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Ultrafast dynamics of high-contrast nano-grating formation on gold film induced by temporally shaped femtosecond laser

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ABSTRACT

We theoretically investigated the ultrafast dynamics of high-contrast nano-grating formation on gold film surface with respect to non-equilibrium thermal excitation processes. It is proposed that the high-contrast nano-grating can be desirably achieved by optimizing the non-equilibrium thermal dynamics processes. The grating contrast can be largely promoted by 64% with adjusting thermal dynamics via tailoring temporally shaped femtosecond laser. The results are attributed to the competitive energy transfer routes between electrons thermal diffusion and electron–phonon relaxation processes during grating formation, which can be well manipulated by temporally shaped femtosecond laser. The study provides for strategy for production of high-quality periodic surface structures with sharp grating profiles.

1. Introduction

Laser induced periodic nanostructures, especially the nano-gratings have been widely studied because of their potential interests for both scientific and practical aspects [1–4]. The high-quality nano-grating would be extremely beneficial for promoting performance of periodic structured devices, such as surface plasmons sensors, polarizing beam splitter, solar cells and mechanical friction devices, *etc*. Generally, the nano-grating formation is widely accepted as the interference between incident laser with scattering surface wave, which may originate from surface roughness, surface electron excitation, surface instability [5–8]. Unfortunately, laser patterned grating usually presents poor appearance with low-contrast and quasi-periodicity due to thermal recast effect during grating formation process. Recently, the temporally shaped femtosecond laser, namely, multi-pulse sequence with variable temporal separation have found potential advantages in patterning of microstructures and periodic nano-grating, such as high ablation efficiency and less thermal recast effect [9–13]. It becomes possible to manipulate grating contrast via tailoring the temporally shaped femtosecond laser. When temporally shaped femtosecond laser interactions with metallic materials, the non-equilibrium thermal relaxation dynamics, which are closely related to pulse-to-pulse relevance can be mainly responsible for regulating ablation features [14,15]. It is demonstrated that the interplay between the electron thermal diffusion and electron–phonon coupling processes can definitely influence the grating contrast [16–18]. However, it is currently challenging to control the processes of interplay between electron thermal diffusion and electron–phonon coupling for a given target for optimizing the grating features for a wide range of applications.

In this Letter, we present the dynamics of grating contrast tuning on gold via manipulating the temporally shaped femtosecond laser. For femtosecond laser ablation, the target can be removed during the non-equilibrium electron–phonon relaxation period in the ablation regime. As a result, the condition of simulations is limited to the non-equilibrium processes within several picoseconds in the early stage of grating formation. The thermal relaxation mechanism in the early stage of grating formation is proposed for exploring grating contrast modulation dynamics. It is revealing that the interplay of competitive energy transfer routes between the electrons thermal diffusion and the electron–phonon relaxation processes can be optimized via temporally shaping the femtosecond laser pulses for generation of high contrast grating. In this Letter, we focus on the ultrafast thermal relaxation dynamics in the early stage of grating formation for analysis of the grating-contrast features. The interference between surface plasmon polaritions and the wide-spectrum femtosecond pulse are taken as the nano-grating formation mechanism. The generation of surface wave like the surface plasmon polaritons can physically originate from surface roughness of gold film. The interference patterns for regulating grating profiles are equalized as the periodically modulated laser source. As the ultrashort laser pulses irradiation of gold film, the target can be excited out of equilibrium dramatically [19]. Namely, the electrons and phonons can be treated as respective

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systems, which can be presented by the two-temperature model. Here, the two-temperature model with respect to the periodically modulated laser source is introduced for investigations of the thermal relaxation dynamics during the nano-grating formation on gold film. Following the termination of laser energy absorption by electrons, the phonon system of gold film is periodically perturbed on the timescale of several picoseconds due to the sustaining electron–phonon coupling process. At about tens of picoseconds, the electron and phonon systems reach the thermal equilibrium state, during which the grating most likely forms as a result of periodic temperature distributions and the phase explosion mechanism. The ultrafast non-equilibrium thermal relaxation dynamics plays an important role in affecting the spatially modulated phonon thermalization process, which can be manipulated by the temporally shaped femtosecond laser.

The thermal excitation and two-temperature relaxation processes of femtosecond laser interactions with gold film are described as follows [20]:

$$C_e[T_e,T_p]\frac{\partial T_e}{\partial t}=\nabla(K_e[T_e,T_p]\nabla T_e)-G[T_e,T_p](T_e-T_p)+Q \tag{1}$$

$$C_p\frac{\partial T_p}{\partial t}=G[T_e,T_p](T_e-T_p) \tag{2}$$

Here, the coupled Eqs. (1) and (2) describe ultrashort laser pulses excitation and the following thermal relaxation processes.

For a wide range of electron temperature ranging from 300 K to Femi temperature, the temperature-dependent electron thermal conductivity during the two-temperature relaxation processes is expressed as follows [21]:

$$K_e[T_e,T_p]=\chi\frac{(\theta_e^2+0.16)^{5/4}(\theta_e^2+0.44)\theta_e}{(\theta_e^2+0.092)^{1/2}(\theta_e^2+\eta\theta_p)} \tag{3}$$

An analytical expression of the electron–phonon coupling strength was proposed by Zhang and Chen, which can be represented as follows [22]:

$$G[T_e,T_p]=G_0[A_e/B_p(T_e+T_p)+1] \tag{4}$$

Where, G_0 is the electron–phonon coupling strength in room temperature, and the coefficients A_e and B_p are constants.

At the early stage of the nano-grating formation, the laser spot is instantaneously modulated on gold film surface due to interference mechanism originating from the surface roughness, leading to appearance of periodic modulated laser field on gold film surface. The modulated laser field is instantly coupled into the electron system of gold film via the photon–electron collisions. The periodic modulation of laser field energy absorption rate Q can be written as

$$\begin{aligned}Q(x,y,t)=&\sqrt{\frac{4\ln 2}{\pi}}\frac{1-R}{(\delta+\delta_b)}\frac{F_i}{t_{pi}}\cos[(2\pi/\Lambda)(y-y_0)]\\&\times\exp\left(-\frac{x}{\delta+\delta_b}\right)\exp\left[-\frac{(y-y_0)}{y_s}\right]^2\\&\cdot\sum_{i=1}^{n}\exp\left[-4\ln 2\left(\frac{t-2t_{pi}-(i-1)\Delta}{t_{pi}}\right)^2\right]\end{aligned} \tag{5}$$

Here, R is the gold film surface reflectivity, which is temperature and wavelength dependent parameter, δ is the optical skin depth, and δ_b is the electron ballistic transfer length for gold film, taken as 100 nm. F_i is the laser fluence of respective pulses of temporally shaped pulses sequence. t_{pi} is the FWHM pulse duration. Λ is nano-grating period, y_s denotes the Gaussian profile parameter. n is pulse number and Δ denotes the temporal separation between pulses.

In this Letter, the optical skin depth is treated as wavelength and temperature dependent function written as

$$\delta[T_e,T_p,\omega]=\left(\frac{2\omega\mathrm{Im}(\sqrt{\varepsilon})}{c}\right)^{-1} \tag{6}$$

Here, ε is the complex dielectric function, which can be split into the real and imaginary parts as follows:

$$\varepsilon=1-\frac{\omega_p^2}{\omega^2+\nu_m^2}+i\frac{\nu_m}{\omega}\frac{\omega_p^2}{\omega^2+\nu_m^2} \tag{7}$$

According to Matthiessen's rule within the relaxation time approximation, the total scattering rate of electrons is the sum of the rates of the separate mechanisms: $\nu_m=1/\tau_{ee}+1/\tau_{ep}$, where τ_{ee} and τ_{ep} are the electron–electron and electron–phonon scattering times, which is temperature dependent parameters, described as $1/A_eT_e^2$ and $1/B_pT_p$, respectively. Because of the instantaneous electron and phonon temperature changes during the two-temperature relaxation processes, therefore, the instantaneous dielectric function of the gold can be well taken into account in simulations.

The spatio-temporal evolution of periodically modulated temperature fields on two-dimensional (2-D) gold film surface excited by temporally shaped femtosecond laser double pulses is shown in Figure 1. We can see that at the very beginning of the laser excitation, the electron temperature within subsurface of the gold film exhibits periodic modulation at 120 fs, while the phonon system keeps undisturbed at this time. With time, the periodic modulation of electron temperature is obscured at 1 ps, while, the phonon temperature modulation becomes visible at 1 ps due to the persistent electron–phonon coupling process, which is taking place on picosecond timescale. At 1.2 ps, a time of the arrival of second pulse of the temporally shaped femtosecond double pulses, the electron system is violently excited again, the periodic electron temperature modulation becomes even more obvious at this time, meanwhile the periodic phonon temperature field becomes more visible. It can be seen that the periodic modulation of electron temperature becomes fuzzy at 5 ps, however the phonon temperature modulation at this time gets more distinct because of the persistent energy exchange from electron system to phonon system.

At 10 ps, the periodically modulated temperature of electron system and phonon system get their equilibrium distribution. The periodically modulated temperature field takes shape at electron–phonon relaxation termination, indicating the possible generation of grating as laser fluence is high enough for causing gold film damage at the temperature modulation region. It is expected that the formed grating can be influenced by adjusting thermal properties of materials via tailoring laser pulses, which will provide for flexible route for well controlling the grating contrast for a wide range of applications.

Figure 2 shows the normalized phonon temperature modulation on 2-D gold film surface with respect to the electron thermal conductivity and electron–phonon coupling strength, respectively. We can see that the large electron thermal conductivity of 1.5 k_e definitely causes the decline of phonon temperature modulation contrast [Figure 2a]. However, a large electron–phonon coupling strength of 1.5g will inversely gives rise to the phonon temperature modulation contrast [Figure 2b]. It indicates that the electron thermal diffusion and the electron–phonon coupling can be mutually competitive processes in regulating the phonon temperature modulation contrast. As the electron–phonon coupling strength increases, the phonon temperature is localized on gold film surface, leading to enhanced modulation contrast of the phonon temperature. On the contrary, the increase of electron thermal conductivity can result in significant diffusion of the electron thermal energy into inner bulk of gold film, which is unfavorable for enhancing the phonon temperature modulation on gold film surface. According to the first principle predictions by Lin et al., the electron thermal conductivity and electron–phonon coupling strength can be

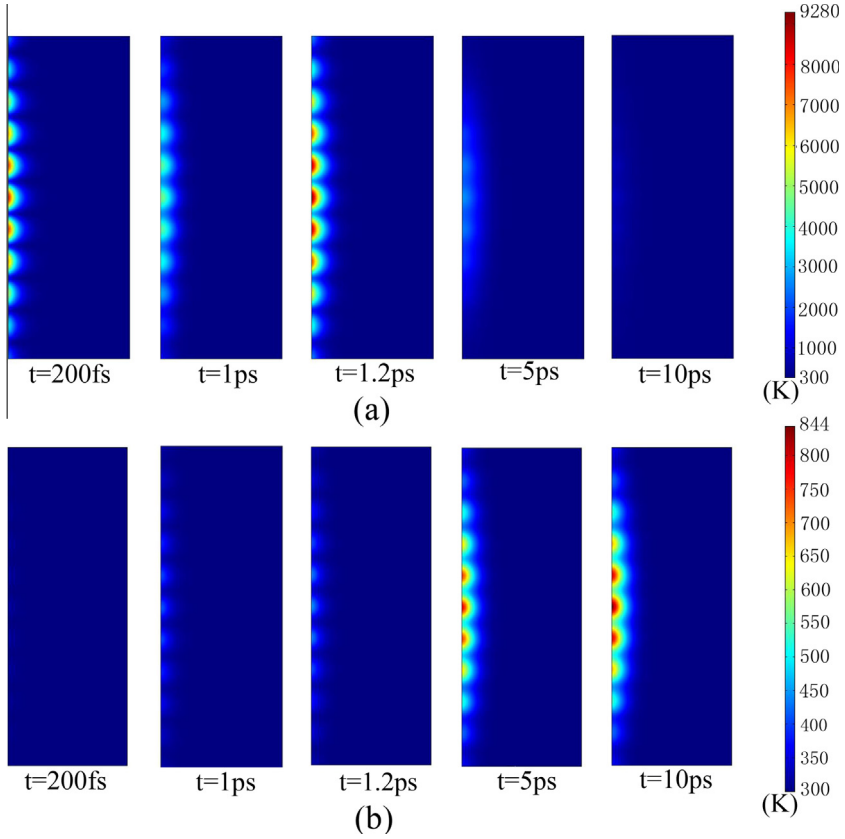

Figure 1. The spatio-temporal evolution of two-dimensional (2-D) periodically modulated temperature field on gold film excited by temporally shaped femtosecond laser double pulses. The laser wavelength 800 nm, pulse duration 60 fs, laser fluence 0.5 J/cm^2, pulse separation Δ = 1 ps.

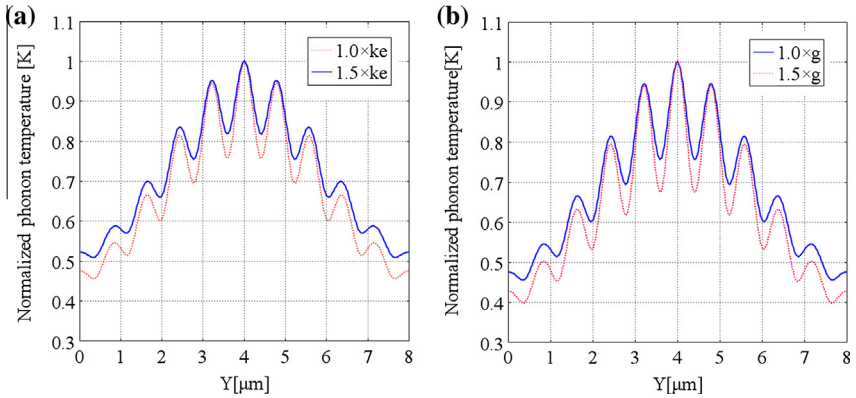

Figure 2. The normalized phonon temperature modulations on 2-D gold film with respect to the thermal parameters of electron thermal conductivity and electron–phonon coupling strength, respectively.

affected significantly by material temperature [23]. In addition, considering that the temperature of phonon system can be properly adjusted by optimizing the parameters of temporally shaped femtosecond laser [14,15]. Therefore, it is expected that the periodic phonon temperature modulations on gold film surface can exhibit close dependences on temporally shaped femtosecond laser parameters.

In the current investigations, we will focus on the nano-grating formation dynamics with respect to the temporally shaped multi-pulse sequences with variable pulse number and pulse separation. The frequency shaping like the frequency chip which mostly plays an important role in the nonlinear processes of femtosecond laser processing of dielectrics is not taken into account for the gold target. For the gold, the absorption enhancement of the double pulses interactions which is closely related to pulse-to-pulse relevance can be mainly responsible for regulating the material ablation. Therefore, it is very important to take the pulse-to-pulse relevance parameters such as pulse separation and pulse number into account in the two-temperature for well exploring the processes of thermal dynamics during the nano-grating formation.

The grating contrast defined as the periodic phonon temperature modulation and maximal phonon temperature on gold film surface at termination of electron–phonon relaxation period as functions of pulse number of temporally shaped femtosecond laser is shown in Figure 3. We can see that the grating contrast and phonon temperature all present rise tendency with increasing pulse number. It can calculated out that the increase rate of the grating contrast reaches 64% as the pulse number increases from 1 to 15,

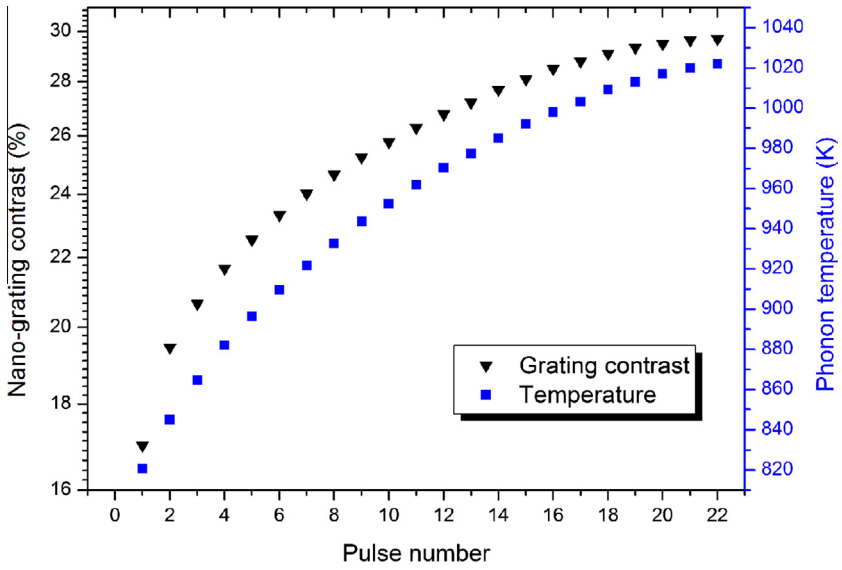

Figure 3. The grating contrast on gold film surface at termination of electron–phonon relaxation period and phonon temperature as functions of pulse number of temporally shaped double femtosecond laser pulses. $F = 0.45$ J/cm^2, laser wavelength $\lambda = 800$ nm, pulse duration $t_p = 60$ fs, pulse separation $\Delta = 1$ ps.

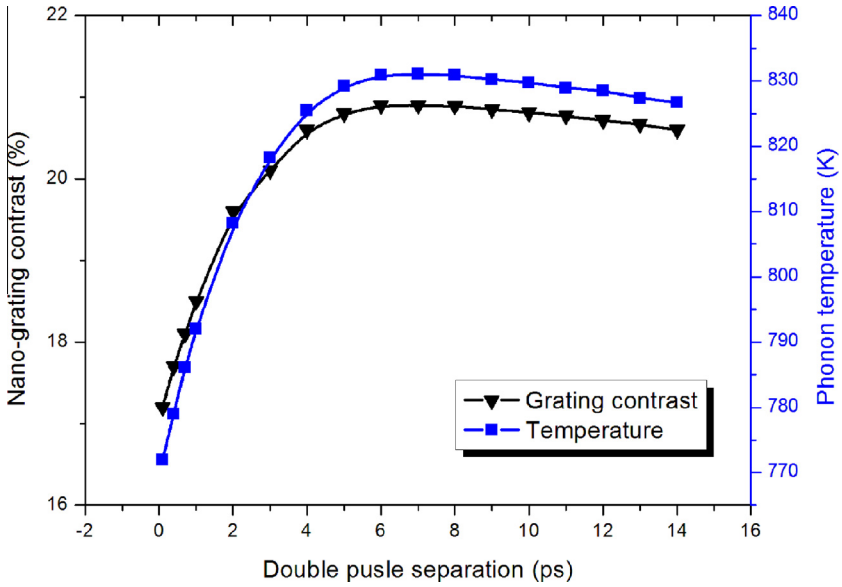

Figure 4. The grating contrast on gold film surface at termination of electron–phonon relaxation period as functions of pulse separation of temporally shaped double femtosecond laser pulses. Total double pulses fluence $F = 0.45$ J/cm^2, laser wavelength $\lambda = 800$ nm, pulse duration $t_{p1} = t_{p2} = 60$ fs.

but only 5.69% for pulse number changing from 15 pulses to 22. The surface localized phonon temperature also presents similar trendency with the grating contrast increase rate. It indicates that the electron–phonon coupling process is dominatingly triumphing over the electron diffusion process as the pulse number increases from 1 to 15. For pulse number changing from 15 to 22, the surface localized phonon temperature presents slow rise. The saturated rise of grating contrast indicates suppressing of electron–phonon coupling process and enhancement of electron thermal diffusion process during grating formation. The results are basically helpful for controlling the periodic phonon temperature modulation for optimizing the grating contrast via manipulating the pulse number of temporally shaped femtosecond laser.

The grating contrast and maximal phonon temperature of gold film surface at termination of the electron–phonon relaxation period as functions of pulse separation of temporally shaped double femtosecond pulses are shown in Figure 4. The grating contrast increases quickly with increasing pulse separation as it is less than 5 ps. It can be calculated that the grating contrast can be promoted by 21% by the optimal pulse separation of 5 ps. Once the pulse separation exceeds 5 ps, the grating contrast presents slow drop. The grating contrast dependences on the temporal separation of shaped double femtosecond pulses can be attributed to the competitive energy transportation routes between the electron diffusion and electron–phonon coupling in gold film, whose prevalence can be guaranteed by adjusting shaped double pulse separation. As the pulse separation is less than 5 ps, the localized phonon temperature on gold film surface increases quickly with increasing the pulse separation, indicating domination of electron–phonon coupling mechanism over electron thermal diffusion mechanism. As a result, the grating contrast presents rapid rise with increasing the pulse separation. However, as the pulse separation exceeds 5 ps, the localized

phonon temperature of gold film surface drops slowly. It shows that the electron–phonon coupling process is being impaired, while the electron thermal diffusion process strengthening with increasing double pulse separation. The grating contrast is lowered due to the strengthening of the electron thermal diffusion conductivity and weakening of the electron–phonon coupling, which was also experimentally observed for different metals materials [16–18].

In conclusion, we have theoretically investigated the ultrafast dynamics of high-contrast periodic grating formation on gold film induced by temporally shaped femtosecond laser. It is revealed that The increase rate of the grating contrast reaches 64% as the pulse number increases from 1 to 15, but only 5.69% for pulse number changing from 15 to 22. The grating contrast increases quickly with increasing the pulse separation as it is less than 5 ps. Once the pulse separation exceeds 5 ps, the grating contrast presents slow drop. The results are equally attributed to the competitive energy transportation routes between the electron diffusion and electron–phonon coupling processes. The high-contrast grating structures can be produced as the electron–phonon coupling process dominates over the electron diffusion process, which can be assured by optimizing the temporally shaped femtosecond laser. The study provides for basic strategy for production of high-contrast periodic nano-grating via tailoring temporally shaped femtosecond laser.

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References

[1] Q. Zhao, F. Ciobanu, S. Malzer, L. Wang, Appl. Phys. Lett. 91 (2007) 121107.
[2] C. Crouch, J. Carey, J. Warrender, M. Aziz, E. Mazur, F. Génin, Appl. Phys. Lett. 84 (2004) 1850.
[3] J. Chen, W. Lai, Y. Kao, Y. Yang, J. Sheu, Opt. Express 20 (2012) 5689.
[4] Y. Shimotsuma, P. Kazansky, J. Qiu, K. Hirao, Phys. Rev. Lett. 91 (2003) 247405.
[5] Y. Yang, J. Yang, L. Xue, Y. Guo, Appl. Phys. Lett. 97 (2010) 141101.
[6] J. Bonse, A. Rosenfeld, J. Krüger, J. Appl. Phys. 106 (2009) 104910.
[7] G. Du et al., Laser Phys. Lett. 10 (2013) 026003.
[8] J. Reif, F. Costache, M. Bestehorn, in: J. Perriere, E. Millon, E. Fogarassy (Eds.), Recent Advances in Laser Processing of Materials, Elsevier, Amsterdam, 2006, p. p. 275ff (Chapter 9).
[9] S. Juodkazis, K. Nishimura, H. Misawa, Chin. Opt. Lett. 5 (2007) S198.
[10] I. Chowdhury, X. Xu, A. Weiner, Appl. Phys. Lett. 86 (2005) 151110.
[11] C. Liebig, P. Srisungsitthisunti, A. Weiner, X. Xu, Appl. Phys. A 101 (2010) 487.
[12] R. Stoian, M. Boyle, A. Thoss, A. Rosenfeld, G. Korn, I. Hertel, E. Campbell, Appl. Phys. Lett. 80 (2002) 353.
[13] M. Rohloff, S. Das, S. Höhm, R. Grunwald, A. Rosenfeld, J. Krüger, J. Bonse, J. Appl. Phys. 110 (2011) 014910.
[14] G. Du, F. Chen, Q. Yang, J. Si, X. Hou, Opt. Commun. 284 (2011) 640.
[15] L. Jiang, H.L. Tsai, Appl. Phys. Lett. 87 (2005) 151104.
[16] J.P. Colombier et al., J. Appl. Phys. 111 (2012) 024902.
[17] J. Wang, C. Guo, Appl. Phys. Lett. 87 (2005) 251914.
[18] J. Wang, C. Guo, J. Appl. Phys. 102 (2007) 053522.
[19] E.G. Gamaly, B. Luther-Davies, L. Hallo, P. Nicolai, V.T. Tikhonchuk, Phys. Rev. B 73 (2006) 214101.
[20] S.I. Anisimov, B.L. Kapeliovich, T.L. Perel'man, Sov. Phys. JETP 39 (1974) 375.
[21] J.K. Chen, D.Y. Tzou, J.E. Beraun, Int. J. Heat Mass Transfer 49 (2006) 307.
[22] Y. Zhang, J.K. Chen, Appl. Phys. A 88 (2007) 289.
[23] Z. Lin, L.V. Zhigilei, Phys. Rev. B 77 (2008) 075133.