REPORT on
Laser plasma advanced studies: application of ps pulses for plasma diagnostic by laser shadowgraphy and laser induced forward transfer
ESF reference numbers 3312, 3313

Period: March 7 – 19, 2010

Experiment purpose

According to the approved working plan, our activity was focused to the achievement of 2 main objectives, namely:

1. study of craters developing as a result of high-intensity nano- or femtosecond vs. picosecond multipulse laser irradiation of solid targets (metal oxides) used in the PLD of nanostructured thin films, with a particular attention paid to nanoparticulates forming during various stages of the laser interaction process: the initial interaction with the target, subsequent propagation in plasma, and film growth on substrates, and
2. correlation between the induced surface nano-morphologys, parameters of the plasma initiating and evolving in front of the target surface, and general characteristics of nanostructured coatings growing on nearby substrates.

We worked in a common team with Prof. Dimitri Batani, Dr. Yas Fadel Al-Hadeethi, Dr. Rashida Jafer and PhD student Mohammed Khair.
The main results we obtained till now can be summarized as follows:

I. Experiments at the University of Milano – Bicocca

All experiments were conducted using a Quanta Nd:YAG laser system capable of delivering a linearly P-polarised 1064 nm laser radiation with an energy per pulse of 120 mJ in 40 ps (FWHM). The system can be operated from 1 to 10 Hz repetition rate depending upon the requirement. It is an active-passive mode-locked Nd:YAG system and consists of a laser oscillator, an amplifier and a nonlinear KDP crystal for second harmonic conversion.
To generate the plasma, we have used 532 nm laser beam to irradiate the target placed inside the vacuum chamber evacuated down to 10^{-3} torr. The beam was focused using a plano-convex lens with f = 9 cm to a spot area of 10 mm^2. The incident laser fluence was of 28 J/cm^2 (40 ps pulse duration).

1. Plasma plume recording using time resolved optical shadowgraphy

We have set-up optical shadowgraphy technique to simultaneously record the extent of plasma plume along with the crater formation. Shadowgraphy technique requires a probe beam having a different wavelength from the main beam used for plasma generation. This is necessary to avoid scattered light from the main beam to completely masking the interesting signal. The probe beam is incident perpendicular to the plasma expansion and its absorption by the high density plasma casts a shadow, while the low density plasma remains transparent to the probe beam.
Output of the 1064 nm and its harmonic radiations were delivered through different exit apertures of the laser system. For the preliminary investigations, probe beam was incident

onto the expanding plasma close to the target surface with a delay of 1.5 ns after the interaction of main laser with the target surface. Probe delay could be adjusted by changing the optical path of the probe beam. The shadowgraphy setup is shown below in figure 1.

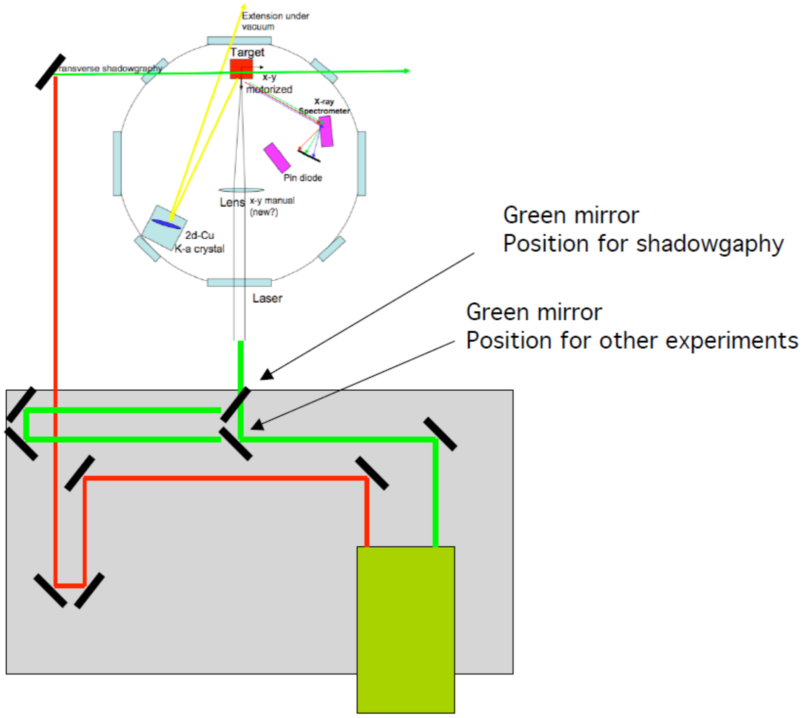


Fig 1: Shadowgraphy setup

Target surface and expanding plasma were independently recorded on CCD camera. An IR interference filter was placed at the entrance of the CCD camera along with the necessary neutral density filters.

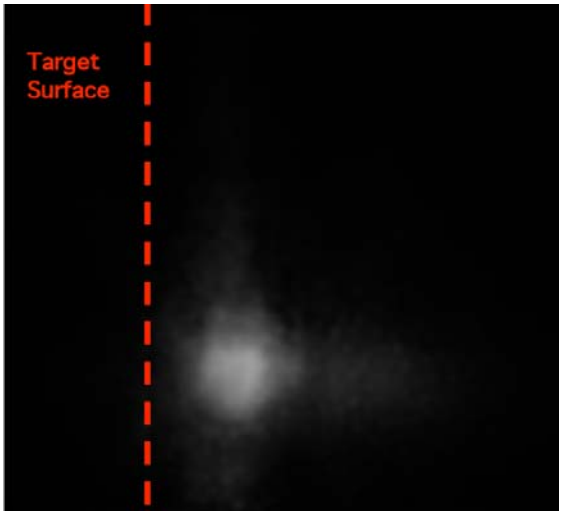


Fig 2. Self-emission of green light from the plasma

Initial images by the CCD camera showed a self-emission of green light from the plasma (Fig. 2).
Experiments were finalised by recording the shadowgraphs in case of plasma generated at different levels of incident laser energy. The recorded data are under processing and interpretation.

2. PLD experiments

The depositions were carried out with 532 nm laser radiation. The ablated material was collected onto double polished (111) Si or quartz wafers placed parallel to the target at a separation distance of 7 mm. The deposited samples and experimental conditions are given in Table 1.

Table 1. Experimental conditions in 40 ps PLD

Sample no.	Target	Substrate	Radiation	Pressure
1	ZnO	Quartz	532 nm	10^{-3} mbar
2	ZnO	Si(111)dp	532 nm	10^{-3} mbar
3	ITO	Si(111)dp	532 nm	10^{-3} mbar

The laser beam was incident at 45° while the laser fluence was adjusted so that the generated plasma extended from target to collector. For the deposition of one film we applied 30000 laser pulses. In order to avoid target drilling, 1000 subsequent laser pulses were applied inside the same irradiation spot. Then, the target was shifted with 1 mm to a new fresh location and the deposition was resumed with another 1000 subsequent laser pulses. This way, identical craters were digged into the target for the deposition of one film. At visual inspection the films looked uniform and covered all surface of the deposition substrate. The craters appeared elliptical.

II. All prepared structures were preserved in special boxes and were carefully investigated in Bucuresti by AFM, UV-Vis and FT-IR. The results of our investigations are presented below.

a. UV-Vis investigations

These studies were performed with a Cintra 10e spectrometer. It has true double beam, high efficiency, all-reflective optics, the full complement of automated accessories and the power of the fully-integrated Spectral software package. It has a fixed 1.5 nm slit width and a silicon photo-diode detector, covering an extended wavelength range of 190 to 1,200 nm.
The spectrum recorded for the ZnO film deposited on quartz is presented in Fig. 3.

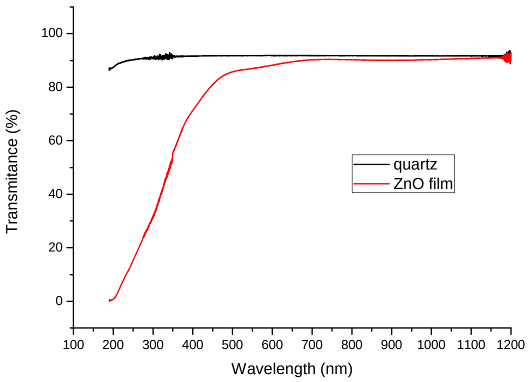


Fig. 3. UV-Vis spectrum of ZnO film obtained with 40 ps@532 nm laser source

From Fig. 3 we noticed a deposition with a high transmittance (~90%) consisting of ZnO. The accentuated fall of the transmittance signal at 350 nm is indicative for the formation of pure ZnO.

b. FT-IR studies

The investigations were conducted with a Shimadzu 8400S spectrophotometer equipped with an AIM 8000 microscope. The investigations were performed in reflection. The recorded spectra for ZnO and ITO depositions were given in Figs. 4 and 5, respectively.

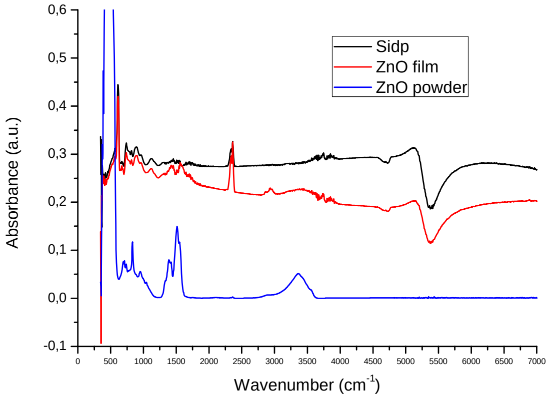


Fig. 4. FT-IR spectra of ZnO film obtained with 40 ps@532 nm laser source along with Si(111) substrate and the respective powder

From the spectra in Fig. 4 we can observe the presence of some lines at 1393 and 1515 cm^{-1} as well as a broad band situated at 3364 cm^{-1} for both ZnO film and powder. The other characteristic lines of ZnO at 700, 836 and 960 cm^{-1} are superposing to the ones of the substrate, (111) Si double polished.

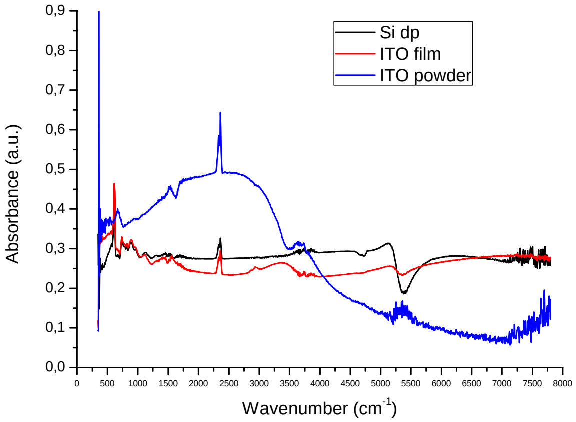


Fig. 5. FT-IR spectra of ITO film obtained with 40 ps@532 nm laser source along with Si(111) substrate and the respective powder

In case of ITO deposition, the film, visible on the substrate, was thin and the FTIR signal too low to record the lines specific for the starting material (Fig. 5).

c. Optical microscopy and AFM investigations

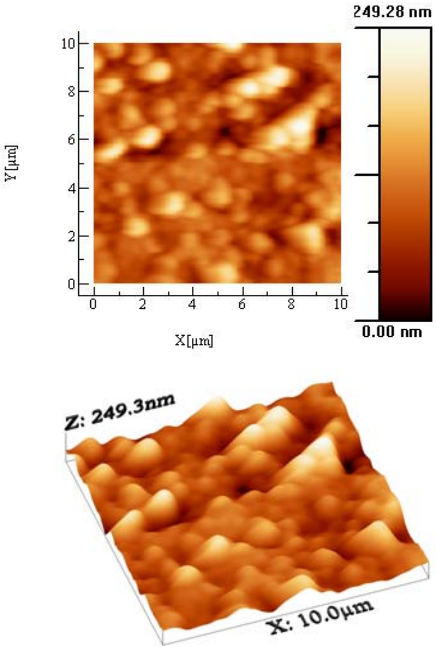
The surface morphology of the deposited films was examined by optical and atomic force microscopies (AFM) in AC mode with a Nanonics MV 4000TM Microscope. The observations by optical microscopy are illustrated in Fig. 6.

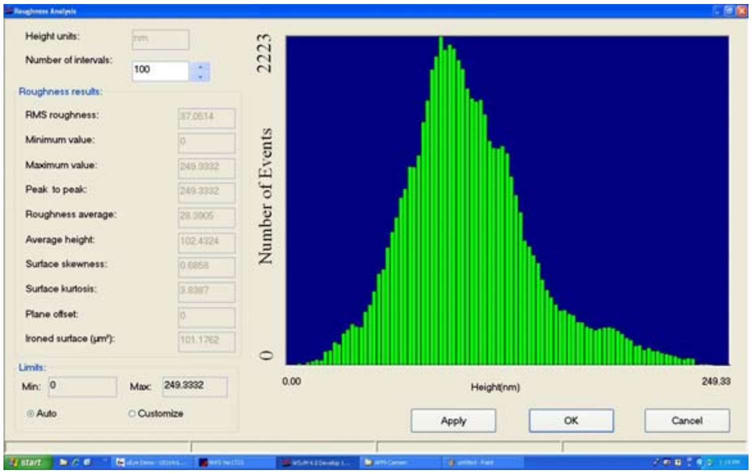
a b c

Fig. 6. Optical microscopy images obtained for ZnO film deposited on (a) quartz and (b) Si(111) and (c) ITO on Si(111) (100X) with 40 ps@532 nm laser source

The films look uniform over the entire investigated area.

Typical AFM recordings for an investigation area of 10x10 μm^2 are given in Figs. 7, 8 and 9 for ZnO films deposited on quartz and Si(111) and of ITO on Si(111), respectively.





Height units: nm

Number of intervals: 100

Roughness results:

RMS roughness: 37.0514

Minimum value: 0

Maximum value: 249.3332

Peak to peak: 249.3332

Roughness average: 28.3905

Average height: 102.4324

Surface skewness: 0.6858

Surface kurtosis: 3.8387

Plane offset: 0

Ironed surface (µm²): 101.1762

Limits:

Min: 0 Max: 249.3332

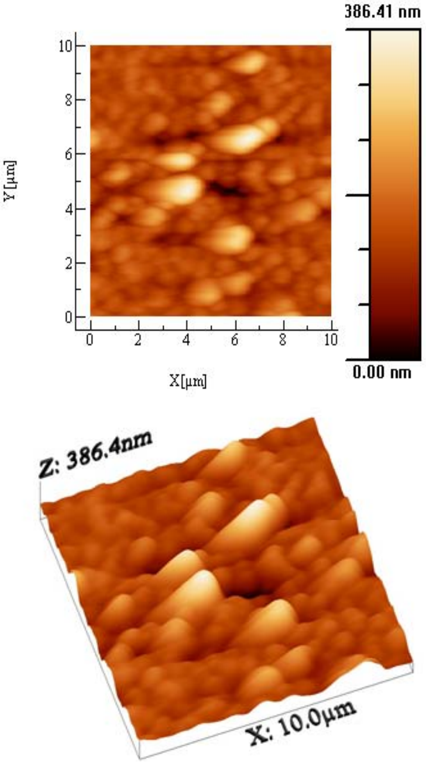
● Auto ○ Customize

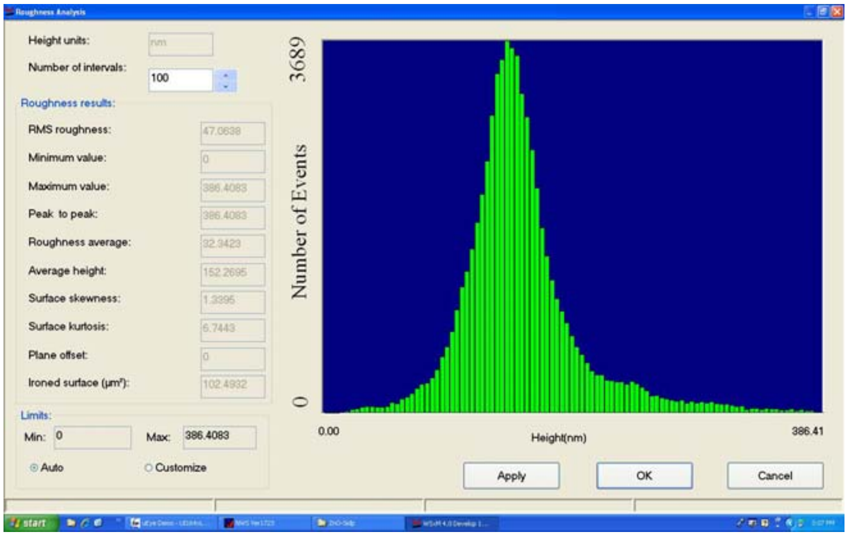
Fig. 7. AFM images of the ZnO film deposited on quartz with 40 ps@532 nm laser source

The characteristic profile roughness parameters as root mean squared (Rms), roughness arithmetic average (Ra) and the average height (Rz) values inferred from Figs. 6 to 8 were collected in Table 2.

Table 2: Roughness parameters (Rms, Ra and Rz)

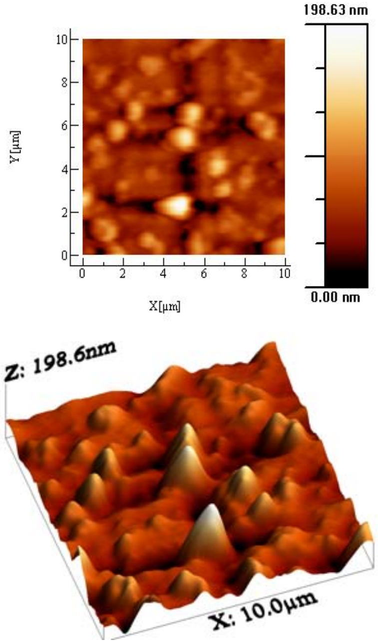
Sample	**Rms (nm)**	**Ra (nm)**	**Rz (nm)**
ZnO/quartz	37.05	28.39	102.43
ZnO/Si(111)dp	47.06	32.34	152.26
ITO/Si(111)dp	23.46	16.70	60.13

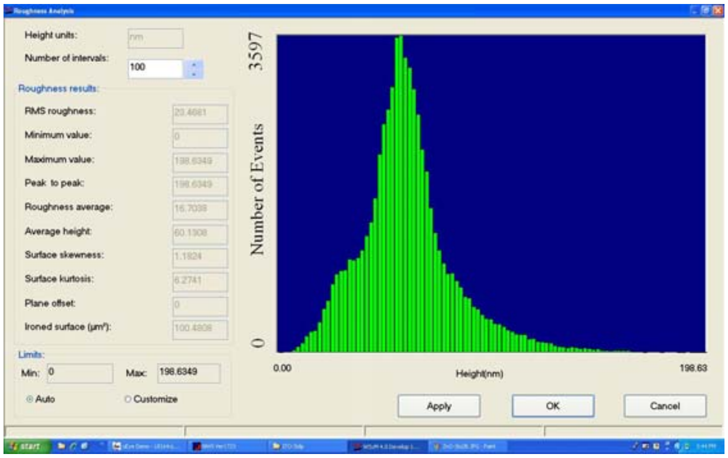




Height units: nm
Number of intervals: 100
Roughness results:
RMS roughness: 47.0638
Minimum value: 0
Maximum value: 386.4083
Peak to peak: 386.4083
Roughness average: 32.3423
Average height: 152.2695
Surface skewness: 1.3395
Surface kurtosis: 6.7443
Plane offset: 0
Ironed surface (µm²): 102.4932
Limits:
Min: 0 Max: 386.4083
● Auto ○ Customize

Fig. 8. AFM images of the ZnO film obtained on Si(111) dp with 40 ps@532 nm laser source





Height units: nm
Number of intervals: 100
Roughness results:
RMS roughness: 23.4681
Minimum value: 0
Maximum value: 198.6349
Peak to peak: 198.6349
Roughness average: 16.7038
Average height: 60.1308
Surface skewness: 1.1924
Surface kurtosis: 6.2741
Plane offset: 0
Ironed surface (µm²): 100.4808
Limits:
Min: 0 Max: 198.6349
● Auto ○ Customize

Fig. 9. AFM images of the ITO film deposited on Si(111) dp with 40 ps@532 nm laser source

The most important observation is that the obtained nanostructures are rougher than the ones obtained with ns laser pulses, but a bit smoother as compared with the ones deposited using fs pulses. The obtained results are under processing for critical comparison wit theoretical models of ns, ps, and fs laser pulse interactions provided in literature and with experimental results obtained by ns (25 ns @ 248 nm) and fs (150 fs @ 800 nm) laser ablation performed previously by Romanian team.

The partners agreed that the communication of first results be done at the 7th International Conference on Photo-Excited Processes and Applications (ICPEPA'7) which will be held in Copenhagen, Denmark, in August 15-20, 2010. The proceedings of this conference will be published in Applied Physics A. After complete processing of obtained data and interpretations with theoretical and experimental models, another paper will be submitted to a regular journal (Thin Solid Films).

During the stage we presented a seminar on *"MAPLE: a new laser technique for transferring / depositing very "delicate" substances"* scheduled on March 15, 2010.

References:

1. "Nanostructured thin optical sensors for detection of gas traces", C. Ristoscu, I. N. Mihailescu, D. Caiteanu, C. N. Mihailescu, Th. Mazingue, L. Escoubas, A. Perrone, H. Du, "Functionalized Nanoscale Materials, Devices, & Systems", Edited by A. Vaseashta, and I. N. Mihailescu, SPRINGER SCIENCE + BUSINESS MEDIA B.V., (2008), p. 27 - 50
2. "Laser Plasma Interactions", I. N. Mihailescu, J. Hermann, Chapter 4 in "Laser Processing of Materials: Fundamentals, Applications, and Developments", Ed. P. Schaaf, Springer Series in Materials Science, Springer Heidelberg (2010) pp. 51 – 90

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