

## Nano-Second Surface Modification of Titanium Nitride Thin Film by Nd:YAG and TEA CO<sub>2</sub> Lasers

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**Abstract.** In this work we investigated the interaction of ns laser pulses (TEA CO<sub>2</sub> and Nd:YAG) with a titanium nitride (TiN) thin film. The TiN thin film of 1 μm thickness was deposited by PVD method on silicon substrate. Modification of TiN film was induced by laser pulses with power densities of about 10<sup>8</sup> and 10<sup>9</sup> W/cm<sup>2</sup>. Part of the laser energy absorbed on the target surface was converted into thermal energy and effects such as melting, vaporization and exfoliation were observed. Nd:YAG laser produced craters with sharp periphery, while TEA CO<sub>2</sub> laser created damages with broad boundary zone. Hydrodynamic effects were especially pronounced during irradiation with TEA CO<sub>2</sub> laser.

### Introduction

Interaction of laser light with matter has been investigated for many years [1,2]. However, laser-beam induced modification of solid materials in the form of thin films is still an expanding field in fundamental sciences as well as in engineering and material processing. Titanium nitride (TiN) films play an important role in wear resistance and in decorative coating applications, as well as in microelectronic and semiconductor manufacturing. Conventional microstructuring of this material is extremely difficult because of its hardness and brittleness [3]. A possible solution to this problem is the application of laser processing [4,5].

The present paper deals with the effects of a pulsed, ns, Nd:YAG laser, emitting in the near-IR (1.064 μm), and a pulsed, ns, TEA CO<sub>2</sub> laser, emitting in IR (10.64 μm), on titanium nitride thin film, deposited by PVD method on silicon substrate. In our previous work we have already investigated laser-induced modifications of titanium based thin films, deposited on steel substrate [6,7,8,9]. In this study by using two different types of lasers, we compare the influence of the number of successive laser pulses on ablated areas. From these results we may conclude that, in this case, for most precise and effective processing of this material, the Nd:YAG laser offers a better choice of pulse parameters.

### Experimental

Sample irradiation was performed using focused laser beams. The angle of incidence of the laser beam with respect to the surface plane was 90°. The irradiation was carried out in air atmosphere. The utilized experimental parameters were: (i) nano-second Q switched Nd:YAG laser at its fundamental wavelength (1.064 μm), pulse energy 3 mJ, pulse duration 10 ns, power density I=2.73·10<sup>9</sup> W/cm<sup>2</sup>, repetition rate 1Hz (ii) TEA CO<sub>2</sub> laser-wavelength= 10.06 μm, pulse duration FWHM (initial spike)=100 ns and the tail duration of 2 μs, pulse energy 70 mJ, peak power density I=5·10<sup>8</sup> W/cm<sup>2</sup>, repetition rate 1Hz (iii) TiN thin film thickness=1 μm, deposited on silicon wafer by physical vapor deposition method. Laser beam diameters on the target surface were up to 150 μm (Nd:YAG laser) and up to 450 μm. (TEA CO<sub>2</sub> laser).

Surface morphology was monitored by optical microscopy (OM) and by scanning electron microscopy (SEM). To estimate the size of laser beam modified areas we used Optical Images Analyzer (OIA). The reflectivity of TiN before laser irradiation was measured by a spectrophotometer.

## Results and Discussions

The surface of deposited TiN on silicon substrate acted like a mirror with high reflectivity ( $R$ ). Measured reflectivity values for TiN film, prior to the laser irradiation, were approximately 98% at  $10.6 \mu\text{m}$  and 91% at  $1.064 \mu\text{m}$ . Higher reflectivity of the sample at  $\lambda=10.6 \mu\text{m}$  in comparison to  $1.064 \mu\text{m}$  implies that the coupling between laser radiation, during the first laser pulse, and target was better for the latter wavelength. Successive irradiation of surface changed  $R$ -values for both laser wavelengths, and in the same time the absorptivity increased. The deposited energy of the laser beam is partially converted into thermal energy, which causes various effects such as vaporization, melting, cracking, formation of shock waves in the vapor and solid phase, appearance of plasma, etc. After multi-pulse irradiation of samples, the photon energy transforms into heat that causes, most likely, thermomechanical ablation (material removal caused by high-intensity laser pulses).

A quantitative estimation of modified areas can be made according to OIA data (Fig. 1). Increasing number of successive pulses  $N$  (at constant value of pulse energy) caused an increase in size of modified areas. This increase was more obvious in the case of irradiation by TEA  $\text{CO}_2$  laser than for Nd:YAG laser. The presence of a tail in the temporal shape of the laser pulse [9] had a direct effect on broadening of the heat affected zone.

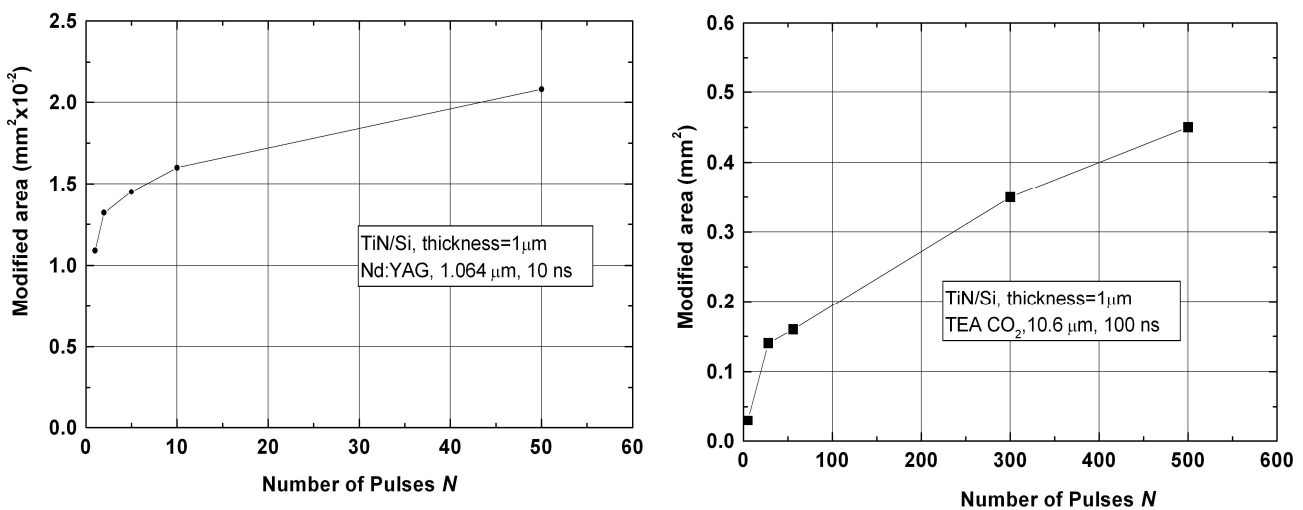


Fig. 1 (a and b) The size of modified areas versus number of laser pulses  $N$  (a)- Nd:YAG laser ( $\text{TEM}_{00}$  mode,  $I=2.73 \cdot 10^9 \text{ W/cm}^2$ ) and (b)- TEA  $\text{CO}_2$  laser ( $\text{TEM}_{00}$  mode,  $I=5 \cdot 10^8 \text{ W/cm}^2$ ).

Morphology investigation of changes induced by Nd:YAG and TEA  $\text{CO}_2$  laser multi pulse irradiation was carried out by OM (Figs. 2 and 3). More detailed analysis can be based on SEM microphotography (Fig. 4 a and b).

### Nd:YAG Laser Induced Morphological Changes

For a single pulse, only corrugation of TiN thin film appeared, there was no manifestation of exfoliation or expelled droplets (Fig. 2 B1, B2; Fig.4a.A); after two laser pulses the first indication of exfoliation processes occurred, based on observation of silicon substrate in the central zone (Fig. 4 a.B); after five pulses we registered a complete exfoliation of TiN (Fig. 4 a.C); even more drastic morphological changes and droplet formation occurred after application of fifty laser pulses (Fig. 2 D1 and D2; Fig. 4 a.D).

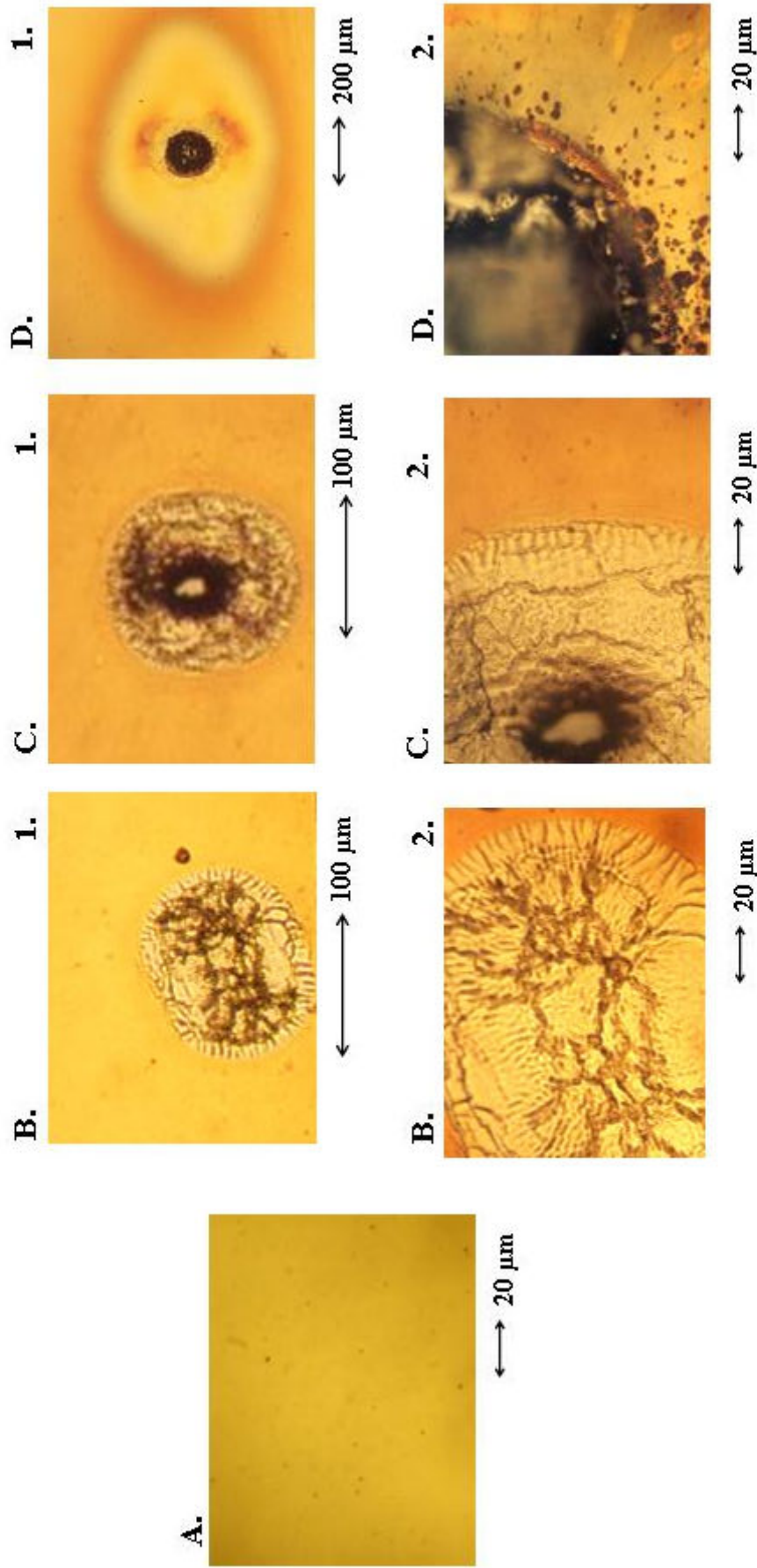


Fig. 2 Nd:YAG laser-induced morphology changes of TiN thin film on silicon (thickness, 1  $\mu\text{m}$ ). Analysis was carried out by optical microscopy. (A)- The view of TiN on silicon prior to laser action; (B1, B2) TiN/Si after one laser pulse action; (C1, C2)- TiN/Si after applying 2 laser impulses; (D1, D2)- TiN/Si after applying 50 laser pulses (TEM<sub>00</sub> mode,  $I = 2.73 \cdot 10^9 \text{ W/cm}^2$ ).

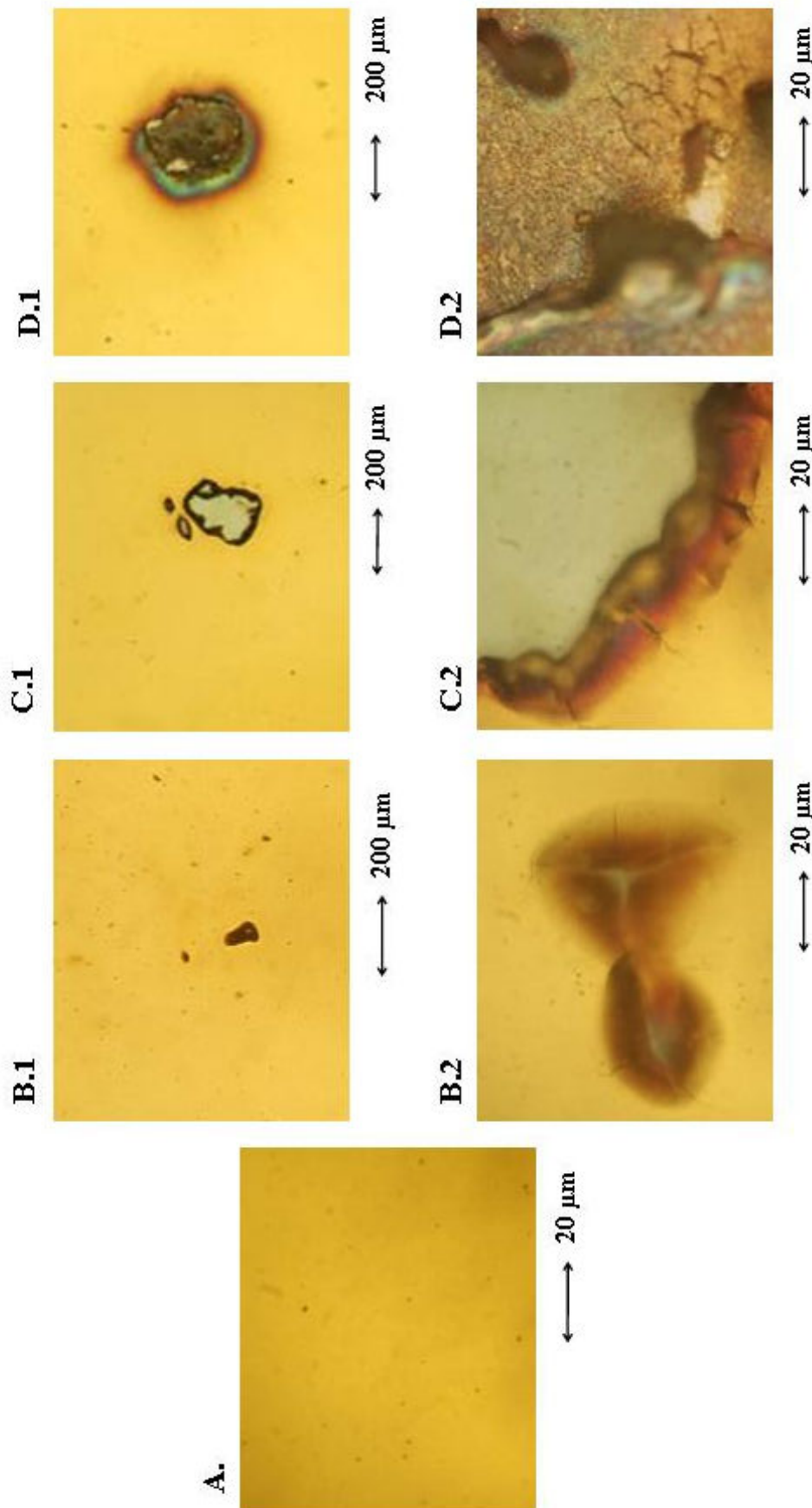


Fig. 3 TEA CO<sub>2</sub> laser-induced morphology changes of TiN thin film on silicon. Analysis was carried out by optical microscopy. (A) The view of TiN before laser action; (B1,B2) TiN/Si after 2 laser impulses action, different magnification; (C1;C2)- TiN/Si after 5 laser impulses action; (D1,D2)- TiN/Si after 28 laser impulses action (TEM<sub>00</sub> mode, I= 5·10<sup>8</sup> W/cm<sup>2</sup>).

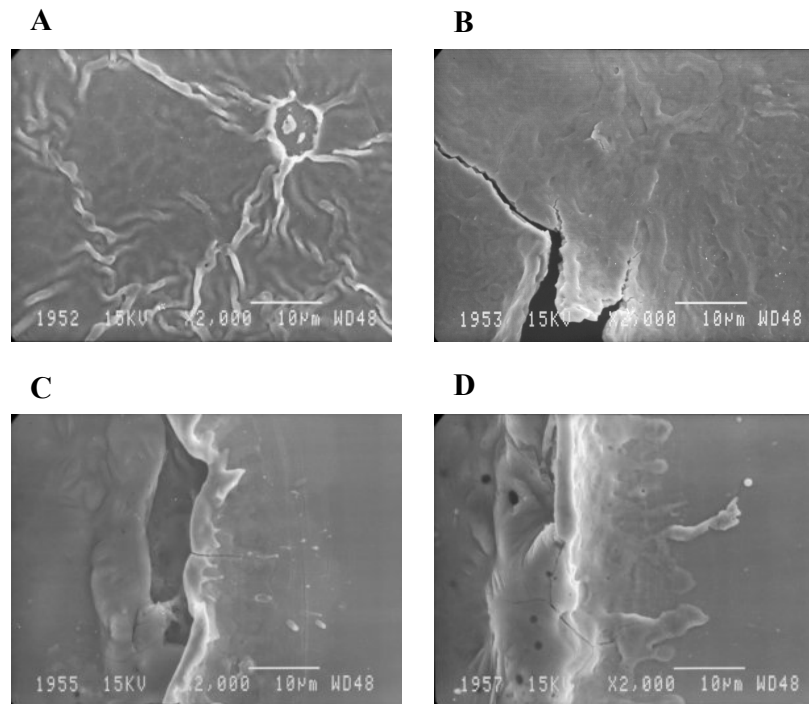


Fig. 4a Nd:YAG laser-induced morphology changes of TiN/Si- SEM micrographs. (A)- TiN/Si after one laser pulse action; (B) after two pulses action; (C)- after applying 5 laser pulses; (D)- after applying 50 laser pulses ( $TEM_{00}$  mode,  $I = 2.73 \cdot 10^9$  W/cm<sup>2</sup>).

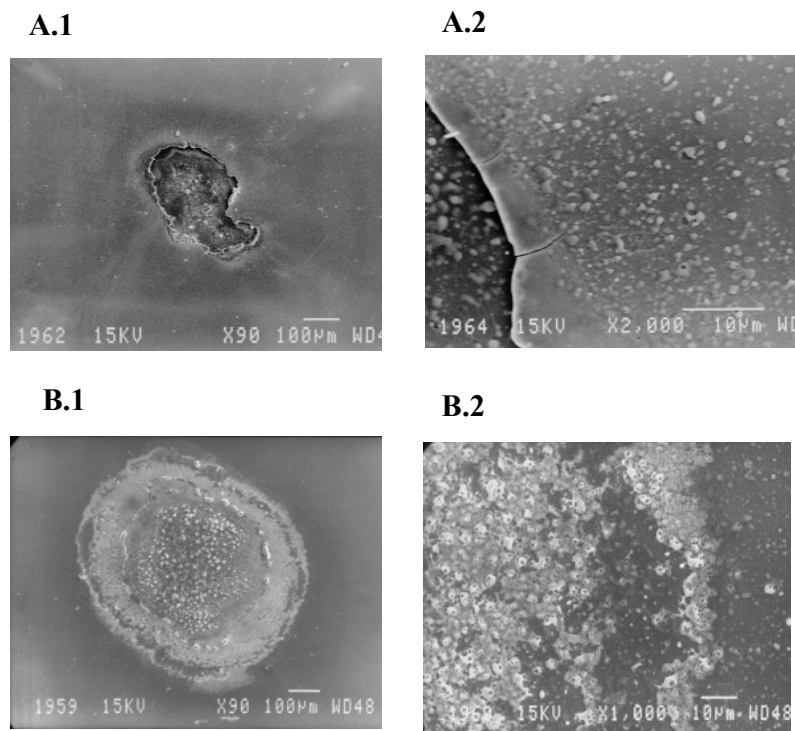


Fig. 4b TEA CO<sub>2</sub> laser-induced morphology changes of TiN/Si - SEM micrographs. (A1,A2)- after action of 56 laser pulses; (B1,B2)- after 504 laser pulses ( $TEM_{00}$  mode,  $I = 5 \cdot 10^8$  W/cm<sup>2</sup>).

#### TEA CO<sub>2</sub> laser induced morphological changes

After application of one or two laser pulses, only small cracking of TiN film and color changes appeared (Fig. 3 B1,B2); after five pulses manifestation of complete exfoliation of TiN and silicon

substrate took place (Fig. 3 C1,C2); similar morphological changes including other hydrodynamic effects such as droplet formation, etc. occurred after application of N= 28, 56 and 504 laser pulses (Fig. 3 D1,D2 and Fig. 4b).

## Conclusion

A qualitative and quantitative study of morphological changes on TiN thin film, deposited on silicon substrate, induced by Nd:YAG ( $\lambda_1= 1.064 \mu\text{m}$ ) and TEA CO<sub>2</sub> laser ( $\lambda_2= 10.6 \mu\text{m}$ ) pulses irradiation is presented.

The morphological modifications of TiN thin film on a qualitative level can be summarized as followed: (i) Surface modification was registered for both lasers; (ii) The initial Nd:YAG laser pulse induced corrugation in irradiated area, while the initial laser TEA CO<sub>2</sub> pulse induced only reflectivity changes; (iii) The exfoliation of TiN film appeared after two Nd:YAG laser pulses and after five TEA CO<sub>2</sub> laser pulses; (iv) Appearance of hydrodynamic features like resolidified rim and droplets of the material were registered after more than 5 and 28 successive laser pulses for the Nd:YAG and the TEA CO<sub>2</sub> laser, respectively; (v) In front of sample surface plasma was observed after first and all subsequent laser pulses.

The dependence of the size of modified area versus number of successive laser pulses was determined quantitatively. It is shown that the broadening of modified area as a result of rise in number of successive pulses was less obvious in the case of Nd:YAG laser. Nd:YAG laser is a better choice due to shorter wavelength and short duration for effective and precise material processing.

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## References

- [1] I. Boyd: *Laser Processing of Thin Films and Microstructure*, Springer Series in Material Sci. (Springer-Verlag 1987).
- [2] I. Ursu, I. Mihailescu, A. Prokhorov and V. Konov: *Laser Heating of Metals* (Accad. R.S.R. Bucuresti 1991).
- [3] J. Sundgren and H. Hentzell: *J. Vac. Sci. Technol. A* Vol. 4 (1986), p. 2259.
- [4] D. Bauerle: *Laser Processing and Chemistry* (Springer, 2003).
- [5] J. Bonse, H. Sturm, D. Schmidt and W. Kautek: *Applied Physics A* Vol. 71 (2000), p. 657.
- [6] B. Gaković, M. Trtica, T. Nenadović and B. Obradović: *Thin Solid Films* Vol. 343 (1999), p. 267.
- [7] B.M. Gaković, Z.S. Ristić, S.M. Petrović and M.S. Trtica: 5<sup>th</sup> General Conference of the Balkan Physical Union – BPU 5, electronic version (ISBN 86-902537-4-2)(2003), p. 985.
- [8] M. Trtica, B. Gakovic, Lj. Petkovska, V. Tarasenko, A. Fedenev, E. Lipatov and M. Shulepov: *Applied Surface Sciences* Vol. 225 (2004), p. 362.
- [9] M.S. Trtica, V.F. Tarasenko, B.M. Gaković, A.V. Fedenev, Lj.T. Petkovska, B.B. Radak, E.I. Lipatov and M.A. Shulepov: *Applied Physics A* Vol. 252/2 (2005), p. 474.