

Laser-induced periodic surface structures on bismuth thin films with ns laser pulses below ablation threshold

A. REYES-CONTRERAS,^{1,2} M. CAMACHO-LÓPEZ,^{2,8} S. CAMACHO-LÓPEZ,^{3,9}
O. OLEA-MEJÍA,⁴ A. ESPARZA-GARCÍA,⁵ J. G. BAÑUELOS-MUÑETÓN,⁶
AND M. A. CAMACHO-LÓPEZ⁷

¹Posgrado en Ciencia de Materiales, Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón y Tollocan, Toluca, 50110, México

²Laboratorio de Investigación y Desarrollo de Materiales Avanzados, Facultad de Química, Universidad Autónoma del Estado de México, Campus Rosedal, Km 14.5 Carretera Toluca-Atlaconulco, San Cayetano de Morelos, Toluca, 50295, México

³Departamento de Óptica, Centro de Investigación Científica y de Educación Superior de Ensenada, Carretera Ensenada-Tijuana 3918, Zona Playitas, Ensenada, Baja California, 22860, México

⁴Centro Conjunto de Investigación en Química Sustentable, Km 14.5 Carretera Toluca-Atlaconulco Campus UAEMéx "El Rosedal", San Cayetano-Toluca, 50200, México

⁵Fotofísica y Películas Delgadas, Departamento de Tecnociencias, Centro de Ciencias Aplicadas y Desarrollo Tecnológico, UNAM, Circuito Exterior s/n, Cd. Universitaria, 04510, México

⁶Materiales y Nanotecnología, Departamento de Tecnociencias, Centro de Ciencias Aplicadas y Desarrollo Tecnológico, UNAM, Circuito Exterior s/n, Cd. Universitaria, 04510, México

⁷Laboratorio de Fotomedicina, Biofotónica y Espectroscopía Láser de Pulsos Ultracortos, Facultad de Medicina, Universidad Autónoma del Estado de México, Jesús Carranza y Paseo Tollocan s/n, Toluca, 50120, México

⁸macamacholo@uaemex.mx

⁹camachol@cicese.mx

Abstract: We demonstrate the formation of laser-induced periodic surface structures (LIPSS) in bismuth (Bi) thin films by irradiation with nanosecond laser pulses. We report on the formation and the destruction of the LIPSS as a result of the delivered number of pulses; both the formation and destruction threshold were very well determined. Results show that the obtained LIPSS are perpendicular to the laser polarization, and their ripple periodicity is on the order of the irradiation wavelength. Although all the irradiation experiments were done in ambient air, Raman micro-spectroscopy indicates that the LIPSS are constituted by metallic bismuth, i. e. the LIPSS formation is oxidation free.

© 2017 Optical Society of America

OCIS codes: (350.0350) Other areas of optics; (350.3390) Laser materials processing; (310.0310) Thin films; (310.6628) Subwavelength structures, nanostructures.

References and links

1. G. F. Nordberg, Bruce A. Fowler and M. Nordberg, *Handbook on the Toxicology of Metals. Vol II: Specific Metals* (Elsevier 2015) Chap. 31.
2. L. Kumari, J.-H. Lin, and Y.-R. Ma, "Laser oxidation and wide-band photoluminescence of thermal evaporated bismuth thin films," *J. Phys. D Appl. Phys.* **41**(2), 025405 (2008).
3. J. C. G. de Sande, T. Missana, and C. N. Afonso, "Optical properties of pulsed laser deposited bismuth films," *J. Appl. Phys.* **80**(12), 7023–7027 (1996).
4. Y. Ahn, Y. H. Kim, S. I. Kim, and K. H. Jeong, "Thickness dependent surface microstructure evolution of bismuth thin film prepared by molecular beam deposition method," *Curr. Appl. Phys.* **12**(6), 1518–1522 (2012).
5. C. M. Bedoya-Hincapié, J. de la Roche, E. Restrepo-Parra, J. E. Alfonso, and J. J. Olaya-Florez, "Structural and morphological behavior of bismuth thin films grown through DC-magnetron sputtering," *Ing. Rev. Chil. Ing.* **23**(1), 92–97 (2015).
6. E. Camps, S. E. Rodil, J. A. Salas, and H. V. Estrada, "A detailed study of the synthesis of bismuth thin films by PVD-Methods and their Structural Characterization," in *Proceedings of Material Research Society Symposium*. **1477** 2012.
7. R. A. Ganeev, *Laser Surface Interactions* (Springer Netherlands, 2014).

8. M. Siegrist, G. Kaech, and F. K. Kneubühl, "Formation of a periodic wave structure on the dry surface of a solid by TEA-CO₂ laser pulses," *Appl. Phys. (Berl.)* **2**(1), 45–46 (1973).
9. A. K. Jain, V. N. Kulkarni, D. K. Sood, and J. S. Uppal, "Periodic surface ripples in laser-treated aluminum and their use to determine absorbed power," *J. Appl. Phys.* **52**(7), 4882–4884 (1981).
10. H. M. van Driel, J. E. Sipe, and J. F. Young, "Laser-induced periodic surface structures on solids: a universal phenomenon," *Phys. Rev. Lett.* **49**(26), 1955–1958 (1982).
11. J. E. Sipe, J. F. Young, J. S. Preston, and H. M. van Driel, "Laser-induced periodic surface structure. I. Theory," *Phys. Rev. B* **27**(2), 1141–1154 (1983).
12. J. F. Young, J. S. Preston, H. M. van Driel, and J. E. Sipe, "Laser-induced periodic surface structure. II. Experiments on Ge, Si, Al, and brass," *Phys. Rev. B* **27**(2), 1155–1172 (1983).
13. E. L. Gurevich and S. V. Gurevich, "Laser Induced Periodic Surface Structures induced by surface plasmons coupled via roughness," *Appl. Surf. Sci.* **302**, 118–123 (2014).
14. M. Huang, Y. Cheng, F. Zhao, and Z. Xu, "The significant role of plasmonic effects in femtosecond laser-induced grating fabrication on the nanoscale," *Ann. Phys.* **525**(1–2), 74–86 (2013).
15. S. Camacho-López, R. Evans, L. Escobar-Alarcón, and A. Miguel, "Camacho-Lopez and Marco A. Camacho-López, "Polarization-dependent single-beam laser-induced grating-like effects on titanium films," *Appl. Surf. Sci.* **255**(5), 3028–3032 (2008).
16. V. S. Mitko, G. R. B. E. Römerb, A. J. H. Veldb, J. Z. P. Skolskia, J. V. Obonad, V. Ocelikd and J. T. M. D. Hossond, "Properties of High-Frequency sub-wavelength ripples on stainless steel 304L under ultra-short Pulse Laser Irradiation," *Phys. Procedia* **12**, 99–104 (2011).
17. T. Hwang and C. Guo, "Angular effects of nanostructure-covered femtosecond laser induced periodic surface structures on metals," *J. Appl. Phys.* **108**(7), 073523 (2010).
18. B. Tan and K. Venkatakrishnan, "A femtosecond laser-induced periodical surface structure on crystalline silicon," *J. Micromech. Microeng.* **16**(5), 1080–1085 (2006).
19. M. Sanz, E. Rebollar, R. A. Ganeev, and M. Castillejo, "Nanosecond laser-induced periodic surface structures on wide band-gap semiconductors," *Appl. Surf. Sci.* **278**, 325–329 (2013).
20. X. J. Wu, T. Q. Jia, F. L. Zhao, M. Huang, N. S. Xu, H. Kuroda, and Z. Z. Xu, "Formation mechanisms of uniform arrays of periodic nanoparticles and nanoripples on 6H-SiC crystal surface induced by femtosecond laser ablation," *Appl. Phys., A Mater. Sci. Process.* **86**(4), 491–495 (2007).
21. M. Castillejo, T. A. Ezquerro, M. Martín, M. Oujja, S. Pérez, and E. Rebollar, "Laser nanostructuring of polymers: Ripples and applications," in *Proceedings of AIP Conference*. 1464, 372–380 (2012).
22. M. Berta, E. Biver, S. Maria, T. N. T. Phan, A. D'Aleo, P. Delaporte, F. Fages, and D. Gigmes, "Nanosecond laser-induced periodic surface structuring of cross-linked azo-polymer films," *Appl. Surf. Sci.* **282**, 880–886 (2013).
23. M. A. Zepeda, M. Picquart, and E. Haro-Poniatowski, "Laser Induced Oxidation Effects in Bismuth Thin Films," in *Proceedings of Material Research Society Symposium*. 1477 (2012)
24. J. A. Steele and R. A. Lewis, "In situ micro-Raman studies of laser-induced bismuth oxidation reveals metastability of β -Bi₂O₃ microislands," *Opt. Mater. Express* **4**(10), 2133–2142 (2014).
25. A. Reyes-Contreras, M. Hautefeuille, A. Esparza-García, O. Olea-Mejía, and M. A. Camacho-López, "Inexpensive laser-induced surface modification in bismuth thin films," *Appl. Surf. Sci.* **336**, 212–216 (2015).
26. A. Venegas-Castro, A. Reyes-Contreras, M. Camacho-López, O. Olea-Mejía, S. Camacho-López, and A. Esparza-García, "Study of the integrated fluence threshold condition for the formation of β -Bi₂O₃ on Bi thin films by using ns laser pulses," *J. Opt. Laser Technol.* **81**, 50–54 (2016).
27. A. L. J. Pereira, J. A. Sans, R. Vilaplana, O. Gomis, F. J. Manjón, P. Rodríguez-Hernández, A. Muñoz, C. Popescu, and A. Beltrán, "Isostructural Second-Order Phase Transition of β -Bi₂O₃ at High Pressures: An Experimental and Theoretical Study," *J. Phys. Chem. C* **118**(40), 23189–23201 (2014).
28. J. S. Lannin, J. M. Calleja, and M. Cardona, "Second-order Raman scattering in the group-Vb semimetals: Bi, Sb, and As," *Phys. Rev. B* **12**(2), 585–593 (1975).
29. J. Toudert, R. Serna, I. Camps, J. Wojcik, P. Mascher, E. Rebollar, T. A. Ezquerro, "Unveiling the Far Infrared – to – Ultraviolet Optical Properties of Bismuth for Application in Plasmonics and Nanophotonics," *J. Phys. Chem. C*. **Just Accepted Manuscript**. DOI: 10.1021/acs.jpcc.6b10331.

1. Introduction

Bismuth (Bi) is an interesting material for technology due to its thermal and electrical properties. Ought to this reason, bismuth is used in thermoelectric applications. Thanks to its low melting point (271 °C), bismuth is commonly used in low melting alloys [1]. At the same time, bismuth is an ideal material to be laser processed since it posses a low laser transformation threshold [2]. It must be noticed that many of its unique properties such as high magnetoresistance, can only be observed at very small-scale sizes. For this reason, in the last two decades there has been a major interest for obtaining nanosized bismuth, in the form of thin films. Bismuth can be obtained in its thin film form by PVD methods like: thermal evaporation, laser ablation, molecular beam epitaxy and magnetron sputtering [2–6]. The

obtained thin films show crystallographic and morphological features that very much depend on the synthesis method.

Laser irradiation is a versatile and powerful tool for micro- and nano-structuring of materials. The interaction of laser radiation with solid materials has been extensively investigated on different materials [7]. The exposure of a solid surface to a single laser beam gives place to the formation of ripple-like periodic structures, denominated LIPSS. LIPSS earliest reports in the literature are from more than three decades ago by Siegrist et al. [8] for quartz and copper, Jain et al. [9] for aluminum, van Driel et al. [10] and Sipe et al. [11] for theory, and Young et al. [12] for semiconductors (Ge, Si) and metals (aluminum and brass). Since then, the generation of LIPSS has gained much attention due to the fundamental challenges of understanding, for instance, the origin of LIPSS formation, which up to date is still controversial. LIPSS are also attractive for potential applications, which include a rapid fabrication method of diffraction gratings; recently it has also been suggested that LIPSS could be used as plasmonic structures [13, 14]. LIPSS can be induced both in bulk and thin films materials as it has been extensively reported in the literature for a wide variety of materials including metals, semiconductors, dielectrics and polymers [15–22]. Either CW or pulsed lasers from microseconds to femtoseconds, at wavelengths in the UV, VIS or IR ranges have been used to generate LIPSS.

It is well known that when nanosecond laser irradiation is incident normal to the surface of the sample, the ripple period of the LIPSS is on the order of the laser wavelength. In general, the ripples have a period, which depends on several factors such as the laser wavelength, the angle of incidence and the material refractive index [12]. M. Sanz et al. have reported a study of LIPSS on wide band-gap semiconductors [19]. They focused their study on varying the per pulse laser fluence and the delivered number of pulses. The laser irradiation experiments were carried out on the following semiconductors InP, GaP, GaAs and SiC by using linearly polarized UV (266 nm) laser pulses of 6 ns duration. They estimated the threshold conditions for obtaining LIPSS, according to their results the per pulse laser fluence and the number of pulses necessary to form the LIPSS in each one of the tested materials are: InP (125 mJ/cm², 200 pulses), GaP (125 mJ/cm², 300 pulses) and GaAs (150 mJ/cm², 200 pulses). LIPSS were not observed to form in SiC. The LIPSS were formed with an orientation perpendicular to the laser polarization, having a ripple period on the order of laser wavelength.

Bismuth thin films have been irradiated with CW laser to obtain Bi₂O₃ [2,23,24]. A. Reyes et al. recently demonstrated low power laser-induced microbumps on a bismuth thin film by using microsecond laser pulses [25]. In a previous work, we have reported a study of laser-induced bismuth oxidation under ns pulsed laser irradiation at 1064 nm; the threshold (number of pulses) for initiating the oxidation process was well determined [26]. We showed that the surface morphology and the composition of the obtained bismuth oxide thin film, strongly depend on the number of delivered laser pulses.

In this work we present the influence of the number of laser pulses on both the formation and the destruction of LIPSS in bismuth thin films. The irradiation experiments were carried out on a very simple way by using the straight output of a Nd:YAG nanosecond laser at 532 nm. Results show that just a dozen of laser pulses are required for LIPSS formation. Hundreds of laser pulses give rise to the destruction of the LIPSS and subsequently to a laser-induced oxidation process, where the β -Bi₂O₃ crystalline phase forms. In fact, several domains were identified were LIPSS start forming, optimize and then deteriorate to finally be destroyed. It is worth noting that from the best of our knowledge this is the first time that LIPSS are generated in bismuth thin films.

2. Experimental

The bismuth thin films were grown onto glass substrates by the DC-sputtering technique using Argon to sputter a bismuth target (99.99% purity from Lesker). The deposition time

was 10 minutes, using a 22 mBar pressure and a discharge power of 10 W. The film thickness was measured to be 500 nm by using a profilometer. The as deposited Bi films showed a roughness on the order of 35 nm, which was measured through AFM.

The experimental setup we used to print LIPSS on the bismuth thin films is very simple, as it is shown in Fig. 1. The bismuth thin film sample was mounted on a translation stage to manually choose each site to be irradiated. The second harmonic emission of a 7 ns pulsed Nd:YAG laser (Minilite II, Continuum) was used to irradiate the bismuth thin films in atmospheric air. These experiments were performed with linearly polarized unfocused laser pulses (2 mm beam size FW1/e^2), the irradiation was set at nearly normal incidence on the sample (the 5° angle is to prevent back reflection to the laser cavity). Since the per pulse laser fluence necessary to remove (laser ablation threshold) the bismuth thin film was determined to be 105 mJ/cm^2 , all the irradiations were carried out at 80 mJ/cm^2 . The number of laser pulses delivered on the samples was varied as follows: 1, 10, 20, 30, 40, 50, 60, 120 and 600 pulses at 1 Hz repetition rate. An additional irradiation delivering 6000 pulses at 15 Hz was also performed.

With the aim to perform a full characterization of the laser irradiated regions on the Bi thin film surface we used: Optical Microscopy (BX41, Olympus), Scanning Electron Microscopy (Jeol JSM6510 LV), Atomic Force Microscopy (Park Scientific Instruments AutoProbe Mod CP), and microRaman spectroscopy (HR-800 LabRaman, Jobin-Yvon-Horiba).

The microRaman spectra were collected in the $50\text{--}500 \text{ cm}^{-1}$ range (3 cm^{-1} spectral resolution) using as the light source a 0.5 mW CW Nd:YAG laser ($\lambda = 532 \text{ nm}$). The 532 nm laser beam was focused on the sample with a 50X objective lens (to a spot size of $8 \mu\text{m}$ FW1/e^2), which is also used for collecting the scattered light. 50 acquisitions were averaged with an exposure time of 5 s each to obtain every single Raman spectrum.

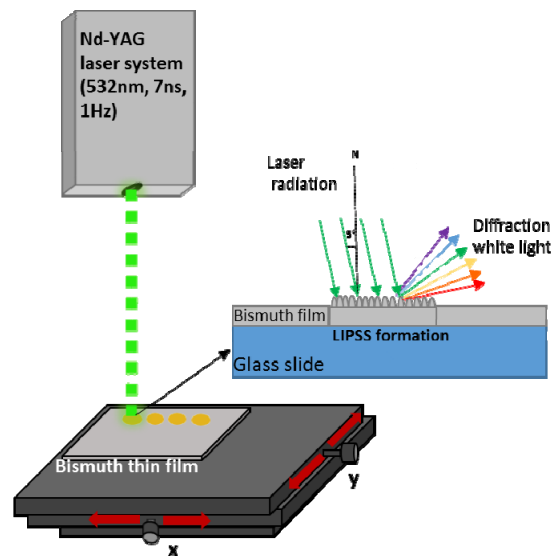


Fig. 1. Experimental setup to generate LIPSS in bismuth films.

3. Results and discussion

Figure 2 shows a photograph of a set of the irradiated regions on a Bi thin film. When the sample is viewed under white light illumination, the irradiated region displays a specific color depending on the viewing angle. The region labeled 1, which was irradiated with a single laser pulse does not show any optical surface modification. For a spot irradiated with 10 pulses the film turns darker than it looks like initially. In contrast, for 20, 30, 40 and 50

pulses, uniform bright green colored marks are displayed. While for 60 and 120 pulses, the uniform green colored marks develop into green-yellow marks with some darkening on the center of the spot. Finally, for 600 and 6000 delivered pulses the film changes its optical appearance significantly by turning up gray with a dark outer edge. The progressive changes on the surface of the bismuth thin film due to the irradiation exposure time (increasing number of laser pulses) are quite clear, an optical modification process occurs with the number of laser pulses. This is due to the presence of well-formed LIPSS within the irradiated spots for the range of 20-50 pulses, which will be confirmed and carefully analyzed in the following sections.

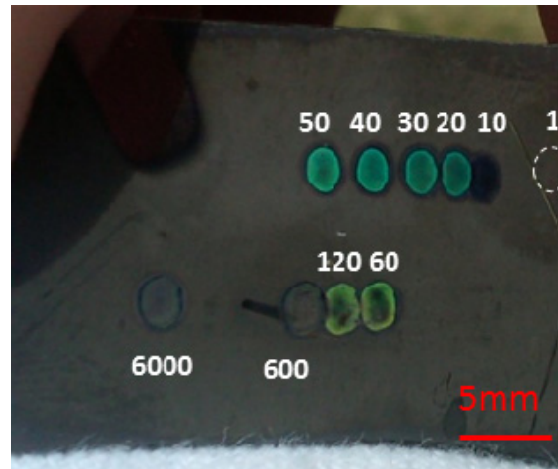


Fig. 2. Photograph of marks generated on a Bi thin film after its irradiation with ns-laser pulses, the labels indicate the number of delivered pulses.

Figure 3 shows a set of photographs (I-V) from the same Bi thin film sample showed in the Fig. 2, taken at different viewing angles. The green spots image corresponds to a normal to the surface view, while the other colored spots images are viewed by tilting the sample in steps of approximately 6° . As the film is tilted the typical effect of a diffraction grating is observed, i. e. a spectral decomposition from red to blue takes place in a lateral angular interval of 30° . As already shown in Fig. 2, a uniform coloration is obtained for irradiated regions with 20, 30, 40 and 50 pulses. While the spots irradiated with 60 and 120 laser pulses present partial darkening inside the colored area, those spots irradiated with 600 and 6000 laser pulses do not display any light diffraction. Notice that if the sample is rotated by 90° around the normal to the sample, while the incidence direction of the white light is kept the same, the diffraction effect disappears. This is due to the well-defined and oriented array of LIPSS [15].

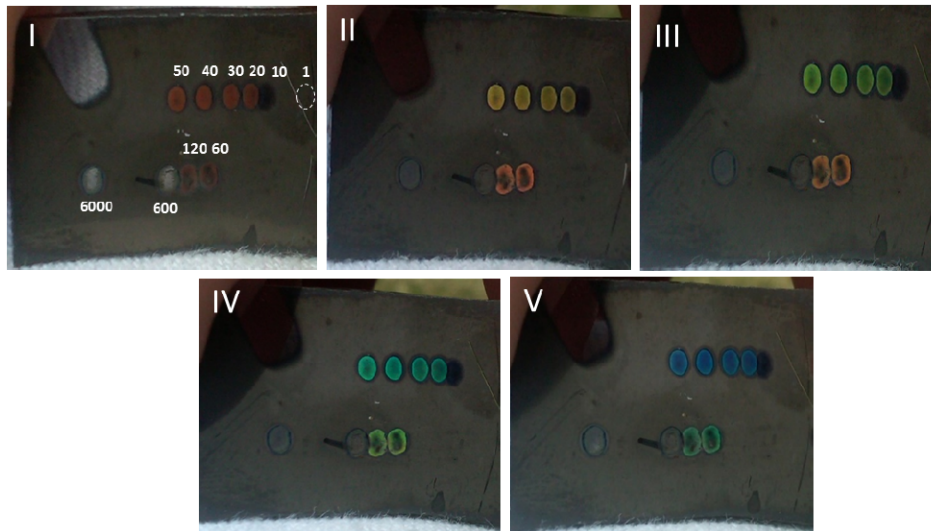


Fig. 3. Diffraction of white light off the irradiated spots (LIPSS regions). I, II, III, IV and V photographs were taken at different viewing angles.

Figure 4 shows the Optical (left) and SEM (right) images of the as-deposited and the laser irradiated regions on the bismuth thin film surface. The SEM micrographs show the center of the irradiated regions. As shown in Fig. 4(a), sub-micrometer grains constitute the surface of the as-deposited Bi thin film; this is the typical morphology of the bismuth films grown by sputtering [26]. This kind of morphology gives an opaque appearance of the thin film surface when seeing in reflection mode. Figure 4(b) shows the bright-green coloured mark on the irradiated zone, a series of well-defined ripples can be clearly identified within that mark by SEM. The ripples orientation is perpendicular to the incident laser polarization. In 4(c) the coloration has faded away and the ripples have been lost; instead, agglomerated material is formed in the irradiated zone. During this process crystalline bismuth oxide is formed as it is shown by microRaman spectroscopy.

The LIPSS formation and the subsequent oxidation for a large number of delivered laser pulses is dominated by a thermal effect. On the one hand, the optical penetration, which is the inverse of the optical absorption coefficient, is only of about 15 nm (for bismuth $\alpha = 6.6 \times 10^5 \text{ cm}^{-1}$ @532 nm). The thermal length can be calculated as $L_{\text{thermal}} = (2D\tau)^{1/2}$ with D the thermal diffusion coefficient and τ the laser pulse duration. For our case the thermal length is of 345 nm. This means that the film gets heated beyond two thirds of its thickness, giving rise to melting and then LIPSS formation on rapid cooling.

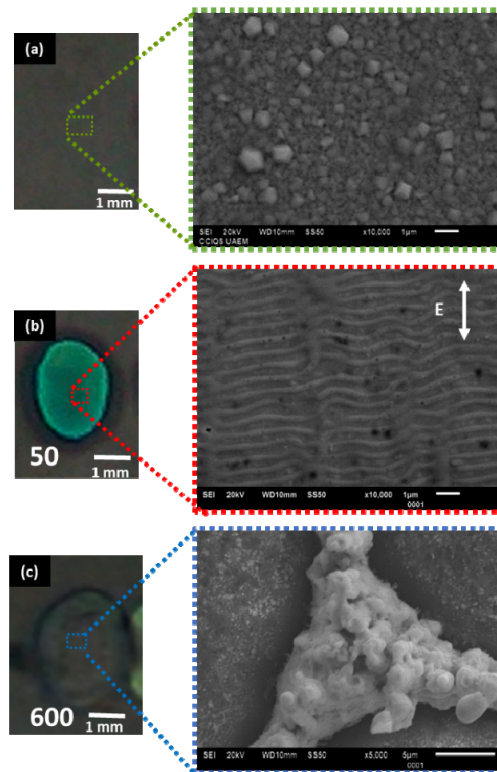


Fig. 4. Optical and SEM images of (a) as-deposited bismuth film, (b) spot with 50 pulses and (c) spot with 600 pulses.

Figure 5 shows the Raman spectra of the as-deposited and laser irradiated bismuth thin film for 50 and 600 pulses. The Raman spectra 5(a) and 5(b) correspond to the as-deposited thin film and the irradiated region with 50 pulses, respectively. These spectra have three characteristic peaks at 65 , 94 , and 186 cm^{-1} , which are in good agreement with those reported by Kumari et al. [2] and M. Zepeda et al. [23], for thermal evaporated bismuth thin films. A further report by Steele et al. shows that the bismuth Raman spectrum has a band located at 188 cm^{-1} . The spectrum 5(c) for the sample irradiated with 600 pulses (re-solidified material shown in SEM micrograph 4(c)), have peaks at 68 , 86 , 94 , 123 , 182 , 313 , 324 and 467 cm^{-1} which correspond to the $\beta\text{-Bi}_2\text{O}_3$ crystalline phase, indicating that the laser irradiated region is composed by crystalline bismuth oxide, in contrast to the LIPSS which remain just bismuth. The observed Raman features are in good agreement with those reported by Pereira et. al. for $\beta\text{-Bi}_2\text{O}_3$ [27]. It is important to notice that LIPSS have fully disappeared for the irradiated region with 600 pulses. Similar features have been identified for the mark irradiated with 6000 laser pulses.

The Raman bands located at 65 and 94 cm^{-1} are assigned to Bi-Bi vibrations and lattice vibrations, respectively [23]. The weak band at 186 cm^{-1} is a second order band (J. S. Lannin et al. [28]). There is a small band between 65 and 94 cm^{-1} , which is located at 84 cm^{-1} , this band is due to oxygen on the bismuth film without the formation of $\beta\text{-Bi}_2\text{O}_3$ (see spectrum d, in Venegas Castro et al. [26]). The weak band at 84 cm^{-1} evolves upon laser-induced oxidation, its intensity increases and shifts towards 86 cm^{-1} as it is observed in 5(c). When the laser-irradiated material is totally oxidized and crystallized, this band shifts to 89 cm^{-1} being the most intense band in the Raman spectrum of $\beta\text{-Bi}_2\text{O}_3$ (Pereira et al. [27]). We must point out that the degree of oxidation and crystallization can be finely controlled by means of the delivered number of laser pulses.

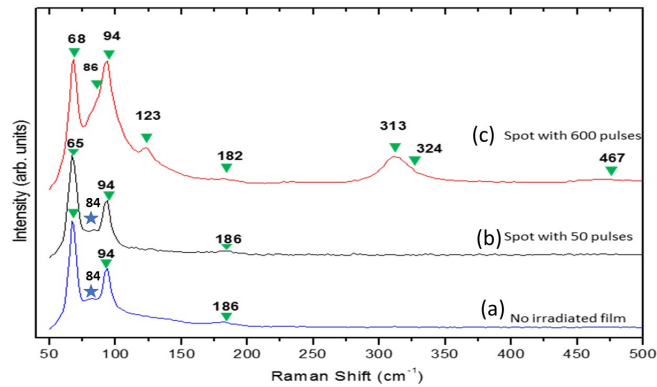


Fig. 5. Raman Spectra for the (a) non irradiated bismuth film, (b) irradiated spot with 50 pulses, (c) irradiated spot with 600 pulses.

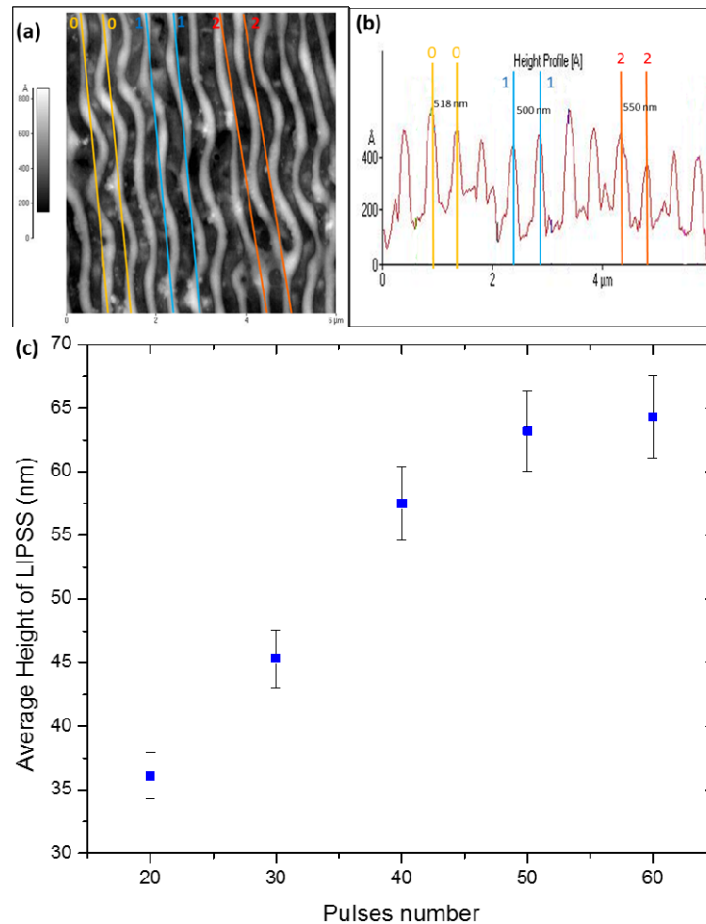


Fig. 6. AFM of LIPSS for 50 laser pulses. a) AFM image, b) LIPSS profile, (c) ripples height as a function of the number of laser pulses.

Figure 6(a-b) show an AFM micrograph of the LIPSS and its cross section profile. The average height of the ripples as a function of the number of laser pulses for the regions irradiated with 20, 30, 40 and 50 pulses is shown in 6(c). The LIPSS ripple period, which was obtained for three different pairs of ripples within the same spot, is 518, 500 and 550 nm (Fig.

6(b)); notice that when averaging over a number of LIPSS spots the period averages 517 ± 30 nm, e. i. it is close to the laser wavelength (532 nm). The ripples height grows linearly with the number of pulses for the range 20-40, and then it gets plateau to reach 65 nm. Hence it can be established that changing the delivered number of pulses can finely control the ripples height.

In Fig. 7(a) we summarize the laser-induced effects on the bismuth thin films presented in this work. Our results clearly indicate that: the Bi thin film does not become optically affected under a single pulse irradiation. When 2 and up to 10 pulses are delivered a darkening effect takes place on the irradiated spot. The LIPSS formation starts at the center of the irradiated region and it expand radially out for 11 and up to 20 pulses. From 21 to 55 pulses the LIPSS formation region grows and it reaches to the spot edge covering the whole irradiated cross section. A gradual degradation of the LIPSS starts at 60 pulses onwards until total destruction of the LIPSS occurs, then giving rise to an oxidation process of the irradiated bismuth. Figure 7(b) shows a photograph of a series of bismuth thin film regions that were irradiated from 1 to 55 pulses at 80 mJ/cm^2 per pulse.

The results of LIPSS formation on bismuth thin films presented here gain relevance in view of the recent work reported by J. Tourdert et al [29], where they present a detailed study of bismuth optical properties aiming applications in plasmonics and nanophotonics. It is well known that plasmonic effects can be excited in well-defined nanostructures, periodic surface arrays are ideal for such a purpose. Therefore the bismuth LIPSS demonstrated in this work are good candidates for plasmonic studies. It is worth noting that the method for obtaining LIPSS is both much more simple and rapid than, for instance, electron or ion beam lithography which are nowadays the standard methods for creating plasmonic nanostructures.

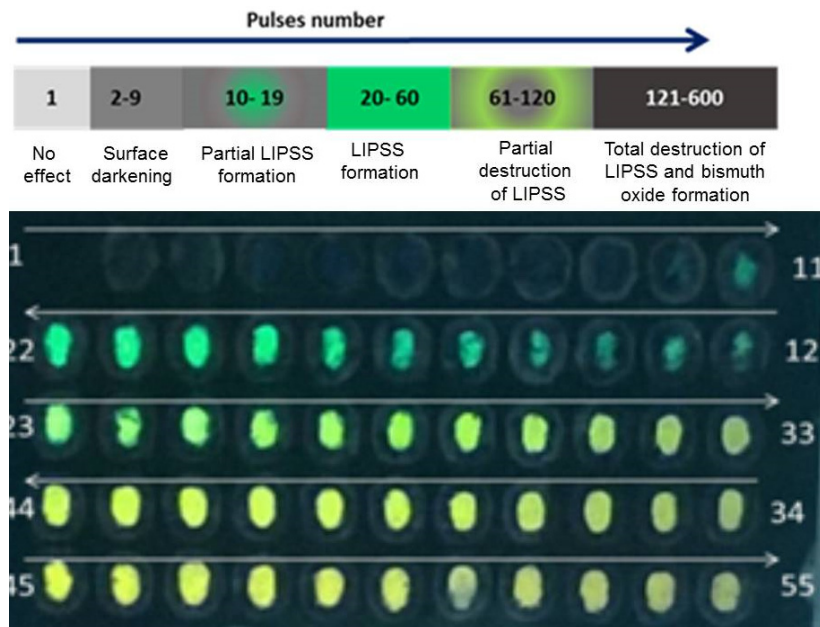


Fig. 7. (a) Phenomenological description of the laser-induced effects on the Bi thin film as a function of number of delivered laser pulses, (b) Photograph showing a set of irradiated spots, on the Bi thin film, for 1 and up to 55 delivered laser pulses at 80 mJ/cm^2 .

4. Conclusions

We demonstrate, for the first time to the best of our knowledge, laser-induced periodic surface structures (LIPSS) on bismuth thin films. Our results clearly show that it is possible to generate LIPSS on Bi thin films by using nanosecond laser pulses with fluence 20% below

the ablation threshold. At 80 mJ/cm^2 only a few tens of laser pulses are required to optimally generate LIPSS. The orientation of the obtained LIPSS is always perpendicular to the polarization of the incident laser beam, and their ripple periodicity is on the order of the irradiation wavelength, or even shorter, as it would be expected for the formation at normal incidence of this kind of LIPSS. We have found that there is a well-suited range of delivered pulses for optimal LIPSS formation and subsequent destruction. Raman characterization proved that the LIPSS are still constituted by bismuth, while over exposing (delivering more than 600 pulses) would cause laser-induced oxidation to form large micron sized $\beta\text{-Bi}_2\text{O}_3$ agglomerates. LIPSS on bismuth thin films could find applications in many technological fields such as surface coloring, color coding, polarization sensitive displays, surface texturing, and rapid and cost effective fabrication of diffraction gratings for miniaturized spectrometry devices. Plasmonic nanostructures based on bismuth LIPSS are also an up coming field of study, according to the new reports on the optical properties of bismuth for an spectral range from far IR to UV.

Funding

Air Force Office of Scientific Research (AFOSR) (FA9550-15-1-0142).

Acknowledgments

Adela Reyes-Contreras thanks CONACyT for supporting her on the postgraduate program at the MSc level. Authors thank Dr. Enrique Camps for making available his Raman facility.