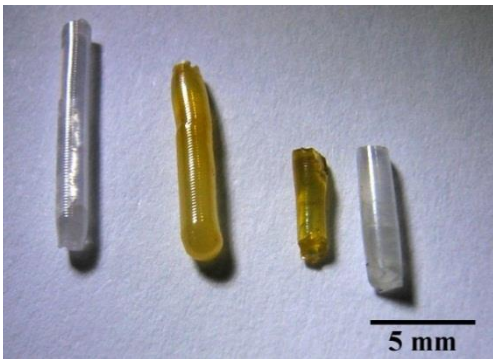



Beam expander
(reflexicon)
CO_2 laser
radiation
textured
fibre
molten
zone
extruded
precursor
Parabolic
mirror
1
2
3
4

Single Crystals

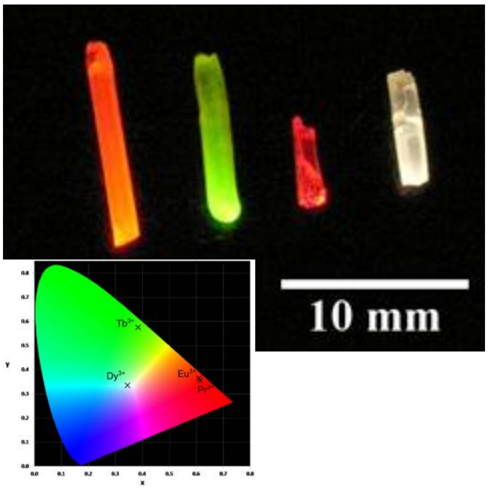


ZrO2 Single Crystal



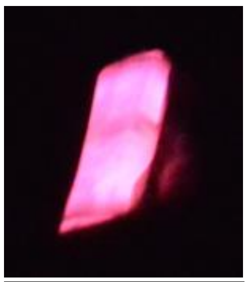
Rare earth doped ZrO2 single crystals

http://dx.doi.org/10.1039/C1JM12564H
http://dx.doi.org/10.1063/1.3527914

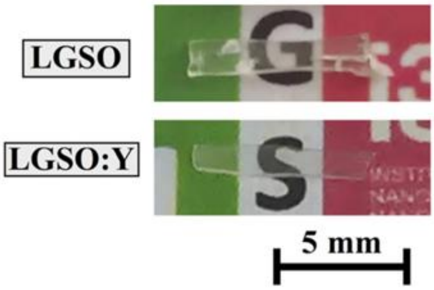


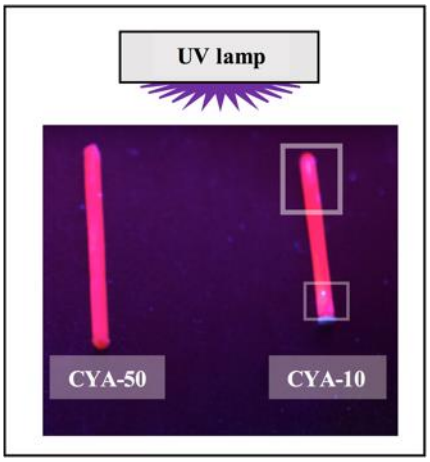
Oxyorthosilicates

Gd_2SiO_5, Gadolinium Oxyorthosilicate (GSO) grown by LFZ



GSO under UV irradiation



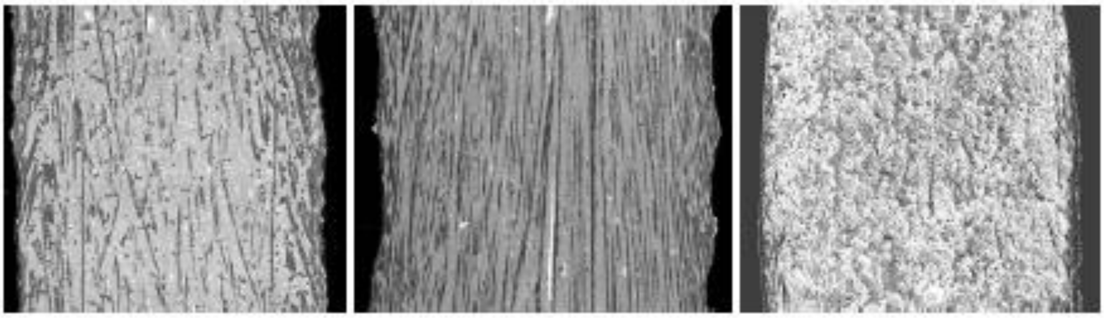


LGSO and LGSO:Y: $(Lu_{0.3}Gd_{0.7})_2SiO_5$ and $(Lu_{0.3}Gd_{0.7})_2SiO_5:Y^{3+}$ (5at%)

CYA derived deep red phosphors: $CaYAlO_4:Y_4Al_2O_9:CaYAl_3O_7:Mn^{4+}$

https://doi.org/10.1016/j.materresbull.2018.04.058
https://doi.org/10.1364/OME.7.000868

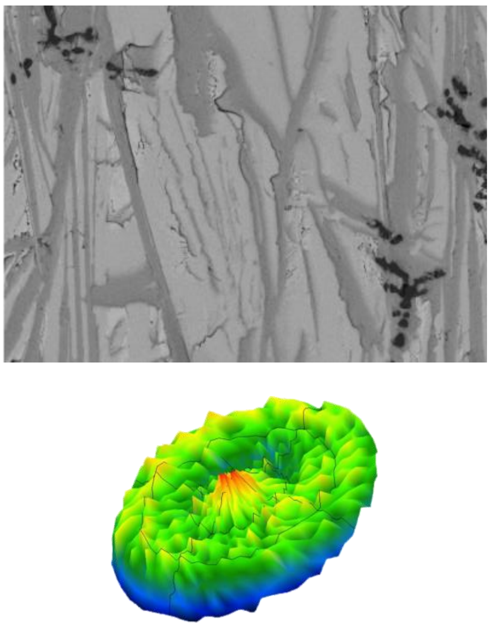
Superconductors & Thermoeletrics



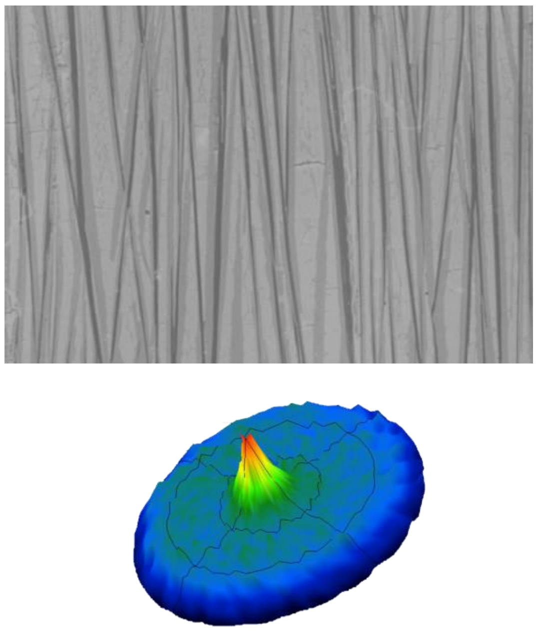
Without current Direct current Reverse current

Superconductors (Bi-Sr-Ca-Cu-O) grown by LFZ (without current) and by EALFZ (with direct and reverse current)

http://dx.doi.org/10.1021/cg5015972
http://dx.doi.org/10.1088/0953-2048/17/4/008



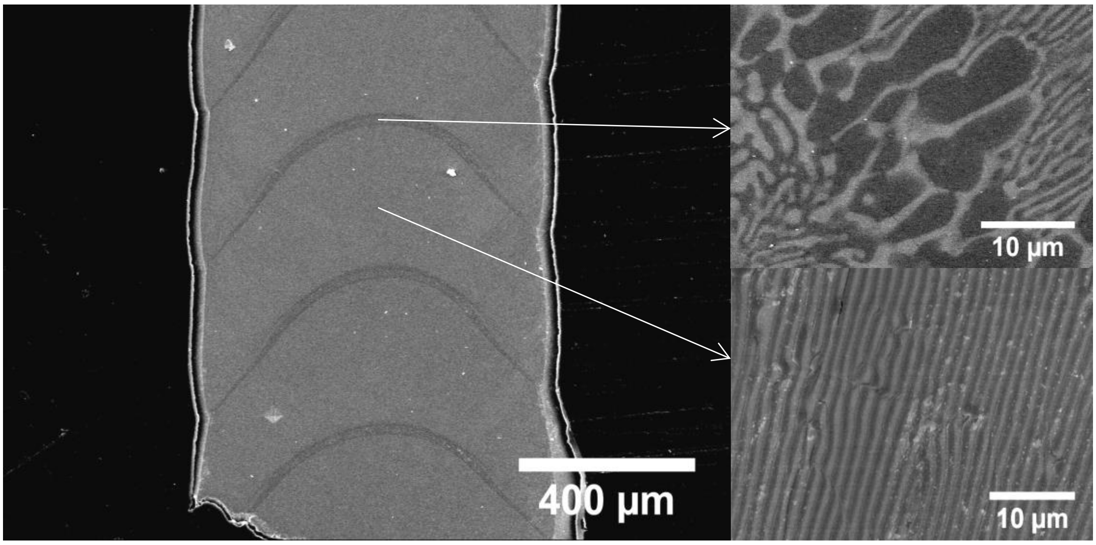
Thermoelectric materials (Bi-Sr-Co-O) grown by LFZ

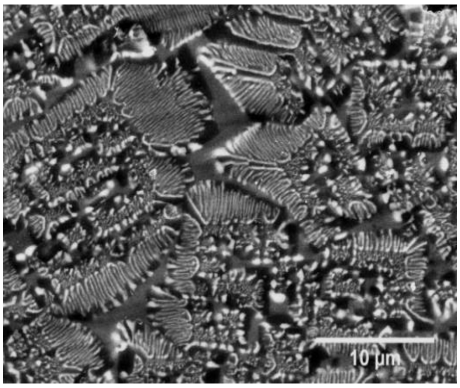


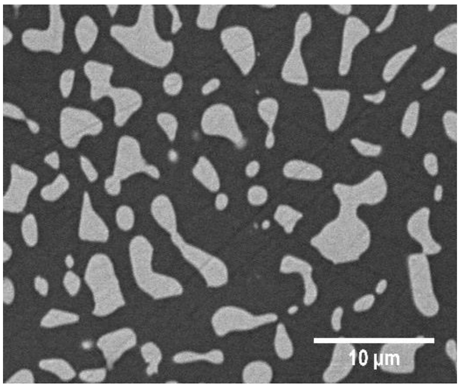
Thermoelectric (Bi-Sr-Co-O) grown by EALFZ

http://dx.doi.org/10.1016/j.matdes.2015.03.005
http://dx.doi.org/10.1016/j.matlet.2012.05.131

Eutectic Oxides





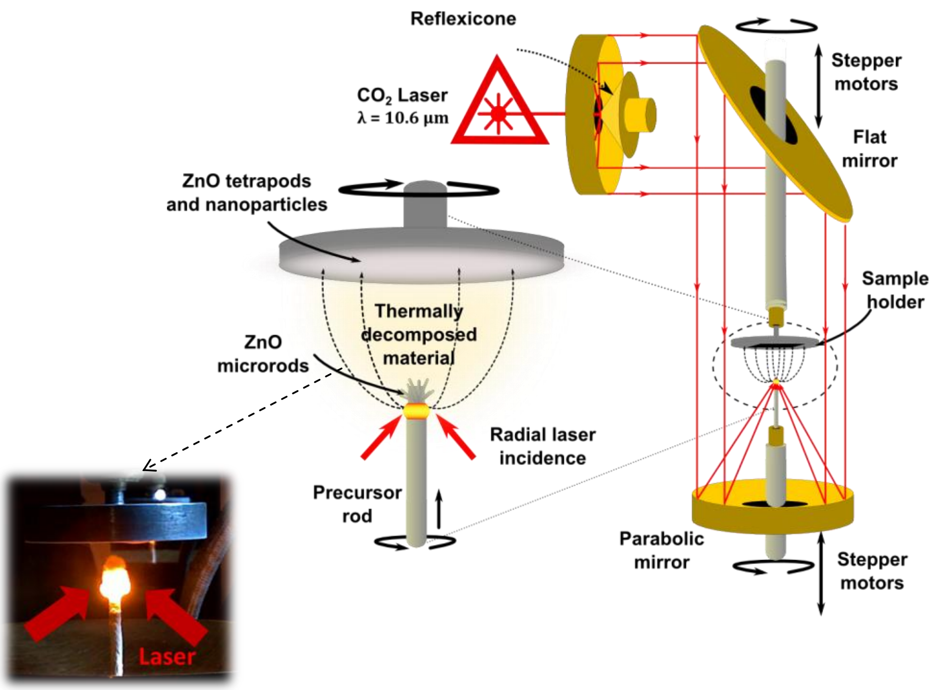


Eutectic Oxides (ZrO_2-$BaZrO_3$) grown by LFZ

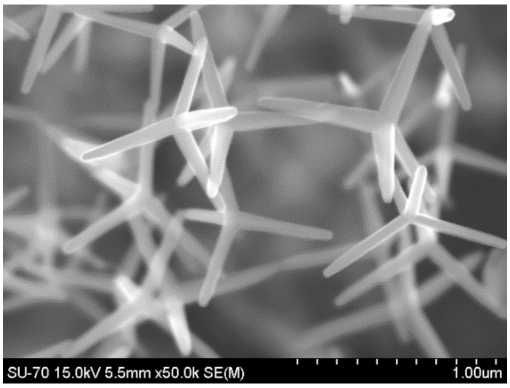
http://dx.doi.org/10.1016/j.matdes.2014.04.050
http://dx.doi.org/10.1016/j.ssi.2013.12.033
http://dx.doi.org/10.1016/j.jeurceramsoc.2012.09.032

Laser-assisted flow deposition (LAFD)

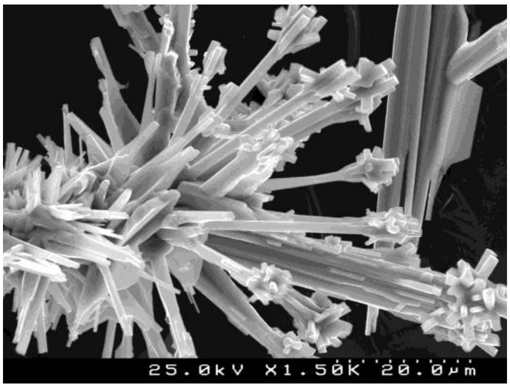
LAFD is a vapour-based method that derives from the LFZ technique. This technique proved to be efficient in the production of ZnO micro/nanocrystals with different morphologies and with a very high crystalline and optical quality. This new process allows high yield of ZnO production, showing great prospects for scalable applications. Moreover, this approach can be employed in the synthesis of other metal oxides (namely SnO_2), as well as composite nanostructures structures in a single processing step (e.g. Ag-decorated ZnO)



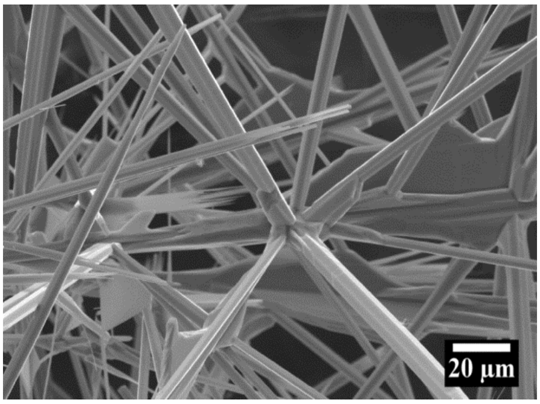
ZnO & SnO_2 Crystals



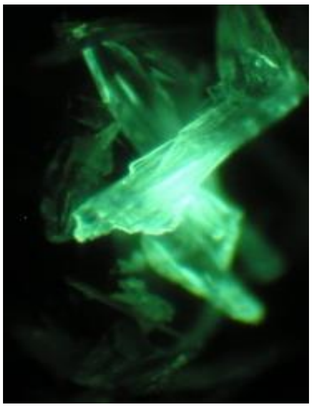
ZnO synthetized by LAFD



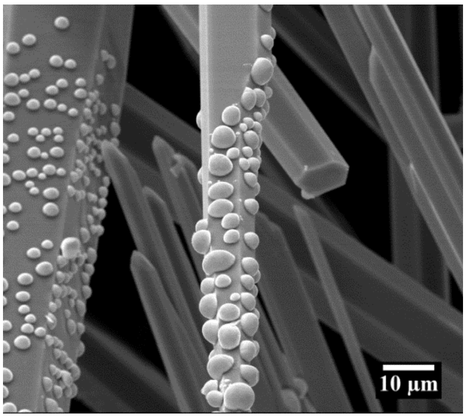
ZnO/Ag synthetized by LAFD



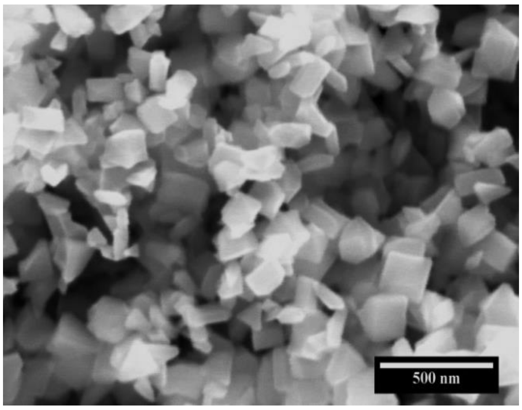
ZnO microrods



ZnO microrods under 325 nm excitation



Ag-decorated ZnO microrods

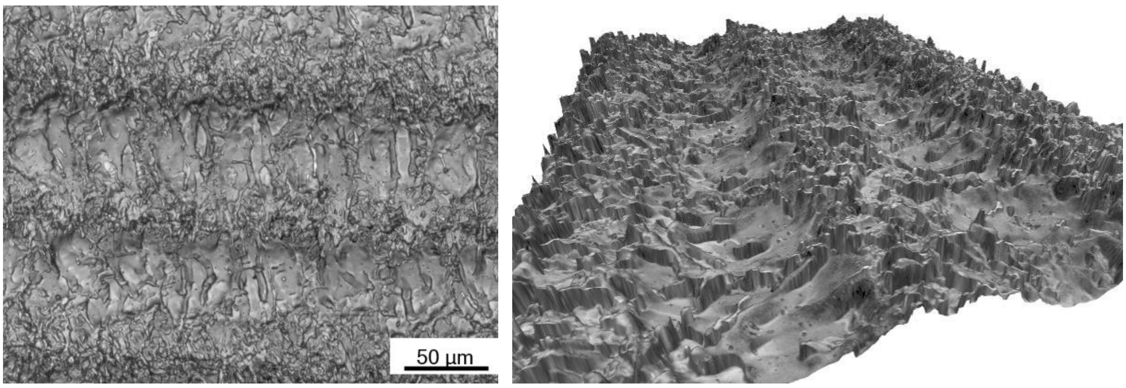


SnO_2

http://dx.doi.org/10.1016/j.matchemphys.2016.04.033
http://dx.doi.org/10.1016/j.tsf.2011.10.208; http://dx.doi.org/10.1039/c4cp06114d

Scanned beam Pulsed Nd:YAG laser

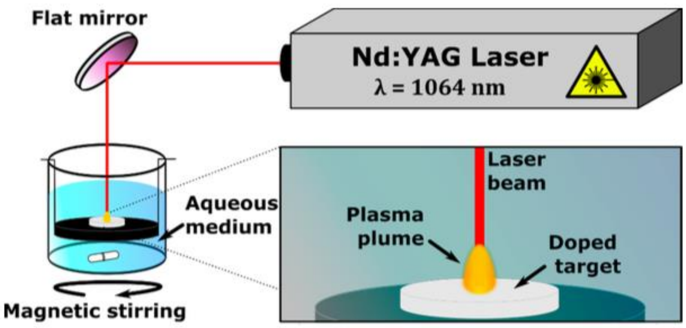
An adapted system for surface treatments is based on a Nd: YAG laser (Rofin Starmark SMP 100 II), that consists in a power unit, a cooling system, a galvanometer head and a moving table, the later allowing sample motion in a controlled speed from 10^{-5}- 1 m/s. The closed-loop water cooled pulsed laser emits at the fundamental wavelength (1064 nm) with a maximum average power of 100 W and a pulse frequency from 4-30kHz. A software driven galvanometric scan head, placed at the exit of the laser body, steers the beam to the desired form of scanning. A vertically moving stage provides focus adjustment.
This system allows the adjustment of several parameters, namely: power, scan speed; pulse frequency; velocity of the sample and scan area.



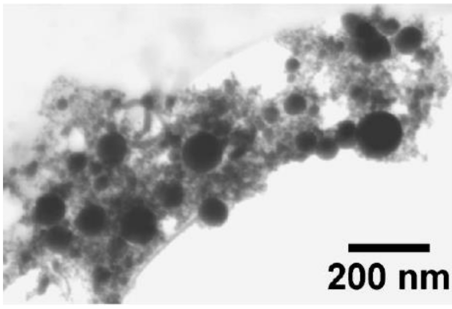
Laser treated copper foil

Pulsed Laser Ablation in Liquids (PLAL)

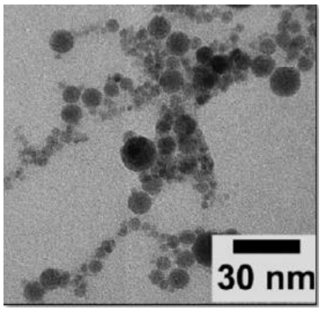
This setup is manly composed by a low frequency high energy pulsed laser, optical components and a glass cell, being exclusively used for Pulsed Laser Ablation in Liquids (PLAL), also referred in literature as liquid-assisted pulsed laser ablation (LA-PLA), liquid-phase pulsed laser ablation (LP-PLA), pulsed laser ablation in aqueous medium (PLAAM) and others.
For this purpose, a nanosecond (7 ns pulse width) Q-switched Nd:YAG laser (Surelite II, Continuum®) emmiting at 1064 nm wavelength and having a maximum pulse repetition rate of 10 Hz energizes this setup. Under unfocused conditions, the laser beam has a spot diameter of 7 mm and a maximum pulse energy of 685 mJ. The radiation produces ablation on the selected targets (metals, oxides, etc.) immersed in adequate liquids, resulting in nanoparticle loaded solutions that can readily be used.



ZrO2 Nanoparticles



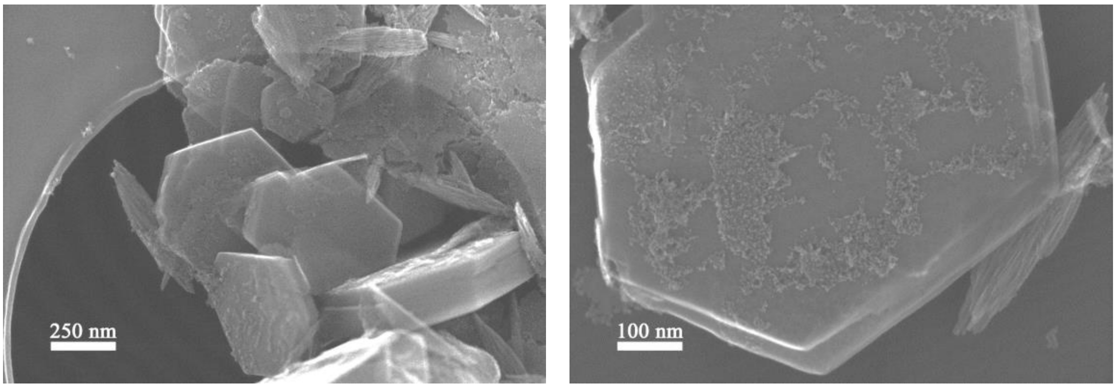
Europium doped ZrO_2 Nanoparticles



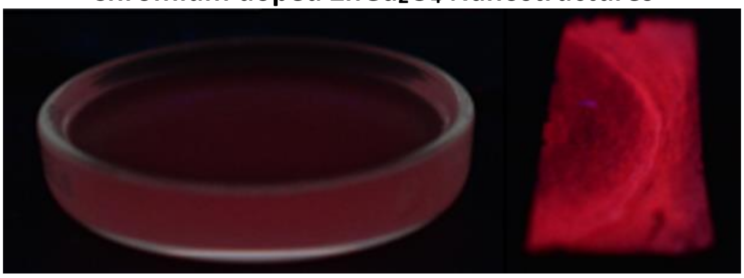
Terbium doped ZrO_2 Nanoparticles

Europium doped ZrO_2 Nanoparticles ablated solution under a 254 nm Lamp as excitation source
http://dx.doi.org/10.1039/c5ra00189g

Terbium doped ZrO_2 Nanoparticles ablated solution under a 254 nm Lamp as excitation source
http://dx.doi.org/10.1039/c5nr04052c



Chromium doped $ZnGa_2O_4$ Nanostructures

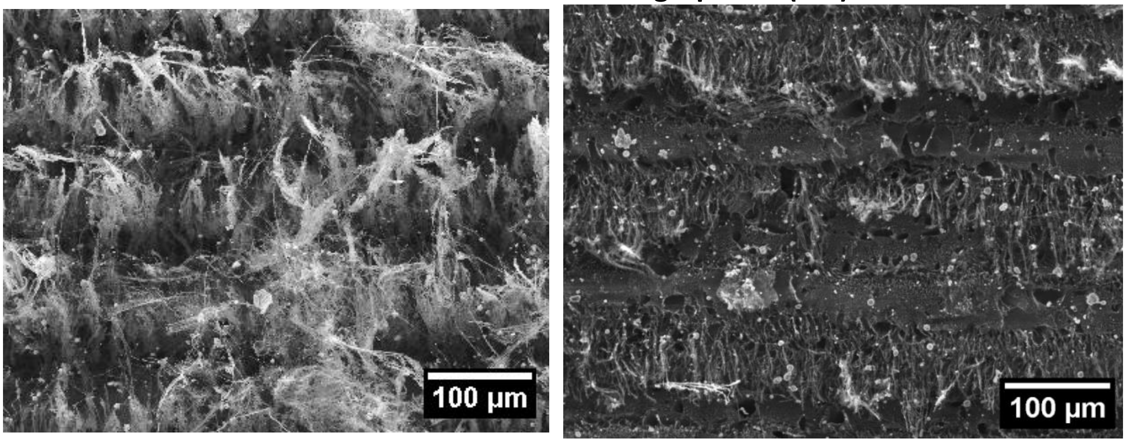


Chromium doped $ZnGa_2O_4$ ablation solution (left) and deposited Nanostructures (right) emission under a 254 nm Lamp as excitation source.

CO_2 XY engraver/cutter

Infrared Laser radiation directly focused onto materials surface promotes changes ranging from melting to different micro- and nanometric patterns, depending on the applied power density. It can be used to chemically and structurally modify surfaces in a wide range of materials, from metals to insulators.
The RedSail M500 CO_2 laser emits a power of up to 50 W at the 10.6 µm wavelength in continuous wave regime. The laser beam is directed through an optical system featuring a moving optical head that allows positioning along the XY plane, achieving a well-focused scribing area of 300 x 500 mm^2 at a maximum speed of 500 mm/s.

ZnO decorated laser-induced graphene (LIG)

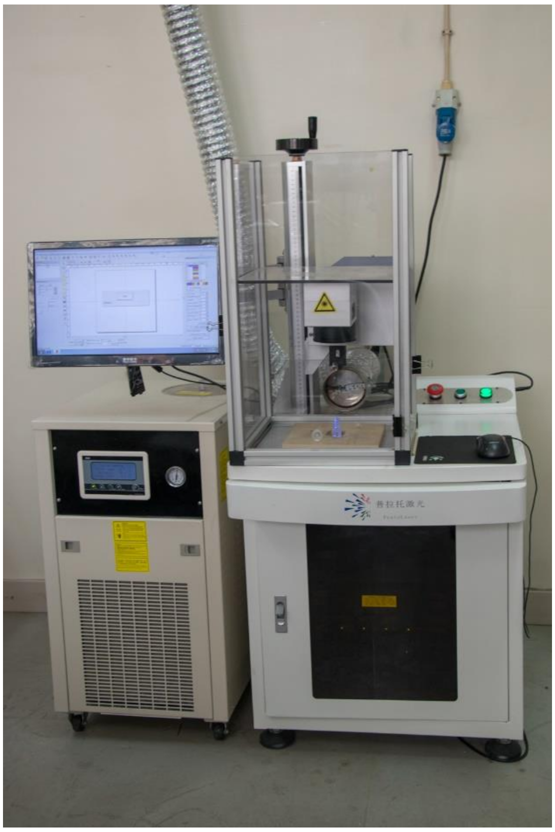


ZnO/LIG (P = 23.9 W, *v* = 300 mm.s^{-1}) **ZnO/LIG (P = 23.9 W, *v* = 200 mm.s^{-1})**

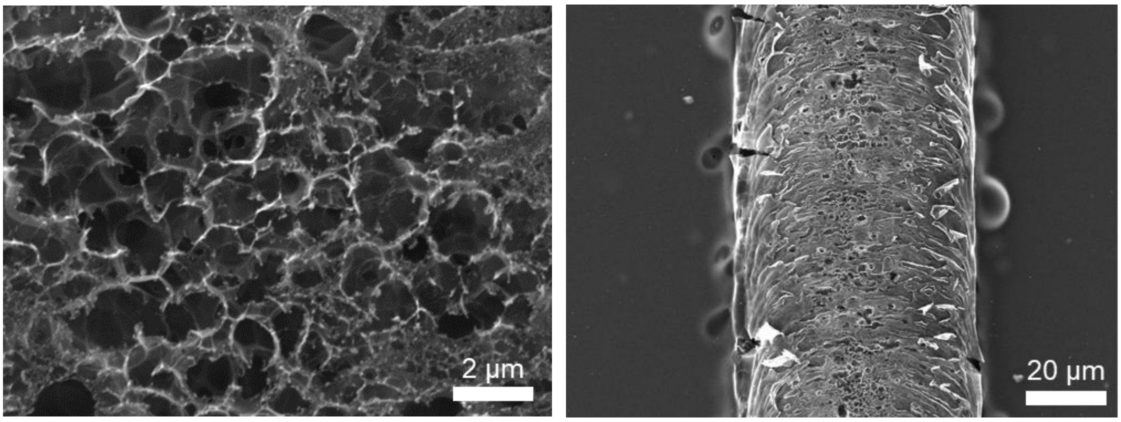
UV Laser Engraver

Laser-processing of solid precursors allows both the synthesis and microfabrication of micro and nanostructured materials. UV lasers can achieve more superficial interactions and higher resolution when comparing to other more conventional systems such as CO_2 lasers, and are able to process other classes of materials, such as metals, with a much lower thermal load to the substrate.

In our group, we have a 3 W pulsed Inngu Laser, with a pulse frequency ranging from 10-150 kHz at a fixed wavelength of 355 nm. It is equipped with a galvanometric scanning head with a 16 mm F-θ Lens, allowing the controllable patterning at high speed in a 10x10 cm working area.



Laser Induced Graphene



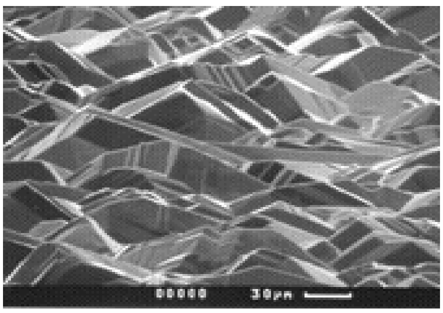
CVD Laboratory

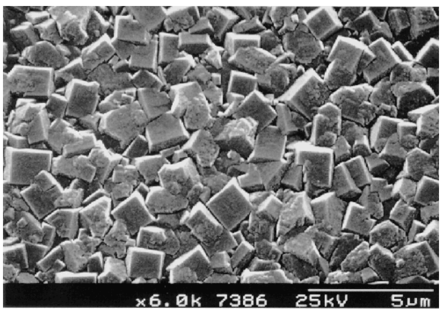
Microwave Plasma Chemical Vapour Deposition (MPCVD)

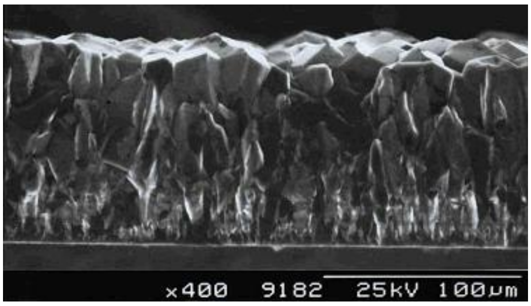
The basic principle of the MPCVD method is to decompose high purity gases in controlled plasma conditions, which further undergo a series of chemical reactions resulting in the deposition of a solid phase in a substrate. This technique permits the growth of several elementary and compound materials with controlled structure and morphologies, such as e.g. monocrystalline, polycrystalline or amorphous films and polycrystalline films with preferential crystal orientation.

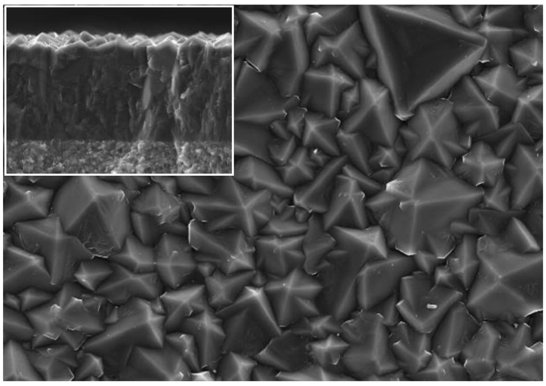
Our group's MPCVD is an ASTeX AX 6350 with 6 kW microwave max. power and is mainly dedicated to the synthesis of carbon allotropes, separately or in the form of hybrid materials, such as high structural quality graphene, carbon nanotubes (CNTs) and diamond films of varying crystal sizes (nano- and micro-crystalline diamond).

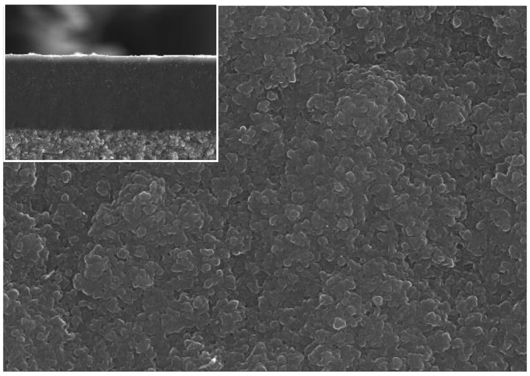
Important parameters are the feed gas chemistry, temperature, microwave power and pressure. The common precursor gases are CH4 (the carbon source), H_2, Ar, N_2 and O_2. The target applications range from wear-resistant cutting tools (diamond coatings), chemical sensors and biosensors (graphene, CNTs) and microelectronics (such as field effect transistors microelectromechanical systems, MEMS), among many others.





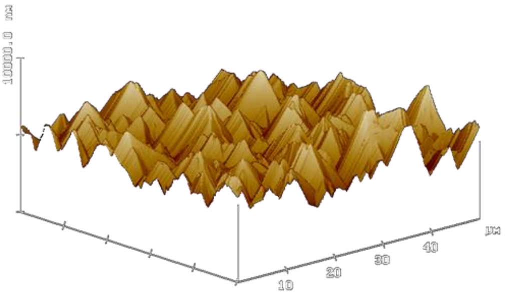


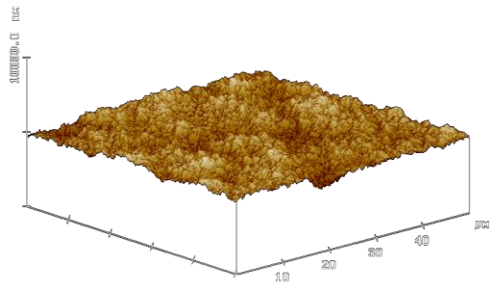




Microcrystalline diamond (MCD)

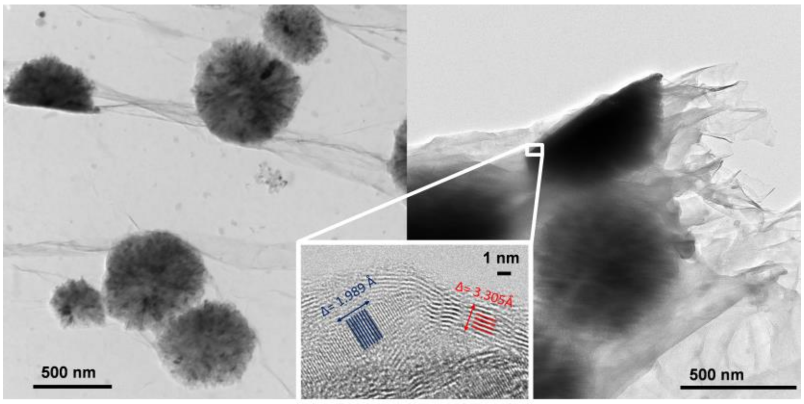
Nanocrystalline diamond (NCD)





http://dx.doi.org/10.1016/j.surfcoat.2010.04.031
http://dx.doi.org/10.1016/j.diamond.2008.08.014

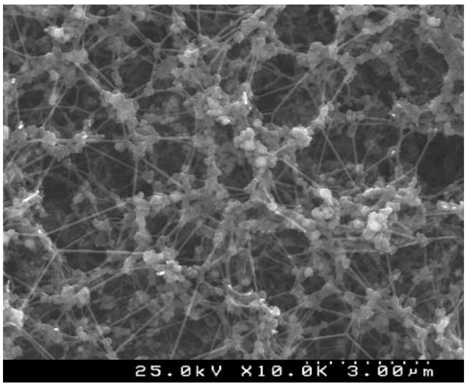
Graphene Diamond Hybrids

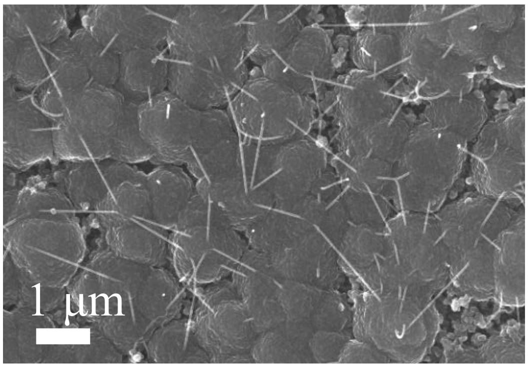


Graphene Diamond Hybrids

http://dx.doi.org/10.1016/j.carbon.2015.10.095
https://doi.org/10.1016/j.carbon.2017.07.024

Carbon Nanotubes Diamond Hybrids

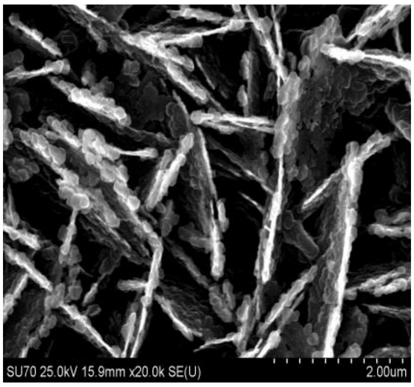


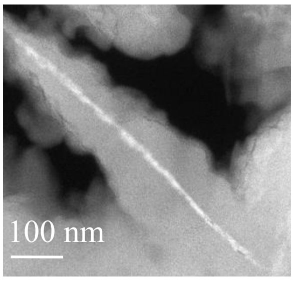


CNT/NCD Hybrid with a neuronal-like network

http://dx.doi.org/10.1016/j.diamond.2008.08.015

Diamond-Graphite Hybrids





EF-TEM
36eV (Diamond plasmon)

Vertically-aligned diamond nanoplatelets having conspicuous edges and high aspect-ratio coated with nanographite

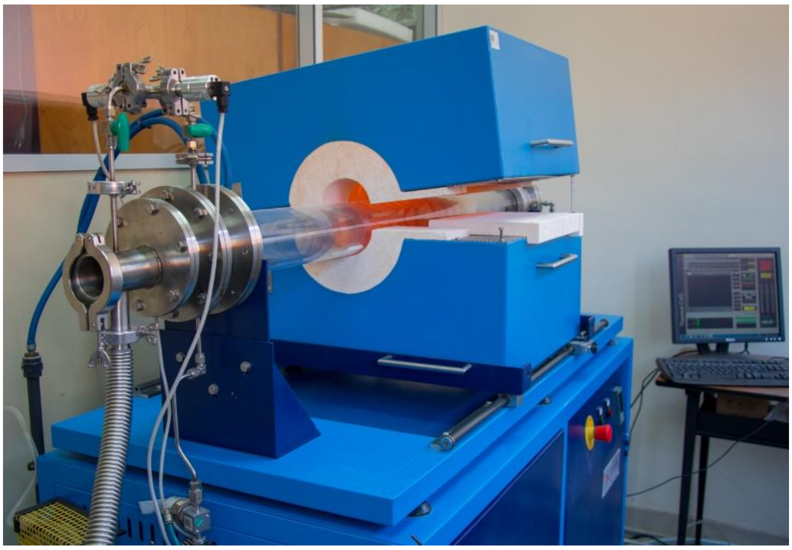
http://dx.doi.org/10.1021/acsami.6b14407

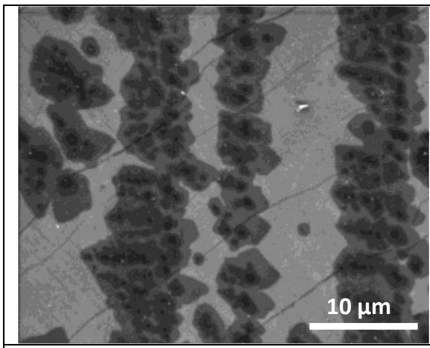
http://dx.doi.org/10.1021/acsami.5b07633

Thermal Chemical Vapor Deposition (TCVD)

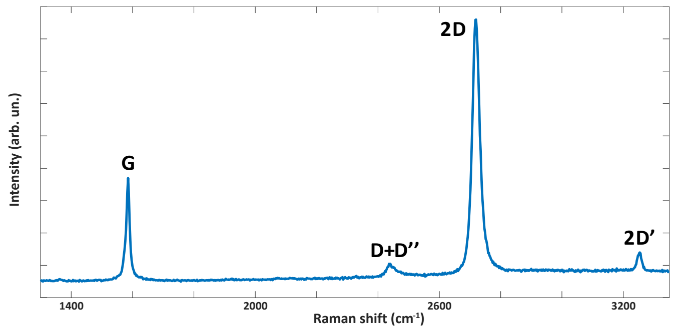
The TCVD relies on the decomposition of precursor compounds (typically, high purity gases) through thermal activation, which posteriorly undergo a series of chemical and physical reactions and processes culminating with the deposition of a solid phase on a substrate.

Our group's TCVD is a home-built system, used primarily for single- and few-layer graphene deposition. The reactor, capable of reaching temperatures of up to 1200°C through resistive heating, is composed of two coaxial quartz tubes (diameter: 75 mm inner tube and 95 mm outer tube; length: 1400 mm inner tube and 1500 outer tube), allowing deposition either between the tubes or in the inner one. The system is equipped with a gas supply of argon, hydrogen and methane, and is capable of growing graphene at either atmospheric or low pressure, with the latter achievable using a roots-type dry pump.





Single-layer graphene with secondary few-layer domains



Raman spectrum of the single-layer areas (442 nm excitation wavelength)

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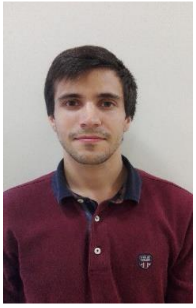

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