AIP | Applied Physics Letters

Simple formula for the interspaces of periodic grating structures self-organized on metal surfaces by femtosecond laser ablation

Masaki Hashida, Yoshinobu Ikuta, Yasuhiro Miyasaka, Shigeki Tokita, and Shuji Sakabe

Citation: Appl. Phys. Lett. **102**, 174106 (2013); doi: 10.1063/1.4803940
View online: http://dx.doi.org/10.1063/1.4803940
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v102/i17
Published by the American Institute of Physics.

Simple formula for the interspaces of periodic grating structures self-organized on metal surfaces by femtosecond laser ablation

Masaki Hashida,[a] Yoshinobu Ikuta, Yasuhiro Miyasaka, Shigeki Tokita, and Shuji Sakabe
ARCBS, Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan and Department of Physics, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyo, Kyoto 606-8502, Japan

(Received 13 February 2013; accepted 19 April 2013; published online 3 May 2013)

Self-organized grating structures formed on Mo and Ti metal surfaces irradiated with femtosecond laser pulses at wavelengths of 800 and 400 nm are investigated by electron microscopy. We observe the formation of the self-organized grating structures on the metals irradiated with 400-nm laser pulses at low laser fluence in narrow fluence ranges. The interspaces of the grating structure depend on the wavelength and fluence of the laser. We find that the dependence of the grating interspaces on laser fluence can be explained by a simple formula for induction of a surface-plasma wave through the parametric decay of laser light. © *2013 AIP Publishing LLC*.
[http://dx.doi.org/10.1063/1.4803940]

The self-organization of periodic grating structures inside or on the surface of materials under femtosecond-pulse laser irradiation at suitable laser fluence is a well-known phenomenon. These structures are characteristic of femtosecond-pulse lasers and are not observed for picosecond- or nanosecond-pulse lasers. These structures have been found in insulators,[1] semiconductors,[2] and metals.[3] For metals irradiated with linearly polarized laser light, the self-organized grating structures on the metal surface are oriented perpendicular to the laser polarization. The interspaces of the grating structures are shorter than the laser wavelength and depend on laser fluence.[3–6] Recently, it was found that, at an appropriate laser fluence, a periodic grating structure is produced with an amorphous state and/or a thin surface layer of metal oxide.[7–9] If periodic nanostructures on amorphous metal can be produced, thin metals with new functionality arising from novel electrical, optical, and thermal properties are expected. The metals with period grating structures have been used not only for industrial applications but also for fundamental research in biochemistry,[10] biomaterials,[11] and tribology.[12] These applications have been expanded through the precise control of periodic grating structures by means of high-repetition femtosecond laser systems. However, the self-organization mechanism of the grating structures remains under investigation. The structures depend on material properties and laser parameters (wavelength, fluence, pulse duration, number of pulses, etc.). Even for the same metal, not all experimental results reported in the literature[3–17] can be directly compared because of experimental differences, for example, in the laser parameters. For discussing the mechanism, a greater amount of systematic experimental data is now needed. One approach to gather systematic experimental data is to investigate the relation between the metal type and the interspaces of grating structures. Another approach is to investigate the relation between the ablation rate and the interspaces for typical metals. We have reported that the grating structure interspaces depend on laser fluence for Cu[3] irradiated with $\leq 100-$ fs laser pulses and for several metals[18] irradiated with 160-fs laser pulses. In the laser fluence ranges where self-organized grating structures are formed, the interspaces of the grating structures are shorter than the laser wavelength of 800 nm. The interspaces increase up to 680 nm as laser fluence is increased. We have reported that the laser fluence dependence of the grating structure interspaces is the same for Ti, Pt, Mo, and W metals on which the self-organized structures are formed.[18,19] We found that, for these metals, the ratio of the grating structure interspaces to the wavelength of the laser light is 0.85 at F_M (the upper limit of the laser fluence range in which the self-organized grating structures are formed). We explained this dependence of the interspaces on laser fluence on the basis of a parametric decay (stimulated Raman scattering) model.[20] In this model, the metal surface is initially covered with pre-formed plasma that is much less dense than solid metal. Surface plasma waves (SP waves) are induced at the interface between free space (air) and laser-produced plasma by parametric decay, resulting in the decay of the incident laser light into a SP wave and a scattered electromagnetic wave. The plasma wave travels slowly at less than 10^{-2} times the speed of light, and an ion-enriched local area appears. Before the next electron wave peak arrives, the ions experience a strong Coulomb repulsive force and can be exploded into a vacuum; in other words, a Coulomb explosion occurs. Through this process, periodic grating structures are formed. The wavelength of the plasma wave induced on the surface depends on only the plasma frequency (electron density) of the surface plasma. The ratio of the wavelength of the SP wave to that of the laser light changes from 0.5 to 0.85 for plasma frequencies in the range of $0 < \omega_p/\sqrt{2} < \omega_L$, where ω_p and ω_L are the frequencies of the plasma and laser light, respectively. When the plasma electron density is dependent on laser fluence, the wavelength of the SP wave in turn depends on laser fluence. This model satisfactorily explains the results reported for Cu[3] and Ti, Pt, Mo, and W.[18] These results indicate that the parametric decay model is valid in regard to only the dependence of the interspaces on laser fluence. At present, however, the body of experimental data is insufficient for verifying this model. The dependence

[a]Author to whom correspondence should be addressed. Electronic mail: hashida@laser.kuicr.kyoto-u.ac.jp

of the interspaces on the wavelength of the incident laser can also be explained in this model. In the present study, we investigated the states of metal surfaces (Ti and Mo) irradiated with femtosecond laser pulses at wavelengths of 800 and 400 nm. We evaluated the dependence of periodic structure interspaces on laser fluence at the different wavelengths. We also examined the dependence of ablation rate on laser fluence at the different wavelengths. We found a relation between the ablation rate and laser fluence at which self-organized periodic structures were formed. In addition, we evaluated the threshold of plasma generation to discuss the extent of the parametric decay models validity.

The targets were Ti and Mo metals, which had been mechanically polished. The surface roughness, as characterized by the arithmetic mean value, was less than 2 nm for both metals. To ablate the metals, we used linear polarized laser pulses at wavelength of 400 nm. A Ti:sapphire chirped-pulse amplification laser system (T6-laser, ICR, Kyoto University) was used to produce pulses (160-fs pulse duration, 800-nm center wavelength, 5-Hz repetition rate). The root-mean-square fluctuation of pulse energy was $\pm 0.3\%$.[21] The second harmonic wavelength of 400 nm was produced by frequency doubling in β-barium borate crystal. The polarizations of the 800- and 400-nm lasers were perpendicular to each other. We experimentally confirmed that the ratio of the energy of the 800-nm laser to that of the 400-nm laser was less than 2.5×10^{-4}. Thus, the 800-nm laser did not contribute to nanostructure formation because the laser fluence of the 800-nm component was much less than the ablation threshold. In air, the 400-nm laser pulses were focused onto the metals by a fused silica convex lens with focal length of 100 mm. To avoid filamentation of 400-nm laser pulses in air at the focal point, the target surfaces were set between the lens and the focal point. The spot size on the target was 90 μm in diameter. The laser pulses were directed at normal incidence onto the target surface. To avoid non-uniformity of structure in the irradiated area on the surface, the laser intensity distribution was adjusted to be spatially uniform by using a super-Gaussian profile.[18] Through a pair of half-wave plates and two polarizers, the energy of 400-nm laser pulses was varied in the range of 3.3–14 μJ, corresponding to fluence of 30–130 mJ/cm^2. Energy (average of 500 pulses) was measured just before irradiating a target at each laser fluence. The number of irradiating pulses was 40 in all experiments. Laser-produced surface structures were examined by scanning electron microscopy (SEM; JSM-5560, JEOL). The periodic grating interspaces were determined by reading the peak value in the frequency domain after taking the Fourier transform for the 6 μm$\times$4.5 μm area of the SEM image. The resolution of the present measurements of the periodic spacing was better than 21 nm. Figure 1 shows typical SEM image and the corresponding Fourier transform spectrum. In addition, we measured the depth of the crater produced by 200 or 1000 laser pulses by confocal laser scanning microscopy (HL-150, Lasertec) and evaluated the ablation rate.

Using linear polarized laser pulses at 400 nm, we observed self-organization of the grating structures on the metal surfaces. The grating structures were oriented perpendicular to the 400-nm laser polarization direction. In Figs. 2(a) and 2(c), the dependence of periodic structure interspaces

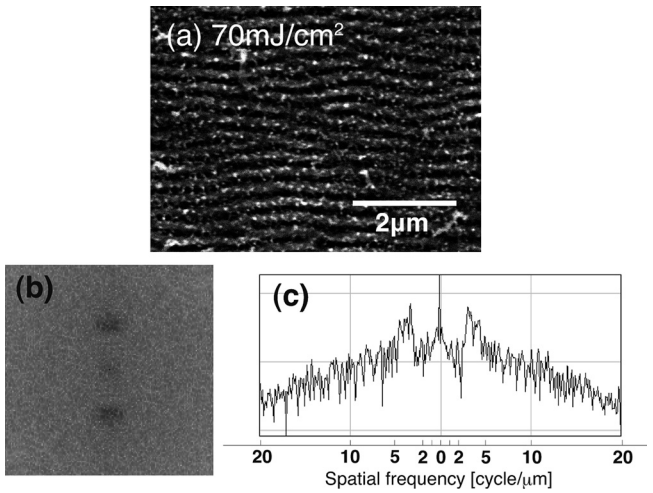

FIG. 1. SEM image of periodic grating structures on the surface of Mo (a), produced by 40 160-fs laser pulses at laser fluence of 70 mJ/cm^2 and Fourier transform spectrum (2D-Fourier transform spectrum (b) and its line spectrum (c)).

on laser fluence for Ti and Mo is shown. The upper limit (F_M) and lower limit (F_S) of the laser fluence range for producing periodic structures can be seen. The interspaces of the grating structures at F_M are about 300 nm, which is shorter than the laser wavelength. The self-organized grating structures are formed in the laser fluence range of 42–75 mJ/cm^2 for Ti and 60–111 mJ/cm^2 for Mo. For the 800-nm pulses,[18] the laser fluence range for grating structure formation is 90–450 mJ/cm^2 for Ti and 187–1120 mJ/cm^2 for Mo. The upper limit of the laser fluence range in which the grating structures are produced is approximately one order of magnitude higher for the 800-nm pulses than for the 400-nm pulses.

The ablation rate was measured in the fluence range of 20–2000 mJ/cm^2. Figure 3 shows the ablation rate dependence on laser fluence; the laser fluence range where grating structures were formed is indicated by dark gray for 400 nm and light gray for 800 nm. The experimental results suggest that the grating structure can be formed in the two metals at ablation rates of 5–10 nm for 400 nm and 4–34 nm for 800 nm. Thus, the ablation threshold is a key parameter for discussing the mechanism of self-organized grating structure formations. In the figure, experimental data are fitted to the well-known function[22,23] $L = \alpha^{-1}\ln(F_L/F_{th})$, where α is the optical absorption coefficient or heat penetration coefficient, F_L is the laser fluence, and F_{th} is the ablation threshold fluence. The experimental results show that F_{th} for Ti was 34 mJ/cm^2 under 400-nm pulses and 74 mJ/cm^2 under 800-nm pulses. In the Mo case, the ablation rate dependence indicates the presence of two different ablation regimes at both wavelengths. The lowest F_{th} value was 24 mJ/cm^2 for 400 nm and 134 mJ/cm^2 for 800 nm. At 90 mJ/cm^2 under 400-nm pulses and at 790 mJ/cm^2 under 800-nm pulses, the ablation rates increase sharply and have different dependences on laser fluence. These two different ablation regimes have been explained by the depths of optical penetration and thermal diffusion.[24,25] The possibility of multiphoton absorption process has also been discussed.[26,27] Table I lists the experimentally obtained physical parameters, namely, F_{th}, F_S, and F_M, related to self-organization of grating structures.

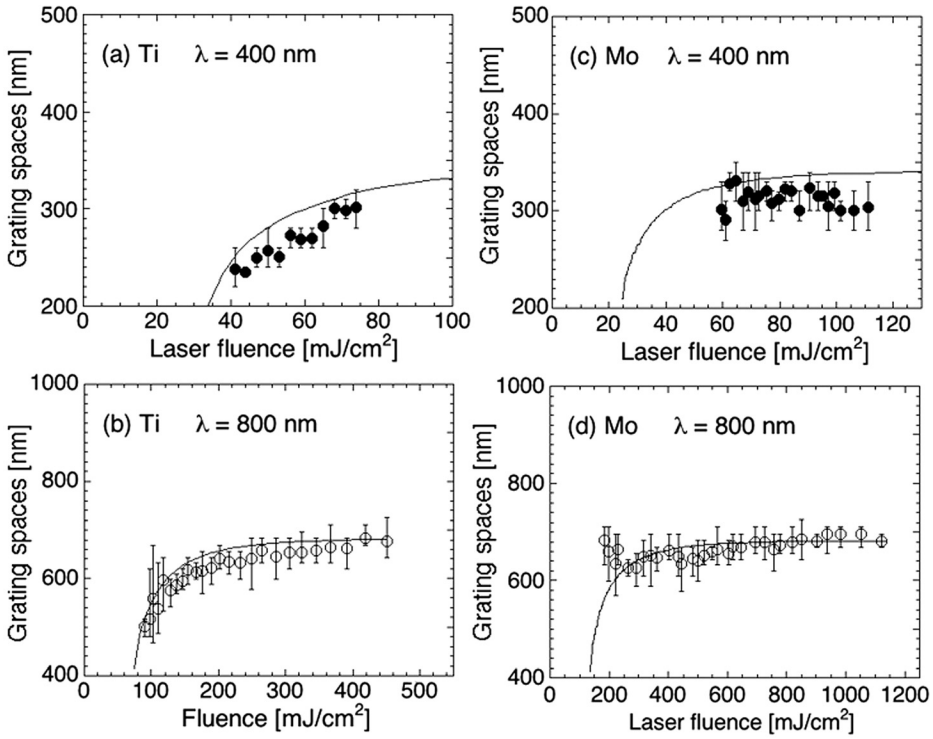

FIG. 2. Laser fluence dependence of the grating structure interspaces produced by femtosecond laser pulses (pulse duration: 160 fs): (a) Ti, 400 nm; (b) Ti, 800 nm; (c) Mo, 400 nm, and (d) Mo, 800 nm. Error bars show the standard deviation of the interspaces. Solid lines show calculation results according to the parametric decay model under the assumption that F_M is defined by $F_{34\text{nm}}$.

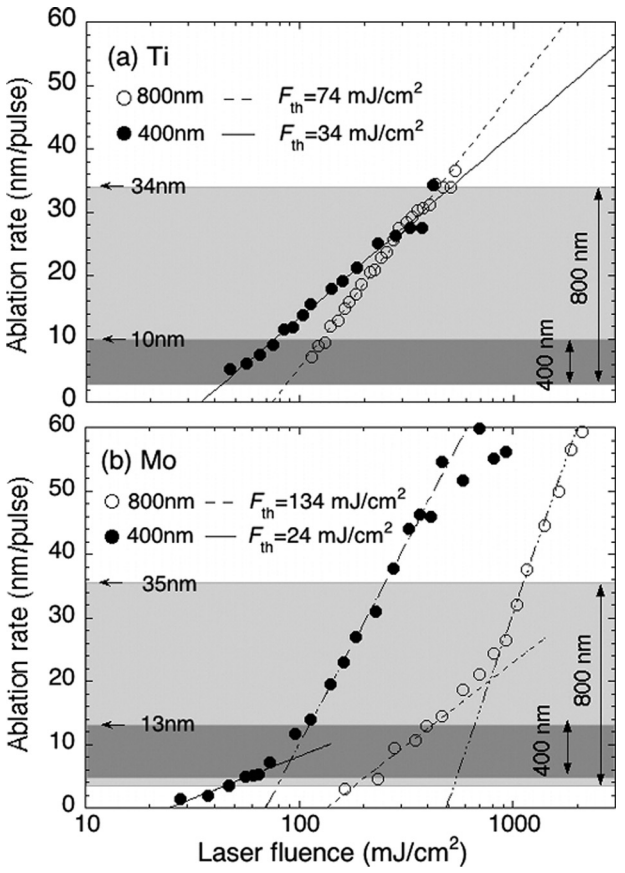

FIG. 3. Laser fluence dependence of ablation rate for laser wavelengths of 400 and 800 nm on the (a) Ti and (b) Mo surfaces where formation of self-organized grating structures occurred. Straight lines indicate fits of the experimental data to $L = \alpha^{-1}\ln(F_L/F_{th})$, where α is the optical absorption coefficient or heat penetration coefficient, F_L is the laser fluence, and F_{th} is the ablation threshold fluence.

Let us compare the experimental data on grating structure interspaces versus laser fluence with the predictions from the model based on plasma wave induction by parametric decay of laser light.[20] Here, the model is briefly described. The parametric process of photon → photon + plasmon can occur on a plasma surface as well as in a bulk plasma (i.e., stimulated Raman scattering). The parametric conditions of $\omega_L = \omega_2 + \omega_{\text{SP}}$ and $\mathbf{k}_L = \mathbf{k}_2 + \mathbf{k}_{\mathbf{SP}}$, where the subscripts L, 2, and SP indicate the incident laser light, scattered light, and surface plasma wave, respectively, are reduced to

$$\omega_L - \omega_{\text{SP}} = ck_{\text{SP}} - ck_L, \quad \omega_L = ck_L,$$
$$\omega_{\text{SP}}^2 = c^2k_{\text{SP}}^2 + \frac{1}{2}\omega_P^2 - \sqrt{c^4k_{\text{SP}}^4 + \frac{1}{4}\omega_P^4}.$$

From this, $k_L/k_{\text{SP}}(=\lambda_{\text{SP}}/\lambda_L)$ can be expressed by the simple formula

$$\lambda_{\text{SP}}/\lambda_L = Ax^3 + Bx^2 + Cx + D,$$

where $x = \omega_{\text{P}}/\sqrt{2}\omega_L$, $A = -0.1731$, $B = 0.316$, $C = 0.2068$, and $D = 0.5013$. Thus, the wavenumber of the plasma wave induced by the parametric process can be related to the plasma frequency, and the k_L/k_{SP} ratio ($=\lambda_{\text{SP}}/\lambda_L$; λ is the wavelength) changes from 0.5 to 0.85 for plasma frequencies in the range of $0 < \omega_{\text{p}}/\sqrt{2} < \omega_L$, where the plasma wavenumber increases as the plasma frequency decreases. As mentioned above, assuming that the self-organization is induced by the plasma wave, the grating spaces correspond to the wavelength of the induced plasma wave, and the fluence dependence of the interspaces can be reduced to plasma density dependence. The dependence of the surface electron density n_{es} on the laser fluence F_L can be interpreted as follows. The electron density n_e of the bulk plasma produced on the surface by the laser is related to the ablation threshold F_{th}:

TABLE I. Ablation threshold fluence (F_{th}) and upper limit (F_M) and lower limit (F_S) of laser fluence for producing periodic structures for investigated wavelengths ($\lambda_L = 400$ and $\lambda_L = 800$ nm) and metals (Mo and Ti).

Metal	λ_L (nm)	F_{th} (J/cm^2)	F_S (J/cm^2)	F_M (J/cm^2)
Mo	400	24	60	111
Mo	800	134	187	1120
Ti	400	34	42	74
Ti	800	74	90	450

$n_e \propto \ln(F_L/F_{th})$. A reasonable assumption is that plasma formation starts at the ablation threshold F_{th}.[28] The heated bulk plasma with temperature T_e expands at the sonic speed $c_s = \sqrt{k_B T_e/m}$, and the surface electron density decreases from the bulk density in accordance with n_e/c_s, and the temperature is proportional to the laser energy: $T_e \propto F_L$. Therefore, the surface electron density is related to the laser fluence as $n_{\text{es}} \propto n_e/c_s \propto n_e/\sqrt{T_e} \propto \ln(F_L/F_{th})/\sqrt{F_L}$. We assume that the plasma frequency is $\omega_{\text{p}} = \sqrt{2}\omega_L$ for the laser fluence F_M because no grating structures are produced at laser fluence greater than F_M. Applying this expression together with $\omega_p = \sqrt{4\pi n_{\text{es}} e^2/m}$ to the dependence of $\lambda_{\text{SP}}/\lambda_L$ on ω_{p}, the spatial dependence of the laser fluence is obtained. This relation is indicated by a solid line in Fig. 2. The experimental results for 800 nm agree reasonably well with this model. For 400 nm, the experimental results are in relatively good agreement with the simple calculation under the assumption that F_M is defined by $F_{34\text{nm}}$, where $F_{34\text{nm}}$ denotes the laser fluence characterized by an ablation rate of 34 nm/pulse. However, the upper limit of the laser fluence range for producing periodic structures appears to be $F_{10\text{nm}}$ for both metals under 400-nm laser irradiation. The calculations suggested that the self-organized grating structures are actually formed up to $F_{34\text{nm}}$, and then destroyed by another mechanism, such as melting. Thus, no grating structures were observed in the laser fluence range of $F_{10\text{nm}} < F_L < F_{34\text{nm}}$. As shown in Fig. 2, the model is in fairly good agreement with the experimental results in the laser fluence range of $F_{5\text{nm}} < F_L < F_{10\,\text{nm}}$. The ranges in which the self-organized grating structures are formed are governed by the ablation rate. These experimental results indicate that the interspaces of the self-organized periodic structure depend not on metal characteristics, but rather on the density of the surface plasma produced by a laser pulse. For high laser fluence ($F_L > F_{34\,\text{nm}}$), the plasma expands too greatly for a clear surface to be constructed, or the plasma density is too high; in such cases, a surface plasma wave is not produced.

In summary, we observed self-organized grating structures formed on the surfaces of Mo and Ti metals irradiated with femtosecond laser pulses at wavelengths of 800 and 400 nm. We found that the self-organized grating structures formed on the metals under 400-nm laser pulses at low laser fluence in narrow fluence ranges. We also found that the grating structure interspaces depended on the wavelength and the laser fluence. The ranges in which the self-organized grating structures are formed were governed by the ablation rate. At ablation rates in the range of 5–30 nm/pulse, the self-organized grating structures are formed and the dependence of the their interspaces on laser fluence can be explained by simple formula for induction of a surface-plasma wave through the parametric decay of laser light, and can be reduced to dependence on the density of laser-produced plasma.

[1]F. Costache, M. Henyk, and J. Reif, Appl. Surf. Sci. **208**, 486–491 (2003).
[2]N. Yasumaru, K. Miyazaki, and J. Kiuchi, Appl. Phys. A **76**, 983–985 (2003).
[3]M. Hashida, M. Fujita, Y. Izawa, and A. F. Semerok, Proc. SPIE **4830**, 452–457 (2003).
[4]A. Y. Vorobyev, V. S. Makin, and C. Guo, J. Appl. Phys. **101**, 034903 (2007).
[5]M. Tsukamoto, K. Asuka, H. Nakano, M. Hashida, M. Katto, N. Abe, and M. Fujita, Vacuum **80**, 1346–1350 (2006).
[6]J. Wang and C. Guo, J. Appl. Phys. **100**, 023511 (2006).
[7]Y. Hirayama, P. A. Atanasov, M. Obara, N. N. Nedialkov, and S. E. Imamova, Jpn. J. Appl. Phys., Part 1 **45**, 792–797 (2006).
[8]S. Valette, R. Le Harzic, E. Audourad, N. Hout, R. Fillit, and R. Fortunier, Appl. Surf. Sci. **252**, 4691–4695 (2006).
[9]M. Hashida, Y. Miyasaka, Y. Ikuta, S. Tokita, and S. Sakabe, Phys. Rev. B **83**, 235413 (2011).
[10]S. Matsumoto, A. Yane, S. Nakashima, M. Hashida, M. Fujita, Y. Goto, and S. Takahashi, J. Am. Chem. Soc. **129**, 3840–3841 (2007).
[11]T. Shinonaga, M. Tsukamoto, S. Maruyama, N. Matsushita, T. Wada, X. Wang, H. Honda, M. Fujita, N. Abe, and A. Inoue, Rev. Laser Eng. **39**, 347–353 (2011).
[12]A. Blatter, M. Maillat, S. M. Pimenov, G. A. Shafeev, and A. V. Simakin, Tribol. Lett. **4**, 237–241 (1998).
[13]J. Wang and C. Guo, Appl. Phys. Lett. **87**, 251914 (2005).
[14]A. Y. Vorobyev and C. Guo, Phys. Rev. B **72**, 195422 (2005).
[15]A. Weck, T. H. R. Crawford, D. S. Wilkinson, H. K. Haugen, and J. S. Preston, Appl. Phys. A **90**, 537–543 (2008).
[16]B. K. Nayak, M. C. Gupta, and K. W. Kolasinski, Appl. Phys. A **90**, 399–402 (2008).
[17]Y. Huang, S. Liu, W. Li, Y. Liu, and W. Yang, Opt. Express **17**, 20756–20761 (2009).
[18]K. Okamuro, M. Hashida, Y. Miyasaka, Y. Ikuta, S. Tokita, and S. Sakabe, Phys. Rev. B **82**, 165417 (2010).
[19]M. Hashida, Y. Miyasaka, Y. Ikuta, K. Otani, S. Tokita, and S. Sakabe, J. Laser Micro/Nanoeng. **7**, 194–197 (2012).
[20]S. Sakabe, M. Hashida, S. Tokita, S. Namba, and K. Okamuro, Phys. Rev. B **79**, 033409 (2009).
[21]S. Tokita, M. Hashida, S. Masuno, S. Namba, and S. Sakabe, Opt. Express **16**, 14875–14881 (2008).
[22]S. Preuss, A. Demchuk, and M. Stuke, Appl. Phys. A **61**, 33–37 (1995).
[23]B. N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, and A. Tunnermann, Appl. Phys. A. **63**, 109–115 (1996).
[24]S. Nolte, C. Momma, H. Jacobs, A. Tunnermann, B. N. Chichkov, B. Wollegehausen, and H. Welling, J. Opt. Soc. Am. B **14**, 2716–2722 (1997).
[25]Y. Hirayama and M. Obara, Appl. Surf. Sci. **197**, 741–745 (2002).
[26]M. Hashida, A. F. Semerok, O. Gobert, G. Petite, Y. Izawa, and J. F -. Wagner, Appl. Surf. Sci. **197**, 862–867 (2002).
[27]M. Hashida, S. Namba, K. Okamuro, S. Tokita, and S. Sakabe, Phys. Rev. B **81**, 115442 (2010).
[28]P. P. Pronko, S. K. Dutta, D. Du, and R. K. Singh, J. Appl. Phys. **78**, 6233–6240 (1995).