Laser Processing

and

Chemical Vapor Deposition

(CVD)

Laboratories
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 CO₂ laser (Spectron SLC, \( \lambda = 10.6 \mu \text{m} \)) 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.
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

Gd₂SiO₅, Gadolinium Oxyorthosilicate (GSO) grown by LFZ

GSO under UV irradiation
LGSO and LGSO:Y: $(\text{Lu}_{0.3}\text{Gd}_{0.7})_2\text{SiO}_5$ and $(\text{Lu}_{0.3}\text{Gd}_{0.7})_2\text{SiO}_5:Y^{3+}$ (5at%)  

CYA derived deep red phosphors: $\text{CaYAlO}_4:Y_4\text{Al}_2\text{O}_9:\text{CaYAl}_3\text{O}_7:\text{Mn}^{4+}$

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

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

http://dx.doi.org/10.1016/j.matdes.2015.03.005
http://dx.doi.org/10.1016/j.matlet.2012.05.131
Eutectic Oxides (ZrO₂-BaZrO₃) 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
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 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
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.
Pulsed Laser Ablation in Liquids (PLAL)

This setup is mainly 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®) emitting 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 ZrO₂ Nanoparticles ablated solution under a 254 nm Lamp as excitation source
http://dx.doi.org/10.1039/c5ra00189g

Terbium doped ZrO₂ Nanoparticles ablated solution under a 254 nm Lamp as excitation source
http://dx.doi.org/10.1039/c5nr04052c

Chromium doped ZnGa₂O₄ Nanostructures

Chromium doped ZnGa₂O₄ ablation solution (left) and deposited Nanostructures (right) emission under a 254 nm Lamp as excitation source.
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, \( v = 300 \text{ mm.s}^{-1} \))

ZnO/LIG (P = 23.9 W, \( v = 200 \text{ mm.s}^{-1} \))
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 CO₂ 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
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), H2, Ar, N2 and O2. 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

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
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
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)