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Synthesis of Multiphase Metallic Oxides by Femtosecond Laser Irradiation of Metallic Thin Films

Santiago Camacho-Lopez
CENTRO DE INVESTIGACION CIENTIFICA Y DE EDUCACION SUPERIOR DE ENSENADA, BAJA CAL
CARR. ENSENADA - TIJUANA NO. 3918
BAJA CALIFORNIA NORT, 22860
MX

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14. ABSTRACT
We studied the formation of metallic oxides under femtosecond (fs) laser irradiation at MHz repetition rate, for different atmospheres on metallic films. We found that the synthesis of molybdenum oxides is significantly affected by the processing atmosphere i. e. ambient air vs pure oxygen. The oxide formation under the same laser irradiation conditions produces distinct crystalline phases depending on the processing atmosphere. In the case of ZnO synthesis by using fs laser pulses we found that the laser irradiation conditions determine the crystalline quality of the obtained ZnO. Under certain laser irradiation conditions the density of point defects increases, which is revealed by microRaman spectroscopy and cathodoluminescence measurements. ZnO nanoparticles (NPs) were proven to produce second harmonic generation when irradiated with fs laser pulses, the features of the SHG signal shows unexpected polarization dependence; it is related to the randomly oriented NPs.

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metallic oxides, synthesis of metallic oxides, SOARD

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Departamento de Óptica

Final report

Southern Office of Aerospace Research and Development (SOARD) – AFOSR (Air Force Office of Scientific Research)

Synthesis of Multiphase Metallic Oxides by Femtosecond Laser Irradiation of Metallic Thin Films

Dr. Santiago Camacho-López

Departamento de Óptica

CICESE

July 31, 2018

Briefing

Program manager: **James M Fillerup, Director-SOARD**

The project entitled "*Synthesis of Multiphase Metallic Oxides by Femtosecond Laser Irradiation of Metallic Thin Films,*" was led by the Dr. Santiago Camacho López (PI, CICESE) and Dr. Guillermo Aguilar (co-PI, UCR) through a subcontract award. The research group is composed as follows:

Laboratory of Ultrashort Pulse Lasers and Processing of Materials, CICESE

Laboratory of Transport Phenomena, UCR

MEXICO

Researchers:

Santiago Camacho-López (CICESE)

Marco Camacho-López (UAEMex)

Students:

Yasmín Esqueda-Barrón (PhD CICESE)

Daniel Huerta-Murillo* (MSc CICESE)

Victoria Ramos-Muñiz (MSc CICESE)

Yryx Luna (BSc UAEM)*

USA

Researchers:

Guillermo Aguilar (UCR)

Students:

Jon Redenius* (MSc UCR)

Kendrick Mensink* (PhD UCR)

Natanael Cuando (PDF UCR)

Note.- the tag * indicates the students who received partial funding through this awarded grant.

Degrees, Conferences and Publications summary

Within this research project the following degrees were either started or completed

Degree program	Mexico (CICESE, UAEMex)	USA (UCR)
MSc	• Victoria Ramos-Muñiz (CICESE) “Síntesis de MoOx por irradiación láser de femtosegundos: estructura, morfología, estequiometría y propiedades ópticas” (**completed**) • Daniel Huerta-Murillo (CICESE) “Estudio de la formación de estructuras periódicas en capas metálicas mediante irradiación láser” (**completed**) • Yryx Y Luna-Palacios (UAEMex) “Estudio de los efectos de generación de segundo armónico y fluorescencia de soluciones coloidales de Np de ZnO sintetizadas por ablación láser” (**completed**)	• Jon Redenius (UCR), *“Pressurized Oxidation Studies of Molybdenum Thin Films Using Femtosecond Pulsed Lasers”* (**completed**)
PhD	• Yasmín Esqueda-Barrón (CICESE) “*Síntesis de los óxidos metálicos inducidos por irradiación láser de pulsos ultracortos: ZnO y SnO*” (**completed**)	• Kendrick Mensink (UCR) *“Material processing above and below the ablation threshold using femtosecond NIR laser”* (**in progress**)

A series of **conferences and seminars** were attended, were work related to this research was presented:

- **Santiago Camacho-López** (April 2018) *Laser-Induced Periodic Surface Structures (LIPSS): Basics and Applied Aspects*. IV Symposium of Nanoscience and Nanomaterials. Ensenada, México.
- **Santiago Camacho-López** (February 2018) *Laser-Induced Periodic Surface Structures (LIPSS): Basics and Applied Aspects*. CARIBMAT 2018. Cartagena de Indias, Colombia.

- **Santiago Camacho-López** (November 2016) *Molybdenum oxides thin films synthesized by ultrashort laser pulses in air and oxygen environments*. CARIBMAT 2016. Santo Domingo, Republica Dominicana.
- **Santiago Camacho-López** (October 2016). *Síntesis de óxidos metálicos mediante irradiación láser con pulsos ultracortos en películas delgadas*. Seminario de física, matemáticas y astronomía del ITESO. Guadalajara, México.
- **Santiago Camacho-López, Yasmín Esqueda-Barrón** (October 2016) *Luminescence and Raman features of fs laser-induced ZnO*. Congreso Nacional de Física. Guanajuato, México.
- **Santiago Camacho-López, Yasmín Esqueda-Barrón, Manuel Herrera-Zaldivar, Alejandro Esparza-García** (August 2016). *Raman spectroscopy and CL from ZnO induced by fs laser irradiation*. ECOSS 32, European Conference on Surface Science. Grenoble, Francia.
- **Yasmín Esqueda-Barrón, René I Rodríguez-Beltrán, Marina C Tristán-Barrios, Marco Camacho-López, Santiago Camacho-López** (October 2015). *Estudio de ZnO y SnO en película delgada inducidos por irradiación láser de pulsos ultracortos*. Congreso Nacional de Física. Mérida, México.
- **Daniel Huerta-Murillo, Santiago Camacho-López** (October 2015). *Formación de LIPSS en películas delgadas de titanio*. Congreso Nacional de Física. Mérida, México.
- **Santiago Camacho-López** (June 2015). *Femtosecond laser-induced micro and nanostructured metallic oxides*. Energy Materials and Nanothecnology. Cancún, México.

The following **journal publications** are related to the present research work:

1. *"Laser fluence dependence of the electrical properties of MoO_2 formed by high repetition femtosecond laser pulses"* **S. Camacho-Lopez**, I. Pérez, M. Cano-Lara, A. Esparza-Garcia, C. Maya-Sánchez, A. Reynoso-Hernandez, M. Camacho-Lopez. Under review in Physica Status Solidi A (2018).
2. *"Influence of oxygen pressure on the fs laser- induced oxidation of molybdenum thin films"* N. Cuando-Espitia, J. Redenius, K. Mensink, M. Camacho-Lopez, **S. Camacho-Lopez**, G. Aguilar. *Opt. Mat. Express* **8**, 581-596 (2018).
3. *"ZnO synthesized in air by fs laser irradiation on metallic Zn thin films"* Y. Esqueda-Barron, M. Herrera, **S. Camacho-Lopez**. *Appl. Surf. Sci.* **439**, 681-688 (2018).
4. *"Second-harmonic generation of ZnO nanoparticles synthesized by laser ablation of solids in liquids"* I. Rocha-Mendozaa, **S. Camacho-Lopez**, Y. Y. Luna-Palacios, Y. Esqueda-Barrón, M. A. Camacho-López, M. Camacho-López, G. Aguilar. *Optics and Laser Technology* **99**, 118-123 (2018).
5. *"Formation of β-Bi_2O_3 and δ-Bi_2O_3 during laser irradiation of Bi films studied in-situ by spatially resolved Raman spectroscopy"* C. Díaz-Guerra, P. Almodovar , M. Camacho-Lopez, **S. Camacho-Lopez**, J. Piqueras. *J. of Alloys and Compounds* **723**, 520-526 (2017).
6. *"Laser-induced periodic surface structures on bismuth thin films with ns laser pulses below ablation threshold"* A. Reyes-Contreras, M. Camacho-Lopez, **S. Camacho-Lopez**, O. Olea-Mejia, A Esparza-Garcia, J. G. Bañuelos-Muñeton, and M. A. Camacho-Lopez. *Opt. Mat. Express* **7**, 1777-1786 (2017).
7. *"Study of the integrated fluence threshold condition for the formation of β-Bi_2O_3 on Bi thin films by using ns laser pulses"* A. Venegas-Castro, A. Reyes-Contreras, M. Camacho-Lopez, O. Olea-Mejia, **S. Camacho-Lopez**, A. Esparza-García. *Optics and Laser Technology* **81**, 50-54 (2016).

8. *"Influence of the per pulse laser fluence on the optical properties of carbón nanoparticles synthesized by laser ablation of solids in liquids"* D. Reyes-Contreras, M. Camacho-Lopez, M. A. Camacho-Lopez, **S. Camacho-Lopez**, R. I. Rodriguez-Beltran, M. Mayorga-Rojas. *Optics and Laser Technology* **74**, 48-52 (2015).

We also filed in a provisional **patent application** through a previous research project, which is now a full application through the present research project

1. S. Camacho-López, M. A. Camacho-López, "Process for obtaining metal oxides by low energy pulsed laser irradiation of metal films" US patent application (Pub No.: US2013/0171373 A1).

The development of the current research project and related, gave place to apply to other sources of funding

Proposal title	Agency	Period	Amount USD	Status
"Estudio de LIPSS y nanoestructuras de óxidos metálicos obtenidas con pulsos láser de femtosegundos"	Cátedras CONACyT	10/01/16-09/31/26	Faculty salary (~$2,000 USD/month)	Awarded

Research results

The main research results are summarized below:

1. **Molybdenum oxide synthesis by fs laser irradiation under air and pure oxygen atmosphere**

Our research group demonstrated in year 2011 the synthesis of molybdenum oxides by femtosecond (fs) laser irradiation, at MHz repetition rate, on thin films under ambient air [1]. In the current project we addressed the problem of synthesizing molybdenum oxides under pure oxygen atmosphere at different pressures. We found that there is a significant difference in the synthesis as it is seen in figure 1, where the synthesis is studied as a function of laser irradiation time for ambient air and pure oxygen at two different per pulse laser fluence. The oxide area is larger for synthesis in ambient air than in pure oxygen, also the type of oxides that are obtained in both cases is different which is clearly seen optically, i. e. the formation of concentric rings displays distinct colors depending on gas atmosphere. This means distinct crystalline phases and stoichiometry as it is shown in figure 2, where Raman spectra are plotted for two representative cases of molybdenum oxide synthesis in ambient air and pure oxygen. Notice also in figure 2 that up to five well defined regions with distinct oxides are identified for the case of the synthesis in ambient air, while only three regions form when the synthesis is carried out under pure oxygen atmosphere.

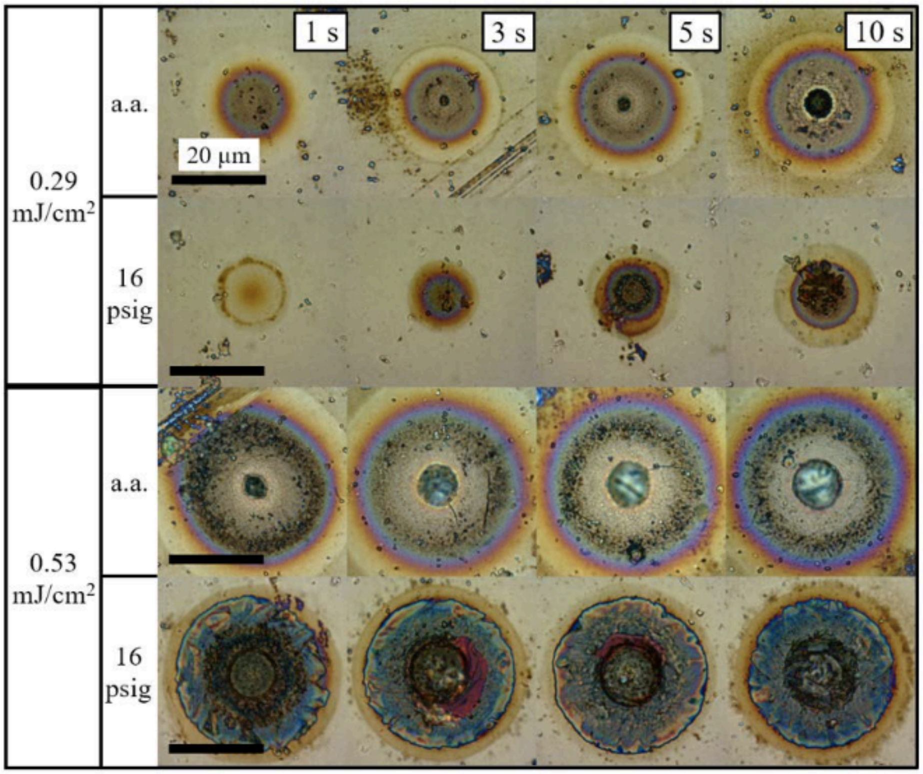

Figure 1. Optical micrographs of molybdenum thin films irradiated for 1, 3, 5 and 10 seconds. Two sets of fluences (0.29 and 0.53 mJ/cm^2) and two atmosphere conditions, ambient air (a.a.) and pressurized oxygen at 16 psig are depicted. The scale bar corresponds to 20 μm. [2]

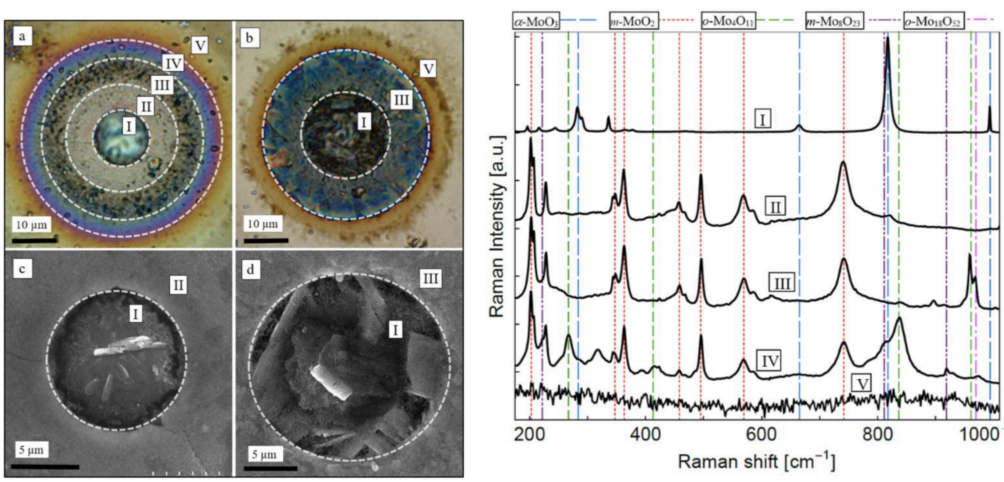

Figure 2. Left: Micrographs of irradiated molybdenum thin films (0.58 mJ/cm^2, 10 s) in atmospheric air (a) and 16 psig O_2 (b). c-d: SEM images from samples depicted in a-b, respectively. Different modified regions can be observed (labeled as I, II, III IV and V). The images suggest a crater-like morphology and crystallites in the inner region. Right: Representative Raman spectra for the different regions shown in Fig. 2. Some of the characteristic peaks of molybdenum oxides have been highlighted. [2]

2. ZnO synthesized by fs laser irradiation on Zn thin films

In addition to molybdenum oxides we synthesized ZnO by using the same method of fs laser irradiation of a metallic film in ambient air. In this case we scanned the laser along the Zn thin film to create tracks of ZnO. The scan speed and laser fluence per pulse were varied, as well as the number of scans on a same track as it is summarized in Table 1. Figure 3 shows scanning electron microcopy (SEM) images of the obtained ZnO formation.

Table 1
Laser irradiation parameters used to print ZnO tracks.

Track labels	E_p [nJ]	F_p [mJ/cm^2]	Scan speed [μm/s]	F_i [kJ/cm^2]	Scans
A	1.1	2.7	100	17.3	1
B					3
C	2.2	5.4	1000	3.5	1
D					3
E	2.6	6.5	100	41.8	1
F			500	8.3	1
G			1000	4.1	1

E_p-per pulse energy, F_p-per pulse energy, F_i-integrated fluence.

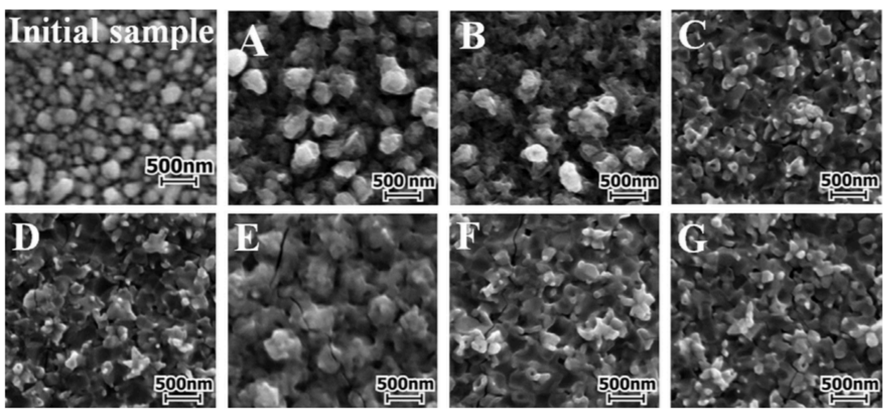

Figure 3. SEM images of the laser fs irradiated regions under different laser irradiation parameters. The labels correspond to the laser irradiation conditions given in table 1. [3]

We found that the initial sample is constituted by smooth round Zn particles (smaller than 200 nm). The effect of the laser irradiation is the formation of faceted ZnO particles, which size depends on the laser irradiation conditions. Low scan speed and increasing integrated laser fluence produce large 500 nm particles, while fast scan speed and low integrated laser fluence produce smaller than 100 nm particles. Micro-Raman spectroscopy (Figure 4) and cathodoluminescence (Figure 5) studies reveled that the synthesis parameters play an important role in the crystalline quality of the formed ZnO. From the Raman assessment, we learned that either a single or three laser scan processing makes no difference. However, the characteristic Raman spectra for the obtained ZnO clearly indicate that an increase in the per pulse laser fluence, no matter that the integrated fluence goes down due to a fast laser scan speed, produces better quality ZnO. Cathodoluminescence measurements confirmed the Raman results and demonstrated that the best quality ZnO is produced for high per pulse laser fluence, medium integrated laser fluences and fast laser scan speed. Interestingly, although single or multiple laser scans make no difference on the morphology and the Raman features, a single laser scan produced better relative $I_{3.3}/I_{2.5}$ intensity ratio than the corresponding intensity ratio for a three scan processed ZnO, meaning that the quality of the synthesized ZnO optimizes (minimizes point defects) under single laser scan synthesis.

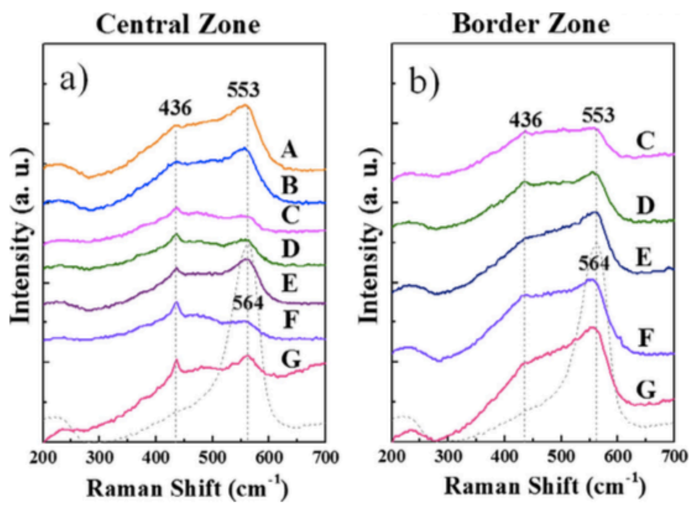

Figure 4. Raman spectra of (a) central zone and (b) border zone of A to G tracks. [3]

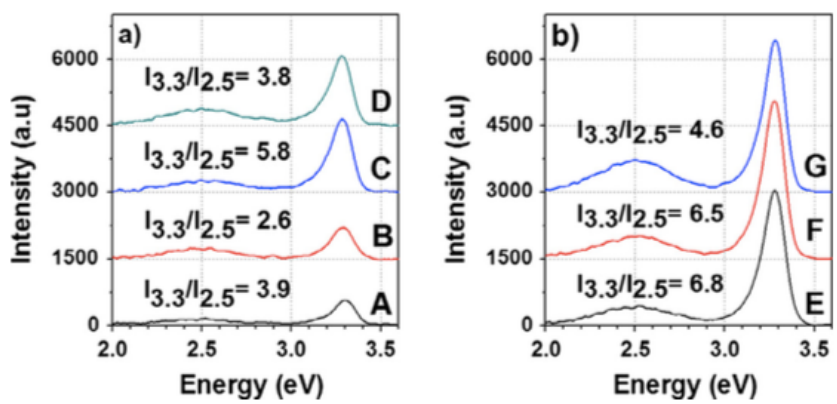

Figure 5. CL spectra of A to G tracks and their respective relative intensity ratio ($I_{3.3}/I_{2.5}$). [3]

The physical mechanisms for ZnO formation, under ultrafast laser pulse irradiation of metallic Zn films are not clear. It seems reasonable to follow a phenomenological model of laser heating, where two time scales drive the synthesis, i. e. the pulse duration and the pulse repetition rate. The ultrashort pulse duration ensures optimal coupling of the optical energy through conduction electrons, and the high laser pulse repetition rate allows for heat accumulation effects. This sets the right conditions for the ZnO synthesis under atmospheric air at room temperature.

3. Nonlinear optical effects of ZnO nanoparticles produced by laser ablation of solids in liquids

We studied the second harmonic generation (SHG) features of ZnO nanoparticles (NPs) produced by laser ablation of solids in liquids (LASL). Bulk ZnO is known to exhibit second order nonlinear optical effects and little work has been done in this field for ZnO NPs. In figure 6 we can see scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) images of the synthesized ZnO NPs, notice that the sample used for the SEM imaging is a dried sample taken from the colloidal solution right after synthesis, in this image we see an agglomerate of a large number of NPs. In the TEM image we can see the size of the NPs is in the order of 5-8 nm. In figure 7 the second harmonic signal produced by the ZnO NPs is shown as recorded by a CCD array. The fundamental source is a fs Ti:sapphire laser with pulses in the order of 30 fs duration at 89 MHz repetition rate. Also in figure 7, the SHG signal is plotted (in log-log scale) as function of the input power, which allows corroborating the second order nature of the signal. The polarization dependence of the SHG signal is plotted in polar coordinates showing an unexpected nearly isotropic response of the produced SHG signal. An anisotropic response was expected due to the noncentrosymmetric structure of the ZnO.

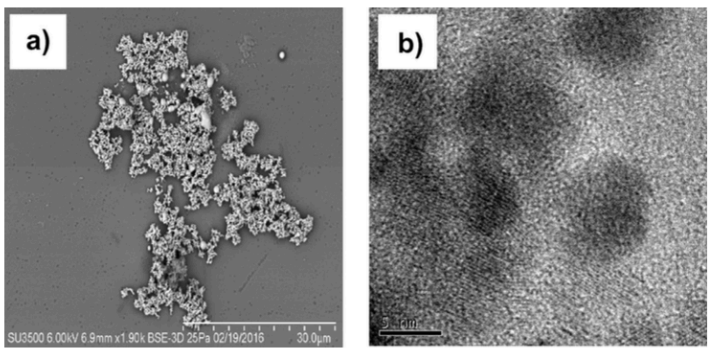

Figure 6. Morphology of synthesized ZnO NPs. (a) SEM image of the ZnO NPs deposited on a glass slide. (b) HRTEM image of ZnO NPs clusters conformed of spheroidal nanoparticles of around 5–8 nm size. [4]

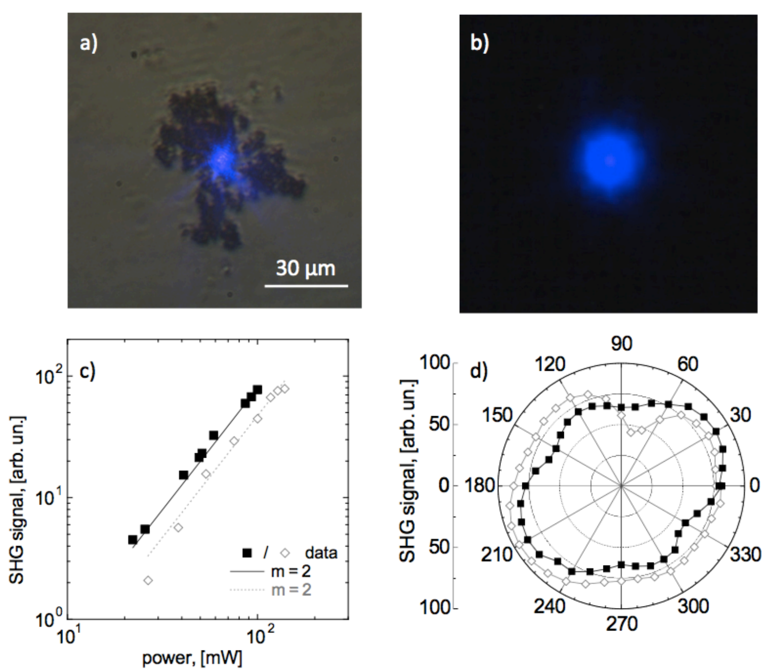

Figure 7. Characterization of SHG signal in ZnO synthetized by LASL. (a) Bright field image of clustered ZnO nanoparticles showing simultaneously the back scattered SHG signal at the laser focus taken in the reflection mode; (b) image of the SHG signal at the confocal plane taken in the transmission mode. (c) Log-log scale plots showing the typical quadratic SHG signal dependence with respect the laser input power (see fitted curves with slopes m = 2) due to a 2nd order optical nonlinear process; and d) polar plot showing the polarization dependence of SHG signal. Figures (c) and (d) show the results taken at two different locations within the sample. [4]

Efficient SHG signal from aggregated ZnO NPs, containing small sized nanoparticles, is observed. While nearly isotropic SHG signal is attributed to randomly distributed ZnO monocrystalline NPs, anisotropic SHG could be originated from the aggregated form of the ZnO NPs microstructures. The comparable amplitude of the signals suggest that the SHG efficiency may not depend on the NPs size or aggregation state. A more detailed study to determine the origin of the SHG efficiency of smaller ZnO NPs is required.

Future work

The future work in view of the present project has to focus on the following issues:

- Modeling of metallic oxide formation under high repetition rate fs laser irradiation.
- Real-time measurements of the changing optical properties of the metallic films during laser irradiation. This is essential for accurate modeling of oxide formation.
- Measuring of electrical and chromic properties of the synthesized oxides.
- The fs laser processing of the metallic thin films under different atmospheres must be continued since it offers a good potential for materials exhibiting novel features.
- Nonlinear optical effects of metallic oxide nanostructures offer new challenges and potential applications, so that it must be pursued.

Benefits

Both knowledge and expertise exchange between three academic institutions CICESE, UCR, UAEMex in two countries, have brought lots of benefits allowing the continuation of the collaboration and mobility between the participating research groups. Various graduate students have continued to enroll in our programs and the interaction is greater than ever. Drs. Camacho and Aguilar are constantly seeking for securing additional funding for the continuation of this and related research projects.

Issues to be faced

Intermittent and small amounts of funding make it difficult to retain students in the program, which affects the continuity of the research program. New joining students take time to catch up, especially if them do not overlap with the experienced students who already left. There exists a joint (USA-MEXICO) program funded by AFOSR-CONACyT, unfortunately our more recent proposal was rejected no matter we had a very productive and unique record within the program. Although we requested referee´s feedback it was not provided, making it difficult to assess possible weaknesses in our proposal.

References

[1] *“Laser-induced molybdenum oxide formation by low energy (nJ)-high repetition rate (MHz) femtosecond pulses”* M. Cano-Lara, **S. Camacho-Lopez**, A. Esparza-Garcia. M. A. Camacho-Lopez. *Opt. Mat*. **33**, 1648-1653 (2011).

[2] *“Influence of oxygen pressure on the fs laser- induced oxidation of molybdenum thin films”* N. Cuando-Espitia, J. Redenius, K. Mensink, M. Camacho-Lopez, **S. Camacho-Lopez**, G. Aguilar. *Opt. Mat. Express* **8**, 581-596 (2018).

[3] *“ZnO synthesized in air by fs laser irradiation on metallic Zn thin films”* Y. Esqueda-Barron, M. Herrera, **S. Camacho-Lopez**. *Appl. Surf. Sci.* **439**, 681-688 (2018).

[4] *“Second-harmonic generation of ZnO nanoparticles synthesized by laser ablation of solids in liquids”* I. Rocha-Mendozaa, **S. Camacho-Lopez**, Y. Y. Luna-Palacios, Y. Esqueda-Barrón, M. A. Camacho-López, M. Camacho-López, G. Aguilar. *Optics and Laser Technology* **99**, 118-123 (2018).