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Self-assembled microcones generated on solid surface through pulsed laser irradiation

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ABSTRACT

We present here our results on surface micro-structuring via nanosecond pulsed laser irradiation of Titanium and Stainless Steel cathode samples. Laser based surface micro-structuring leading to formation of self-assembled micro-tips can potentially enhance field emission efficiency of such surface treated cathodes. Microstructure of the laser treated surfaces has been observed under a Scanning Electron Microscope (SEM) and SEM images were further analyzed using software attached with Optical Microscope. To study the effect of laser fluence on developed surface microstructure, the target surface was irradiated in different regions with laser beams at varying laser fluence levels ranging from 2-10 J/cm^2 for a period of 1 to 15 minutes corresponding to 600 to 9000 laser pulses. Mean height of the generated micro-cones was observed to increase from 17 to 30µm on increasing number of irradiating laser pulses from 3000 to 9000 in case of Stainless Steel samples. In case of laser treated Titanium average periodicity of generated self-assembled micro-cones decreased from 10.8µm to 6.5µm when laser fluence was increased from 5 to 10J/cm^2 with a total of 600 laser pulses used for irradiating the sample. Copyright © 2013 VBRI press.

Keywords: Laser surface micro-structuring; self-aligned microcones; stainless Steel; titanium.

Sucharita Sinha has carried out extensive theoretical and experimental investigations on nonlinear optical phenomena in laser-atom interaction, photo-thermal properties of tunable-laser media and developed novel attractive means to improve the quality of high-average-power laser beams. She received her Ph.D degree in Physics from Mumbai University in 1990 for her work on Optically Pumped Molecular Gas Lasers. Her work on theoretical analysis of quantum size effects in composite materials and semiconductor nanospheres resulting in tailored optical absorption spectrum is widely cited in literature. Among her current research interests, in the field of laser material ablation process she has demonstrated a unique dry laser etching technique required for metallographic examination of nuclear fuel pellets, and laser based surface micro-structuring of electron emitters leading to vastly improved field-emission properties.

Introduction

Generation of laser induced surface micro-structures, either, in a reactive gas atmosphere, or under vacuum has been extensively investigated largely on account of its application potential for a wide range of applications [**1-6**]. Such surface texturing achieved via laser treatment essentially provides a means of tailoring surface properties including mechanical and wetting characteristics [**7**], optical [**8-9**], and electronic behaviour [**10-12**]. Although, various conventional techniques ranging from sand blasting to chemical etching and electrochemical treatment exist for surface treatment, laser based treatment has its unique associated advantages. Typical characteristics of laser light, namely, high energy density and directionality ensure excellent spatial, as well as, temporal resolution that can be achieved through laser processing. In addition, laser treatment is a highly reproducible and contamination free process having remote processing capability.

A novel approach at fabricating a cold cathode possessing high electron emission competence at low operating voltages as compared to conventional single micro-tip cathodes is to use laser based surface micro-structuring resulting in generation of an array of micro-structures on the planar cathode surface [**11**]. Micro-tips formed in this manner protrude above the solid surface. Spatial period of these self assembled structures have been observed to be of an order of magnitude higher than the laser wavelength [**13**]. Formation of these surface structures has been attributed to development of instabilities at the interface between the melt and the plasma of optical breakdown. Capillary waves on the melt surface have been suggested to serve as the initial inhomogeneity of the surface relief [**14**]. Such laser generated surface micro-structures on Silicon have shown a low-threshold field emission behaviour [**11**].

Our investigations on picosecond laser surface treatment of sintered Lanthanum Hexaboride pellets resulting in formation of micro-columnar surface features having sub-micron tip diameter have confirmed enhanced field emission electron emission capability [**15, 16**]. In this paper we present our results on nanosecond laser based surface treatment of Titanium and Stainless Steel electrodes resulting in formation of self-assembled micro-conical surface structures.

Experimental

A set of samples of Titanium and Stainless Steel (SS) were exposed to radiation from a nanosecond pulsed Nd:YAG laser either in air or in low vacuum (10^{-1} to 10^{-2}mb). Second harmonic radiation at 532nm delivered by a pulsed Nd:YAG laser having 6ns (FWHM) pulse duration, operating at 10Hz repetition rate was focused onto the surface of the solid sample. The irradiating laser beam having a Gaussian spatial distribution was focused to a spot of around 400μm diameter. In order to surface treat a larger area of the sample the processing laser beam was translated by a pre-set amount thereby enabling laser surface irradiation of the entire sample surface. Surface morphology of the laser treated surface was studied using a Scanning Electron Microscope (SEM).

Development of instability leading to formation of such self-assembled micro-cones is not a single laser pulse effect. In fact, such surface features have been reported to require a sufficiently high number of laser shots, and a certain minimum level of laser fluence for these to be formed [**17**]. However, despite extensive research, formation of surface micro-structures with multiple laser pulses is yet to be fully understood [**18**]. We have carried out a detailed parametric study to determine the effect of laser parameters such as, number of laser shots and the laser fluence, on generation of these micro-conical structures on samples of Titanium and SS. While imaging the laser treated surface with a SEM the sample surface was inclined at $30\text{-}40^0$ with respect to the horizontal. Viewing the laser treated surface at an angle allowed us to clearly image the generated surface micro-cones. SEM images were then analyzed using a Leica Qwin software attached to a Leica Optical Microscope [Leica DM ILM Inverted Microscope] in order to characterize the surface features, including height, and tip diameter of the generated micro-cones, as well as, their periodicity.

In order to investigate effect of increasing laser fluence on formed surface micro-structures, the laser fluence was varied over 2 - 10J/cm^2 keeping the irradiation time duration and thus the total number of laser pulses irradiating the sample surface fixed. Dependence of developed surface micro-structures on the cumulative number of laser pulses used for irradiating sample surface was also investigated for both Titanium and SS samples.

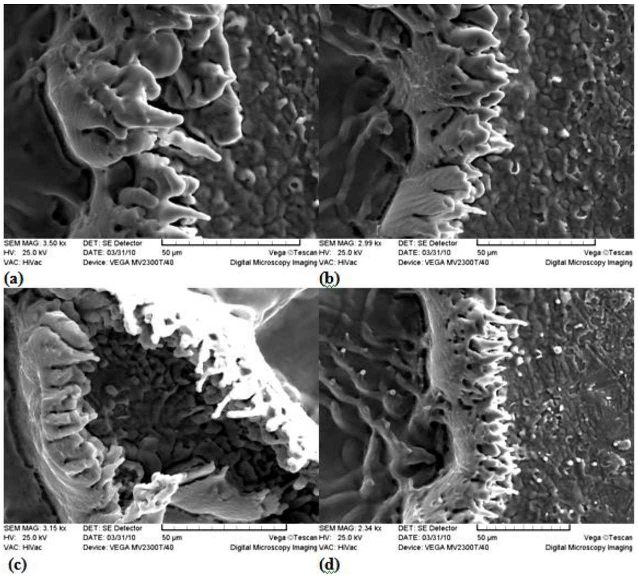

Fig. 1. SEM image of laser treated region showing formation of self-assembled micro conical structures on Titanium sample. Laser treatment done with 600 laser pulses at fluence levels of; (a) 5J/cm^2, (b) 6J/cm^2, (c) 8J/cm^2, and (d) 10J/cm^2, respectively.

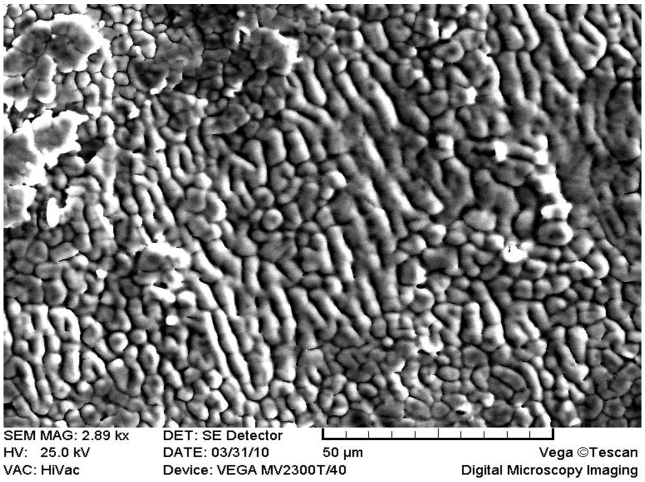

Fig. 2. SEM image of Titanium sample laser treated with laser fluence of 1J/cm^2 and irradiation with 600 laser pulses.

Results and discussion

Laser surface treated Titanium and SS samples when viewed under SEM clearly revealed formation of self-assembled micro-conical structures. Also, axes of these self-assembled micro-structures were observed to be oriented along the direction of the incident laser beam. However, such surface micro-structures were formed reproducibly only when laser irradiation was done at an appropriate level of laser flux and employing multiple number of irradiating laser pulses. In **Fig. 1a-1d** are shown SEM images of typical laser treated regions of Titanium target when irradiated with 600 pulses of laser radiation with incident fluence varied from 5J/ cm^2 to 10J/cm^2. Periodicity or separation between these micro columnar tips decreased from an average value of 10.8μm to 6.5μm as the incident space averaged laser fluence was increased from 5J/cm^2 to 10J/cm^2 with 1minute of laser irradiation, i.e. a total of 600 laser pulses. Titanium samples when irradiated with laser fluence of 1J/cm^2 resulted in formation of surface ripples (**Fig. 2**) although micro-cones were not formed even when irradiation time was extended to beyond 2minutes i.e., in excess of 1200 laser pulses irradiated Titanium sample surface. Such surface ripples were, however, not observed with single laser pulse irradiation. This implies that these highly oriented surface features are a result of a collective mechanism and associated feedback evolving out of irradiation by a series of laser pulses. Also, the smooth surface of the generated micro-cones suggests melt displacement as the dominant mechanism primarily responsible for their formation, rather than laser induced evaporation and re-deposition of target material.

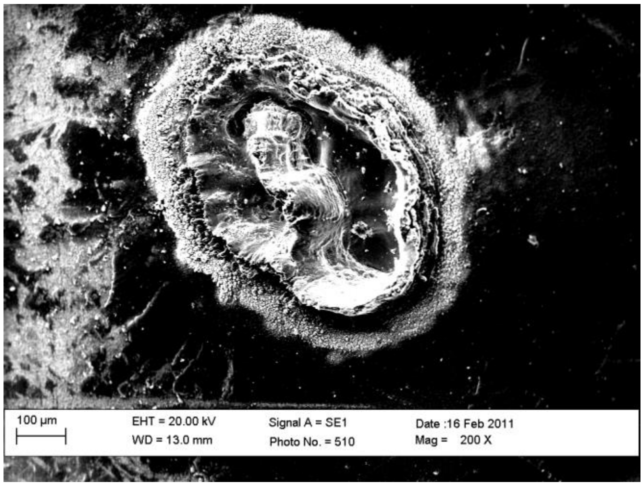

Fig. 3. SEM image of laser treated spot on Stainless Steel cathode surface irradiated with 3000 laser pulses at a fluence level 6 J/cm^2.

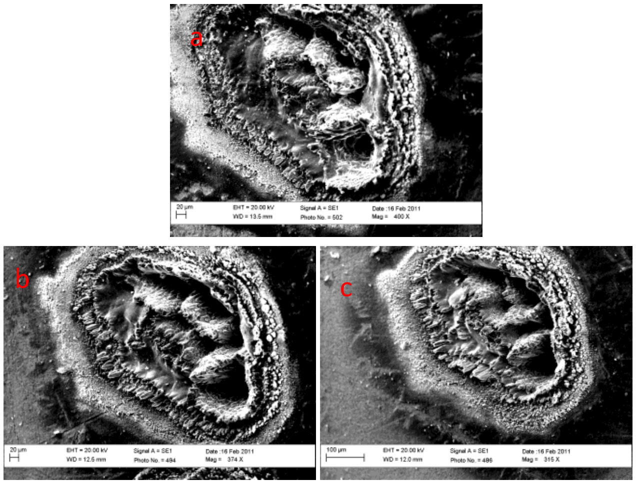

Fig. 4. SEM image of laser treated spot on SS target using (a) 3000, (b) 6000, and (c) 9000 laser pulses, at laser fluence level of 2 J/cm^2, respectively.

Typical SEM images taken of laser treated SS target indicated that for space averaged fluence levels of 4 - 6J/cm^2 prominent craters are formed in the central region of the laser irradiated spot (**Fig. 3**). In order to minimize such crater formation average laser fluence was restricted to 2J/cm^2 while investigating micro-structuring of the SS target via laser irradiation. **Fig. 4**(a,b,c) show SEM images of laser treated spots on the SS target surface when irradiated with 3000, 6000 and 9000 laser pulses at space averaged laser fluence of 2J/cm^2.

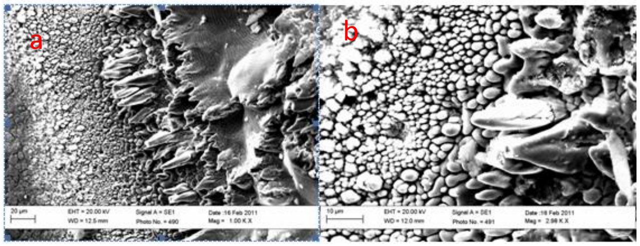

Fig. 5. SEM images taken at higher magnification: (a)1000X and (b) ~ 3000X; of region close to periphery of the laser treated spot on SS target corresponding to ~9000 laser pulses with fluence of 2J/cm^2.

From these **Figs.** it is evident that micro-cones with high aspect ratio have been developed in the laser irradiated surface region, particularly close to the periphery of the treated spot. In **Fig. 5** (a and b) are shown generated micro-cones when the target surface was imaged at higher magnification, 1KX and ~3KX, respectively. **Fig. 5b** is a SEM image taken of a typical region lying close to the edge of the irradiated spot. SEM image 5b reveals that in this particular region, which is farther away from region where sharp cones have been formed, surface ripples and periodic structures have been developed, similar to those that had been observed in the case of Titanium surface for a space averaged laser fluence level of 1J/cm^2. This is likely due to the fact that the laser fluence incident on this region is not high enough to develop sharp cones.

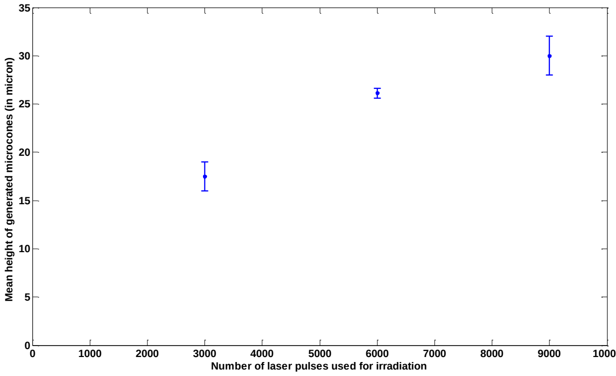

Fig. 6. Variation of mean height of the generated micro-cones on SS surface with number of irradiating laser pulses.

Analysis of the SEM images using Leica Qwin software revealed that mean height of the grown micro-cones in peripheral region increased with increasing number of incident laser pulses. The observed variation of mean height of the generated micro-cones with number of laser pulses used for irradiation is shown in **Fig. 6**. As the number of irradiating laser pulses increased from 3000 to 6000, estimated mean height of the developed microcones increased from 17µm to 26µm. Further, when the target surface was irradiated by 9000 laser pulses, mean height of the microcones rose to 30µm. While, initial growth of micro-cones with increasing number of laser pulses was rapid, subsequently there is a slowing down in this growth and height of individual cones tends to saturate. These observations are in agreement with those reported for micro-structure evolution of laser exposed Silicon targets both with nanosecond and femtosecond laser pulses [**13, 18**].

Our observations on growth of micro-columns with increasing number of laser pulses confirms that a certain minimum number of laser pulses at a particular laser fluence level are needed to stimulate formation of an array of micro-columns. For instance, in case of Titanium even with 1200 pulses at an energy density of 1J/cm ^{2} very few micro-cones were detected. Formation of micro-cones always takes place preferentially on the edges of pits and craters. Formation of crater in the central region of the laser irradiated spot is on account of localized high fluence zones within the laser beam. This leads to enhanced ablation and material ejection and subsequent re-deposition at the crater walls. In the border or periphery region of this crater microcolumns are packed closely while near the centre of the irradiated spot micro-columns are wide and tall, but far apart.

The mechanism of formation of such surface features is different from one involving erosion resistant tips since the observed column growth reported here occurs above the original surface. A mechanism solely based on material removal by selective ablation cannot explain formation and evolution of these structures as they protrude very significantly above the initial surface [**6**]. Melt displacement has been suggested to be a possible mechanism for generation of self assembled microcones on target surface upon irradiation with laser pulses [**5, 6**]. Transport of surface material to tips of these micro-cones i.e. from base to tip of microcones, can occur essentially via flow of liquid pool during laser irradiation. When the laser beam is incident on target surface, melting of target occurs in addition to material being ablated from some areas. Non-uniform heating of the molten pool tends to accumulate liquid in one region as against another, the driving force in this case being a gradient in surface tension generated by thermal gradients in the liquid pool.

Inherent surface irregularities present on the original untreated target surface leads to a non-uniform temperature distribution developing on laser irradiation. With the laser beam depositing energy to the target surface, melting of the surface layer occurs. Non-uniformity in temperature and associated temperature gradient in the molten surface layer of the target gives rise to gradients of surface tension. Typically, surface tension of liquids decreases with increasing temperature and thus liquid tends to be pulled from hotter regions towards cooler regions of the laser irradiated molten surface leading to formation of surface micro-columns and cones. With increasing number of laser shots irradiating the target surface more heating occurs at locations that are oriented normal to the laser beam than those sections of the target surface that are inclined with respect to the incident laser beam such as the side-walls of the micro-cones. Inter-cone gap areas are oriented normal to the laser beam and thus attain a much higher temperature than the side-walls of the micro-cones. Although, tips of micro-cones are also oriented normal to incident laser beam, temperature attained by the tips is not as high, as these tips do not absorb much of the laser energy, area of the tips being small. The inter-cone zones reach the highest temperature also on account of additional laser radiation reaching these regions on account of multiple reflection of laser radiation by the cone sidewalls. Therefore surface tension in these flat zones is the lowest. Consequently, this gradient in surface tension drives the molten target layer towards the walls of the micro-cones leading to further enhancement of these micro-conical surface features. Each subsequent incoming laser pulse contributes towards accumulation of molten target layer on the cooler walls of the micro-cones and causes further enhancement of micro-cone height, as observed.

Conclusion

Self-assembled array of micro-conical surface structures generated on Titanium and SS cathode surface by nanosecond pulsed laser surface treatment has been investigated. Detailed study characterizing these surface micro-features including height and tip diameter of the micro-cones and their periodicity has been carried out. While, mean height of micro-cones increased with increasing number of irradiating pulses for a given level of laser fluence, periodicity, i.e. separation between successive micro-conical structures showed a decreasing trend with increasing incident laser fluence.

Reference

1. Voronov, V.V.; Dolgaev, S.I.; Lavrishchev, S.V.; Lyalin, A.A.; Simakin, A.V.; Shafeev, G.A.; *Quantum Electronics*, **2000,** *30(8)*, 710. **DOI:**10.1070/QE2000v030n08ABEH001795
2. Nayak, B.K.; Gupta, M.C.; *Opts. & Lasers in Engg*., **2010,** *48*, 940. **DOI:**10.1016/j.optlaseng.2010.04.010
3. Bensaoula, A.; Boney, C.; Pillai, R.; Shafeev, G.A.; Simakin, A.V.; Starikov, D.; *Appl Phys. A*, **2004,** *A 79*, 973, **DOI:** 10.1007/s00339-004-2588-z.
4. Zorba, V.; Boukos, N.; Zergioti, I.; Fotakis, C.; *Appl. Opts*, **2008,** *47*, 1846. **DOI:**10.1364/AO.47.001846
5. Lloyd, R.; Abdolvand, A.; Schmidt, A.; Crouse, P.; Whitehead, D.; Liu, Z.; Li, L.; *Appl. Phys. A*, **2008,** *A 93*, 117. **DOI:** 10.1007/s00339-008-4646-4
6. Pedraza, A.J.; Fowlkes, J.D.; Lowndes, D.H.; *Appl. Phys. Lett*., **1999,** *74*, 2322. **DOI**:10.1063/1.123838
7. Zorba,V.; Persano, L.; Pisignano, D.; Athanassiou, A.; Stratakis,E.; Cingolani,R.; Tzanetakis,P.; Fotakis, C.; *Nanotechnology*, **2006,** *17*, 3234. **DOI:**10.1088/0957-4484/17/13/026
8. Wu, C.; Crouch,C.H.; Zhao, L.; Carey, J.E.; Younkin, R.; Levinson, J.A.; Mazur, E.; Farreli, R.M.; Gothoskar, P.; Karger, A.; *Appl. Phys. Lett*., **2001,** *78*, 1850. **DOI:**10.1063/1.1358846
9. Crouch, C.H.; Carey, J.E.; Warrender, J.M.; Aziz, M.J.; Mazur, E.; Genin, F.Y.; *Appl. Phys. Lett*., **2004**, *84*, 1850. **DOI:**10.1063/1.1667004
10. Zorba, V.; Tzanetakis, P.; Fotakis, C.; Spanakis, E.; Stratakis, E.; Papazoglou, D.G.; Zergioti, I.; *Appl. Phys. Lett*., **2006,** *88*, 081103. **DOI:**10.1063/1.2177653
11. Zorba, V.; Alexandrou, I.; Zergioti, I.; Manousaki, A.; Ducati, C.; Neumeister, A.; Fotakis, C.; Amaratunga, G.A.J.; *Thin Solid Films*, **2004,** *453-454*, 492. **DOI:**10.1016/j.tsf.2003.11.144,
12. Karabutov, A.V.; Frolov, V.D.; Loubnin, E.N.; Simakin, A.V.; Shafeev, G.A.; *Appl. Phys. A*, **2003,** *A 76*, 413. **DOI:** 10.1007/s00339-002-1715-y

13. Fowlkes, J.D.; Pedraza, A.J.; Lowndes, D.H.; *Appl. Phys. Lett.*, **2000,** *77*, 1629.
    DOI:10.1063/1.1308538
14. Dolgaev, S.I.; Lavrischev, S.V.; Lyalin, A.A.; Simakin, A.V.; Voronov, V.V.; Shafeev, G.A., *Appl. Phys. A,* **2001,** *A 73***,** 177.
    DOI: 10.1007/s003390100530
15. Late, D.J.; Singh, V.R.; Sinha, S.; More, M.A.; Dasgupta, K.; Joag, D.S.; *Appl. Phys. A,* **2009,** *A 97***,** 905.
    DOI: 10.1007/s00339-009-5357-1
16. Late, D.J.; More, M.A.; Sinha, S.; Dasgupta, K.; Misra, P.; Singh, B.N.; Kukreja, L.M.; Bhoraskar, S.V.; Joag, D.S.; *Appl. Phys. A,* **2011,** *A 104***,** 677.
    DOI: 10.1007/s00339-011-6315-2
17. Hommes, V.; Miclea, M.; Hergenroder, R.; *Appl. Surf. Sci*., **2006,** *252***,** 7449.
    DOI:10.1016/j.apsusc.2005.08.089
18. Bonse, J.; Baudach, S.; Kruger, J.; Kautek, W.; Lenzner, M.; *Appl. Phys*. A, **2002,** *A 74,* 19.
    DOI: 10.1007/s003390100893