Mechanism for self-formation of periodic grating structures on a metal surface by a femtosecond laser pulse

Shuji Sakabe, Masaki Hashida, Shigeki Tokita, Shin Namba, and Kiminori Okamuro
Advanced Research Center for Beam Science, 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 4 November 2008; published 23 January 2009)

Periodic grating structures self-formed on a metal surface under the irradiation of a femtosecond laser pulse are characterized by grating spaces which are shorter than the laser wavelength, as well as by dependence on the laser fluence. This Brief Report presents a different interpretation of these features in terms of the process of parametric decay of laser light to surface plasma waves. Depending on the electron density, grating spaces with lengths of 680 nm to as short as 400 nm can be produced for 800 nm laser wavelength as a result of the interaction of laser pulses with laser-produced surface plasma.

DOI: 10.1103/PhysRevB.79.033409 PACS number(s): 81.16.−c, 78.20.Bh, 79.20.Ds, 82.53.Mj

Since the discovery of periodic structures in optical damages on mirror surfaces induced by laser pulses, self-organization of the periodic grating structures has been actively studied,[1] and the formation of the structures is currently thought to be caused by the interference of incident light with reflected (scattered) light. The interspacing of the periodic grating structures is given by $\lambda/n(1\pm\sin\theta)$, where λ, θ, and n are the laser wavelength, the laser beam incidence angle, and the refractive index of the material, respectively.[2–5] Therefore, the interspacing is greater than the laser wavelength when the incidence is normal to the surface and $n<1$ for laser-produced plasma on the surface. The advancement of intense femtosecond-pulse laser technology has elucidated some phenomena induced by laser-matter interactions which are completely inaccessible to picosecond- and nanosecond-pulse lasers. One of the inherent phenomena related to the irradiation of femtosecond-pulse laser is the emergence of self-formed periodic grating structures on the surface or inside the material. These self-formed structures exhibit certain differences in comparison to the ones mentioned at the exordium, namely, that the interspacing is much shorter than the laser wavelength, which effectively excludes light interference as a possible explanation. Periodic grating structures formed under the irradiation of femtosecond-pulse lasers have been found independently for metals,[6,7] semiconductors,[8] and insulators[9] by different research groups. Since then, the possible applications of the self-production of gratings have been intensively studied and developed for scientific[10,11] and industrial uses.[12,13] However, the physical mechanism for the self-formation of periodic gratings by femtosecond-pulse laser irradiation has remained unexplained with the only exception of self-organized nanogratings in glass materials, where the cause for the gratings is considered to be laser-induced plasma waves in bulk plasma.[14] The present Brief Report proposes a mechanism for the self-formation of gratings on metal surfaces by a femtosecond light pulse, and the spaces of the experimentally observed gratings are successfully accounted for by this interpretation.

One of the authors has reported experimental results of the ablation rates[15,16] and the observation of self-formed periodic grating structures[7] for metals irradiated with a femtosecond-pulse laser. A brief description of the experiment is provided. The metal sample is a mechanically polished copper plate, and optical pulses of a laser with an 800 nm wavelength and with pulse durations of 70 and 100 fs are irradiated on the copper plate in normal direction through a $f=100$ mm lens. The respective depths and sizes of the ablation-produced cavities are measured with optical and atomic force microscopes. Furthermore, the surfaces of the cavities are observed with scanning electron microscopy (SEM), and the ablation rates are estimated from the depth profiles of the ablation-produced cavities in accordance with the laser intensity profiles. Figure 1(a) shows the dependence of the ablation rate on the energy fluence of the irradiated laser beam. The SEM pictures of the grating structures are shown in the insets of the images in Fig. 1(b), and the grating spaces are given as the dependence on the laser energy fluence, as shown in Fig. 1(b). The grating structures self-formed under the influence of the femtosecond-pulse laser irradiation are characterized by the following features: (1) the interspaces are shorter than the laser wavelength ($<0.85\lambda$), (2) the interspaces depend on the laser energy fluence, (3) the interspaces become shorter in a discontinuous manner near the ablation threshold as the laser energy fluence decreases, and (4) the gratings are produced perpendicular to the laser polarization plane. None of these features can be observed for nanosecond-pulse laser ablations.

In this Brief Report, we propose an interpretation of the interspacing of the observed periodic grating structures, where we assume the overall process generating the grating structures as follows: (1) plasma waves are induced on the surface by the femtosecond laser pulse; (2) spatially localized ion clouds Coulomb-explode to vacuum, and consequently the thin layer is ablated, and the interspacing of the gratings is printed at the stage of the first several pulses (it is considered that the number of pulses depends on the laser energy fluence, and at certain high values for the fluence, only a single pulse is involved in this and the following processes); and (3) for the subsequent pulses, the electric field is enhanced near the initially printed structures, and the near field ablates the surface, thus deepening the structures.

For nanosecond-pulse laser-matter interactions, the front phase of a laser pulse heats a solid-state matter, which turns into plasma. The plasma is heated by the subsequent phases of the pulse and expands at sonic speed. Therefore, the major

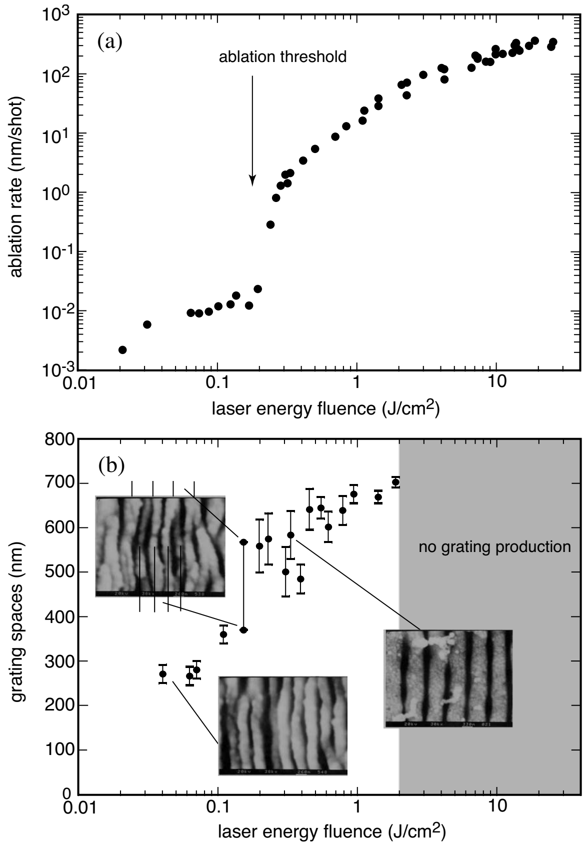

FIG. 1. (a) The dependence of the ablation rate on the energy fluence of the laser pulse (Refs. 6, 15, and 16) (pulse duration 70 fs). (b) The dependence of the interspaces the grating structures produced by femtosecond laser pulses on the laser flux and (inset) the SEM pictures of the laser-ablated surface (Ref. 7) (pulse duration 100 fs).

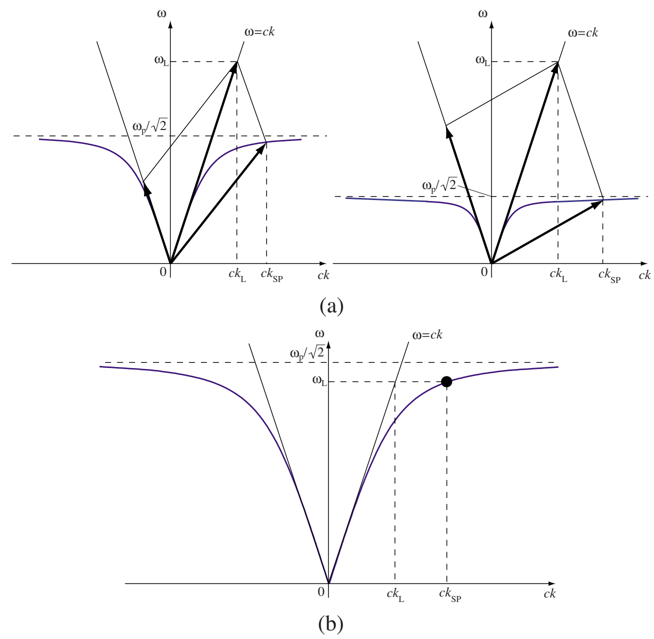

FIG. 2. (Color online) (a) Dispersion diagrams of the parametric process involving the interaction of photon→photon and surface plasma wave. For lower plasma densities, giving lower plasma frequencies (right-hand side), the wave numbers of the decayed photons and the induced plasma waves are larger. (b) Dispersion of surface plasma waves directly induced by the laser. When the surface plasma density is sufficiently high for $\omega_p/\sqrt{2}$ to be close to ω_L, the wave number of the surface plasma wave becomes large.

part of the pulse interacts with the expanding plasma. In laser-bulk plasma interactions, the laser pulse propagates inside the plasma with a dispersion of $\omega^2=\omega_p{}^2+c^2k^2$, where ω and k are the angular frequency and the wave number of the electromagnetic wave (laser light), c is the speed of light in vacuum, and ω_p is the plasma frequency. The laser pulse cannot propagate to depths beyond the point where $n=m\omega^2/(4\pi e^2)$ (n is the electron density, e is the electron charge, and m is the electron mass). On the other hand, for femtosecond-pulse laser-matter interactions, even when the peak of a pulse arrives at the surface of the material, the produced plasma is still in close contact with the solid-state matter. The plasma produced by the laser expands at sonic speed $c_s=\sqrt{k_BT_e/m}$ (k_B, T_e, and m are the Boltzmann constant, the electron temperature, and the electron mass, respectively), and therefore the plasma scale length is of the order of $c_s\tau$, where τ is the pulse duration. For instance, the expansion of the 10 eV plasma is only 100 nm during a 100 fs laser pulse. The plasma scale length is sufficiently short for the plasma to form a surface. Therefore, the pulse can interact with the surface formed by the plasma rather than with the bulk plasma. The dispersion of the surface plasma is given by $ck=\omega\{\varepsilon_1\varepsilon_2/(\varepsilon_1+\varepsilon_2)\}^{1/2}$,[17,18] where ε_1 and ε_2 are the respective permittivities of the materials separated by the surface. Here, if we assume that the surface separates plasma from vacuum, then $\varepsilon_1=1-\omega_p{}^2/\omega^2$ and $\varepsilon_2=1$, and a plasma wave (plasmon) can be induced with the following dispersion:

$$c^2k^2=\omega^2\frac{1-\omega_p{}^2/\omega^2}{2-\omega_p{}^2/\omega^2}.$$

This indicates that laser light with frequency ω_L cannot be transferred into the plasma wave (direct coupling with the plasma wave) for $\omega_L>\omega_p/\sqrt{2}$. In order to have $\omega_L<\omega_p/\sqrt{2}$, the plasma electron density should be higher than 3.5×10^{21} cm^{-3} for 800 nm (375 THz) laser light. However, a high-intensity laser pulse can be transferred into the surface plasma wave by a parametric process, as shown in Fig. 2(a). The parametric process of photon→photon+plasmon is referred to as stimulated Raman scattering for bulk plasma. The parametric conditions of $\omega_L=\omega_2+\omega_{\rm SP}$ and $\mathbf{k}_L=\mathbf{k}_2+\mathbf{k}_{\rm SP}$, where the subscripts L, 2, and SP indicate incident laser light, scattered light, and surface plasma wave, respectively, are reduced to

$$\omega_L-\omega_{\rm SP}=ck_{\rm SP}-ck_L,\qquad \omega_L=ck_L,$$

$$\omega_{\rm SP}{}^2=c^2k_{\rm SP}{}^2+\frac{1}{2}\omega_p{}^2-\left(c^4k_{\rm SP}{}^4+\frac{1}{4}\omega_p{}^2\right)^{1/2}.$$

The wave number of the plasma wave stimulated by the parametric process can be related to the plasma frequency as shown in Fig. 3(a). The $k_L/k_{\rm SP}$ ratio ($=\lambda_{\rm SP}/\lambda_L$, where λ indicates the wavelength) changes from 0.5 to 0.85 for plasma

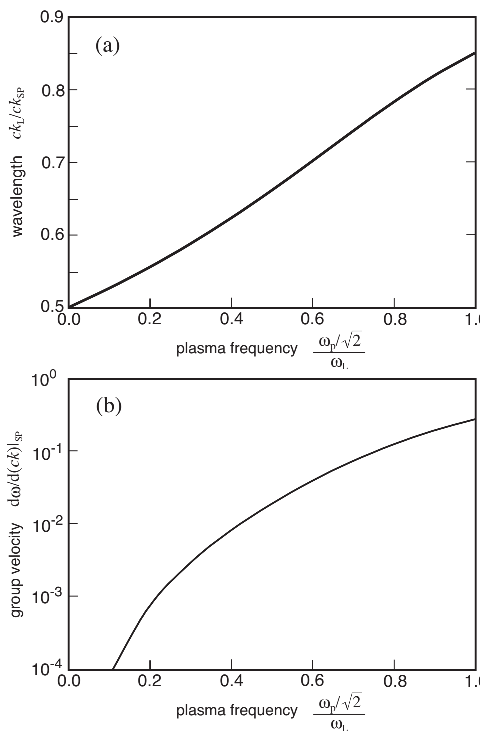

FIG. 3. The dependence of (a) the wave number and (b) the group velocity of the plasma waves induced by the parametric process on the plasma frequency.

frequencies in the range $0<\omega_p/\sqrt{2}<\omega_L$, where the plasma wave number increases as the plasma frequency decreases. The plasma wave travels slowly, as shown in Fig. 3(b), which also describes the group velocity. For instance, a plasma wave whose wavelength is 70% of that of the laser light travels with a speed of 3×10^{-2} times the speed of light. Even for a laser pulse with a duration of 100 fs, the plasma wave moves only 0.9 μm. During this interval, an ion-enriched local area appears, and the ions experience strong Coulomb repulsion until the peak of the next electron wave arrives at that position, which can result in a Coulomb explosion,[19,20] thus giving rise to the formation of periodic grating structures. The depth of these gratings cannot be estimated in a straightforward manner if only the present interpretation is considered. Once such structures are formed, an enhancement process might take place. For instance, the grating structures might be enhanced (become deeper) under the influence of localized static electric fields on the surface (near field effect[21]) for the subsequent laser pulses. Furthermore, the parametric process to surface plasma waves and the following Coulomb explosion can contribute to the formation of the initial printing of periodic grating structures. Here, only the interspaces of the grating structures are discussed.

From the discussion above, it is concluded that the grating spaces correspond to the wavelengths of the induced plasma waves. As k_L/k_{SP} ($=\lambda_{SP}/\lambda_L$) changes from 0.5 to 0.85, the structure interspaces change in the range 400–680 nm. This is in good agreement with the experimental results for values of the laser energy fluence higher than about 0.15 J/cm^2 [shown in Fig. 1(b)], which indicates that when the laser energy fluence is in the range 0.15–2 J/cm^2, the spaces change from 400–560 to 680 nm. The dependence of the surface electron density n_{es} on the laser energy fluence F_L can be interpreted as follows. The electron density n_e of the plasma bulk produced by the laser on the surface is proportional to the laser energy $n_e \propto F_L$. The heated plasma bulk with temperature T_e expands at sonic speed $c_s=\sqrt{k_BT_e/m}$, the surface electron density can decrease from the bulk density as 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 energy fluence as $n_{es} \propto n_e/c_s \propto n_e/T_e^{1/2} \propto F_L{}^{1/2}$. It is reasonable to assume the plasma frequency to be $\omega_p=\sqrt{2}\omega_L$ for laser energy fluence of 2 J/cm^2 since there no grating structures were produced at values for the laser energy fluence of over 2 J/cm^2. In this case, $n_{es}=3.5\times10^{21}(F_L/2)^{1/2}$, where n_{es} is in units of cm^{-3} and F_L is in units of J cm^{-2}. Applying this relation together with $\omega_p=\sqrt{4\pi n_{es}e^2/m}$ to Fig. 3(a), the spatial dependence of the laser energy fluence is obtained, which is indicated with a solid line in Fig. 4 and is in reasonable agreement with the experimental results. Note that near the ablation threshold of 0.15–0.18 J/cm^2, the electron density would be drastically reduced in such manner as $n_{es} \propto \ln(F_L/F_{th})$ (F_{th} is the laser fluence at the ablation threshold) from the value given by the equation $n_{es}=3.5\times10^{21}(F_L/2)^{1/2}$, and therefore the grating space becomes close to 400 nm. Taking into account the fluctuations in the laser energy between pulses and the formation of gratings by multiple laser shots, some interspaces might become intricately entwined near the ablation threshold, and the grating space can be 400 nm when only small amounts of electrons are produced with laser pulses whose energy is accidentally low. In fact, as shown in the inset of Fig. 1(b), two spaces are observed on the ablated surface when the laser energy fluence is near the ablation threshold. The present model gives the ratio of the length of the spaces to the laser wavelength, where the space does not depend on the number of pulses. In fact, in the experiment, even if more pulses are irradiated on the structures produced by the first several shots, the space of the grating structure never changed.

The present interpretation cannot be applied to laser pulses with fluence levels <0.15 J/cm^2 since the minimum of k_L/k_{SP} must be 0.5 (λ_{SP} is 400 nm for $\lambda_L=800$ nm). The experimental results of the ablation rate show that 0.18 J/cm^2 is the ablation threshold; in other words, under this threshold there is only little plasma on the metal surface. However, some small part of the surface is ablated even under this threshold, and on the ablated cavity surface periodical grating structures are still self-formed, with interspaces shorter than 400 nm. The experimental results suggest that even at fluence levels lower than 0.15 J/cm^2, some plasma waves are induced, thus forming periodic structures. These surface plasma waves cannot be induced by parametric processes but are rather produced directly with $\omega_L<\omega_p/\sqrt{2}$, as shown in Fig. 2(b). As the laser energy fluence decreases, the surface plasma layer becomes thinner, and the surface plasma is not only composed of laser-produced plasma on the surface but also of solid-state plasma of non-ablated material. Based on the dispersion of the surface plasma, the wavelength of the plasma waves is written as

$$\frac{\lambda_{SP}}{\lambda_L} = \left\{ 1 + \left(\frac{\omega_p^{\ 2}}{\omega_L^{\ 2}} - 2 \right)^{-1} \right\}^{-1/2}.$$

In order to explain the 270 nm interspaces at the laser energy fluence levels $<0.1\ \mathrm{J/cm^2}$, the plasma frequency must be 3.44×10^{15} rad/s, which corresponds to electron density of $4.23 \times 10^{21}\ \mathrm{cm^{-3}}$. This electron density is lower than $9.59 \times 10^{22}\ \mathrm{cm^{-3}}$ as estimated from the copper solid-state plasma frequency of 1.62×10^{16} rad/s (Ref. 22) and is much higher than that calculated from $n_{es}=3.5\times 10^{21}(F_L/2)^{1/2}=6.71 \times 10^{20}\ \mathrm{cm^{-3}}$ at $F_L=0.1\ \mathrm{J/cm^2}$. The effective plasma electron density can be determined by the densities of both the laser-produced thin surface plasma and the solid-state plasma of the non-ablated metal.

The orientation of the observed gratings discussed here is perpendicular to the laser polarization plane, and it is reasonable to conclude on the basis of this fact that the plasma waves are driven by the electric field of the light. The present parametric process model predicts that the size of the interspaces is 0.5–0.85 times the laser wavelength. Although such interspaces reported for any materials can be interpreted by this model, it is ambiguous with respect to the plasma (electron) density at the surface. The plasma density depends on the laser fluence, and therefore at least the dependence of the interspaces on the laser fluence must be known. Other metals reported in the relevant literature do not show any dependence between the laser fluence and the interspaces. At the moment, the dependence of the interspaces on the laser fluence for metals is given only by Hashida *et al.*[7] for Cu, as discussed in this Brief Report. The results show no interspaces larger than 0.85 times the laser wavelength, which was consistent with the results of this model.

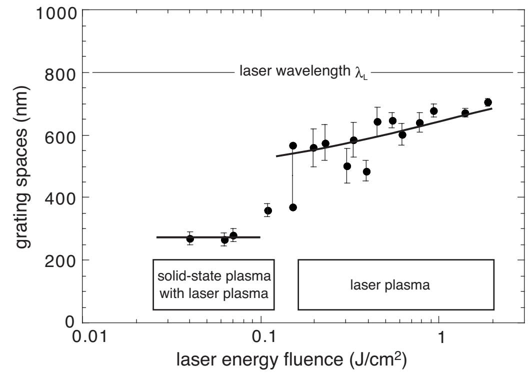

FIG. 4. The interspaces as interpreted on the basis of the parametric induction process and the direct induction process of laser light to surface plasma.

In conclusion, the parametric process involving the interaction of laser light and surface plasma waves, as well as the excitation of surface solid-state plasma, has been proposed for the purpose of providing a physical interpretation of the periodical grating structures self-formed on a copper metal surface by femtosecond-pulse laser irradiation. For the experimentally observed gratings, interspaces with sizes which vary in the range 400–680 nm depending on the laser energy fluence are successfully accounted for by this interpretation.

This work was supported by the Grant-in-Aid for the Global COE Program "The Next Generation of Physics, Spun from Universality and Emergence" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan and partially by the Iketani Science and Technology Foundation and the Amada Foundation for metal work technology.

[1] D. C. Emmony, R. P. Howson, and L. J. Willis, Appl. Phys. Lett. **23**, 598 (1973).
[2] A. K. Jain, V. N. Kulkarni, D. K. Sood, and J. S. Uppal, J. Appl. Phys. **52**, 4882 (1981).
[3] F. Keilmann and Y. H. Bai, Appl. Phys. A: Solids Surf. **A29**, 9 (1982).
[4] Z. Guosheng, P. M. Fauchet, and A. E. Siegman, Phys. Rev. B **26**, 5366 (1982).
[5] J. F. Young, J. S. Preston, H. M. van Driel, and J. E. Sipe, Phys. Rev. B **27**, 1155 (1983).
[6] M. Hashida, M. Fujita, Y. Izawa, and A. F. Semerok, in *Laser Precision Microfabrication*, Proceedings of SPIE, edited by I. Miyamoto *et al.* (SPIE, Washington, 2002), Vol. 4830, pp. 452–457.
[7] M. Hashida, K. Nagashima, M. Fujita, M. Tsukamoto, M. Katto, and Y. Izawa, Proceedings of the 9th Symposium on Microjoining and Assembly Technology in Electronics, edited by K. Atsumi (Japan Welding Society, Tokyo, 2003), Vol. 9, pp. 517–522.
[8] N. Yasumaru, K. Miyazaki, J. Kiuchi, and H. Magara, Proceedings of the 3rd Asian Pacific Laser Symposium (APLS2002), edited by K. Toyoda (Laser Society of Japan, Osaka, 2003), pp. 594–597.
[9] J. Reif, F. Costache, M. Henyk, and S. V. Pandelov, Appl. Surf. Sci. **197-198**, 891 (2002).
[10] S. Matsumoto, A. Yane, S. Nakashima, M. Hashida, M. Fujita, Y. Goto, and S. Takahashi, J. Am. Chem. Soc. **129**, 3840 (2007).
[11] N. Yasumaru, K. Miyazaki, and J. Kiuchi, Appl. Surf. Sci. **254**, 2364 (2008).
[12] H. Sawada, Rev. Laser Eng. **33**, 525 (2005).
[13] T. Katou, N. Abe, M. Yamanaka, and K. Matsumoto, Rev. Laser Eng. **36**, 144 (2008).
[14] Y. Shimotsuma, P. G. Kazansky, J. Qiu, and K. Hirao, Phys. Rev. Lett. **91**, 247405 (2003).
[15] M. Hashida, A. Semerok, O. Gobert, G. Petite, and J. F. Wagner, in *Nonresonant Laser-Matter Interaction (NLMI-10)*, Proceedings of SPIE, edited by M. N. Libenson (SPIE, Washington, 2000), Vol. 4423, pp. 178–185.
[16] M. Hashida, A. F. Semerok, O. Gobert, G. Petite, Y. Izawa, and J. F-. Wagner, Appl. Surf. Sci. **197-198**, 862 (2002).
[17] *Surface Polaritons*, edited by V. M. Agranovivh and D. L. Mills (North-Holland, Amsterdam, 1982).
[18] A. M. Bonch-Bruevich, M. N. Libenson, V. S. Makin, and V. V. Trubaev, Opt. Eng. **31**, 718 (1992).
[19] S. Sakabe, K. Shirai, M. Hashida, S. Shimizu, and S. Masuno, Phys. Rev. A **74**, 043205 (2006).
[20] S. Sakabe *et al.*, Phys. Rev. A **69**, 023203 (2004).
[21] N. Nedyalkov, T. Miyanishi, and M. Obara, Appl. Surf. Sci. **253**, 6558 (2007).
[22] M. Sparks and E. Loh, Jr., J. Opt. Soc. Am. **69**, 847 (1979).