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# Ultrafast electron transport phenomena in highly excited gold films

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## Abstract

Non-equilibrium dynamics of hot electrons in highly excited gold films has been investigated by using the femtosecond transient reflecting grating method. Transport processes which compete with electron-phonon coupling processes were investigated by observing thermal surface displacements. The results were compared with calculations by a simple thermoelastic equation and the two-temperature model with two different conditions for the thermal conductivity. The results suggested that non-thermal states of the hot electrons still contribute transport processes on time scales of several picoseconds. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Gold film; Hot electrons; Transport phenomena; Thermal surface displacement

## 1. Introduction

Ultrafast non-radiative processes in metals, including hot electrons dynamics, play important roles in physical and chemical phenomena occurring on the surface [1]. Direct measurements of the hot electrons in metals have been performed by using a two-photon photoemission method [2] and a transient reflectivity method [3]. For highly excited metal targets, the processes have been investigated in order to understand the initial stage of laser-induced plasma and X-ray generation [4]. According to recent reports, the hot electrons pro-

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duced in metals by fs-laser irradiation affects surface chemical reactions such as laser-induced desorption [5] and surface redox reactions [6]. However, detailed analysis of these chemical reactions have been difficult because the reaction processes compete with hot electrons' energy dissipation processes such as electron-phonon (e-p) coupling and transport processes. In order to investigate the hot electrons effects on the chemical reactions, it is necessary to quantify the energy dissipation processes.

We reported that the transient reflecting grating (TRG) method is a powerful tool to investigate the energy dissipation processes of the hot electrons [7]. In that report, the processes were analyzed by the two-temperature model (TTM) and by the theory of the transient grating method. It was found that the e-p coupling and thermal diffusion processes could be investigated independently. We also

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reported that the TRG method can measure fast surface displacements due to longitudinal acoustic pulse echoes and surface acoustic waves [8]. The surface displacements induced by fs-laser irradiation were analyzed by the TTM coupled with a thermoelastic model. It was found that transport phenomena of the hot electrons can be investigated by the surface displacements analysis. In these reports, temperature dependence of the thermal conductivity  $\kappa$  has been investigated and found to be  $\kappa \propto T_e^{-1}$  or  $\kappa \propto T_e^0$ . The dependence has also been investigated theoretically in a recent report [9].

In this report, we measured surface displacement dynamics of highly excited gold film by the TRG method. The pump laser power dependence of the dynamics was measured and compared along with predictions by the TTM and thermoelastic equation with two different models for the thermal conductivity  $\kappa$ .

## 2. Experimental

A schematic figure of an experimental setup for the TRG method is shown in Fig. 1. TRG responses are measured by a pump-probe technique. A regeneratively amplified Ti : sapphire laser system, which has an autocorrelaton of 200 fs, a wavelength of 800 nm and a repetition rate of 1 kHz, is used as the laser system. Fluence of the pump pulse varies from 0.8 to 3.0 mJ/cm<sup>2</sup>. Two pump pulses of the same wavelength ( $\lambda_{pump} = 400 \text{ nm}$ ) cross on a sample surface with crossing angle of  $2\theta$  and form an optical interference pattern with the fringe spacing  $\Lambda = \lambda_{pump}/(2\sin\theta)$ . The fringe spacing is set to 2.7 µm in this report. The temporally generated interference fringes act as a transient diffraction grating. A probe pulse ( $\lambda_{probe} = 800 \text{ nm}$ ) is incident normal to the grating, after passing through an optical delay line, and is diffracted by the grating. Intensities of the diffracted light are recorded as TRG signals.

A 300 nm-thick polycrystalline gold film deposited on a glass plate was used for the measurements. The penetration depth of the pump pulse was calculated as 16 nm. All the experiments were performed in air at 296 K.



Fig. 1. A schematic figure of the experimental setup for the TRG method. BS, beam splitter; HM, half mirror; ODL, optical delay line; PD, photodiode.

#### 3. Results and discussions

TRG responses of a 300 nm-thick gold film are shown in Fig. 2. The lines (a) and (b) in Fig. 2 represent the responses obtained by pump fluences of 3.0 and  $0.8 \text{ mJ/cm}^2$ , respectively. In both cases, the excitation fringe spacing  $\Lambda$  is set to 2.7 µm. The sharp peaks around 0 ps correspond to dielectric constant changes due to generation and relaxation of the hot electrons. Since analysis of these faster responses have been reported in our previous paper [7], we do not discuss these responses any further in this paper. The TRG response, except the sharp peak represents surface displacement dynamics resulting from temperature rise due to laser irradiation. The response denotes the following processes. At first, the hot electrons energy generated by fslaser irradiation is deposited to lattice system and thermal expansion begins. This thermal expansion brings about surface displacement and the generation of longitudinal acoustic (LA) pulse. The LA pulse reflects at both film/substrate and film/air interfaces. When the LA pulse arrives at the measuring plane (film/air interface) it negates the surface displacement due to thermal expansion. Therefore, periodic decrease of the signal in Fig. 2(b) corresponds to the arrival of the LA pulse echoes.



Fig. 2. Experimental and theoretical TRG responses. (a) Experimental pumped with  $3.0 \text{ mJ/cm}^2$ . (b) Experimental pumped with  $0.8 \text{ mJ/cm}^2$ . (c) Theoretical pumped with  $3.0 \text{ mJ/cm}^2$ . (d) Theoretical pumped with  $0.8 \text{ mJ/cm}^2$ .

Very slow gradual increase of signal is due to the surface acoustic wave (SAW), where wavelength of SAW agrees with the fringe spacing  $\Lambda$  [10,11]. These surface displacement dynamics were confirmed and reported in our earlier paper [8].

In Fig. 2(a) and (b), the first surface expansion peaks around 100 ps are normalized to unit intensity in order to compare the dynamics. The two responses agree with each other almost completely. This result means that the surface expansion and LA pulse generation processes are not affected by changing the pump fluence. When temperaturedependent thermal conductivity is assumed [7], the pulse width of the LA wave becomes broader with higher pump fluence. Therefore, our results shown in Fig. 2(a) and (b) suggest that the temperature dependence of thermal conductivity presented in Ref. [7] is not sufficient to describe the hot electrons dynamics. In this paper, we demonstrate one possible case to explain our results shown in Fig. 2(a) and (b).

In order to analyze the transport phenomena of the hot electrons, the two-temperature model (TTM) was introduced. The TTM assumes that the electron and the lattice systems are in local equilibrium and have characteristic temperatures, which is the electron temperature  $T_e$  and the lattice temperature  $T_1$ . The electron system is not in equilibrium with the lattice system within several picoseconds and  $T_e$  is coupled with  $T_1$  by the electron-phonon coupling. The temporal evolution of the systems can be written by a set of coupled differential equations [12]. Namely,

$$\gamma T_{\rm e} \frac{\partial T_{\rm e}}{\partial t} = V(\kappa V T_{\rm e}) - G(T_{\rm e} - T_{\rm l}) + Q,$$

$$C_{\rm l} \frac{\partial T_{\rm l}}{\partial t} = G(T_{\rm e} - T_{\rm l}), \qquad (1)$$

where  $\gamma T_e$  and  $C_1$  are the electronic and lattice heat capacity, G is the electron-phonon coupling factor and Q is the energy source term. In Eq. (1), diffusion and energy source terms for the lattice systems are neglected because these contributions are small. To calculate the surface displacement u, the simplest form of the thermoelastic equation was introduced and coupled with  $T_1$ . Namely,

$$\frac{\partial u}{\partial t} = \frac{1}{v_{\rm L}^2} \frac{\partial^2 u}{\partial z^2} - \frac{3\beta B}{\rho} \frac{\partial T_1}{\partial z},\tag{2}$$

where z is the axis perpendicular to the surface plane (to thickness direction),  $v_{\rm L}$  is the longitudinal acoustic velocity,  $\beta$  is the linear thermal expansion coefficient, B is the bulk modulus and  $\rho$  is the density. Eq. (2) is coupled with the boundary condition at the free surface. In our analysis, Eqs. (1) and (2) are numerically solved. For the source term Q, a sech<sup>2</sup> function is used for the time-evolution of the pump pulse.

In our analysis,  $\kappa$  is regarded as a constant. Since our previous reports [8] clarified the value for  $\kappa$  in equilibrium state (= 317 W/(m K)) is not sufficient, we use the value 950 W/(m K) for  $\kappa$ , which is suggested in Ref. [7]. The theoretical curves calculated with different pump fluences, 3.0 and 0.8 mJ/cm<sup>2</sup>, are shown in Fig. 2(c) and (d). The two theoretical responses agree well. Therefore, constant thermal conductivity is strongly suggested for the transport process of the hot electrons. In the relaxation time approximation (RTA) theory, the thermal conductivity is expressed as  $\kappa = (1/3)v^2\tau C_e$ , where v is the electronic velocity,  $\tau$  is the relaxation time and  $C_e (= \gamma T_e)$  is the electronic heat capacity. As long as the RTA theory is assumed,  $v^2\tau$  should be proportional to  $T_e^{-1}$ . As electron-electron scattering time is considered to be dominant in the relaxation time in high  $T_e$  region,  $\tau$  may be regarded as electron-electron scattering time. When  $\kappa$  is independent of  $T_e$ , the relaxation time should be expressed as  $\tau \propto T_e^{-1}$ . This temperature dependence does not agree with the well-known relation ship,  $\tau_{e-e} \propto T_e^{-2}$ , where  $\tau_{e-e}$  is the electron-electron scattering time. This inconsistency may be attributed to nonthermal properties of the hot electrons.

## 4. Conclusions

The surface displacement dynamics has been measured on a highly excited gold film. The dynamics has been analyzed by TTM and the thermoelastic equation. In conclusion, temperature independent thermal conductivity is suggested for the transport process of the hot electrons. This non-thermal property of the hot electrons may affect the ultrafast surface chemical reactions. A continual investigation will be made on the relation between the surface redox reactions and the non-thermal properties of the hot electrons, which have been observed at  $Pt/Cl^-$  [6] and  $TiO_2/SCN^-$  [13] interfaces.

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## References

- T. Elsaesser, J.G. Fujimoto, D.A. Wiersma, W. Zinth, Ultrafast Phenomena XI, Springer, Berlin, 1998.
- [2] H. Petek, S. Ogawa, Prog. Surf. Sci. 56 (1997) 239.
- [3] S.D. Brorson, J.G. Fujimoto, E.P. Ippen, Phys. Rev. Lett. 75 (1987) 1962.
- [4] M. Li, S. Menon, J.P. Nibarger, G.N. Gibson, Phys. Rev. Lett. 82 (1999) 2394.
- [5] S. Deliwala, R.J. Finlay, J.R. Goldman, T.H. Her, W.D. Mieher, E. Mazur, Chem. Phys. Lett. 242 (1995) 617.
- [6] A. Hibara, A. Harata, T. Sawada, Chem. Phys. Lett. 272 (1997) 1.
- [7] A. Hibara, T. Morishita, I. Tsuyumoto, A. Harata, T. Kitamori, T. Sawada, Jpn. J. Appl. Phys. 38 (1999) 2983.
- [8] A. Hibara, T. Morishita, I. Tsuyumoto, A. Harata, T. Kitamori, T. Sawada, Proceedings of International Seminar on Photothermal and Photoacoustic Phenomena and Their Application, Tomakomai, Japan, 5–7 Aug. 1998, p. 209.
- [9] A.P. Kanavin, I.V. Smetanin, V.A. Isakov, Y.V. Afanasiev, B.N. Chichkov, B. Wellegehausen, S. Nolte, C. Momma, A. Tünnermann, Phys. Rev. B 57 (1998) 14698.
- [10] Q. Shen, A. Harata, T. Sawada, Jpn. J. Appl. Phys. 35 (1996) 2339.
- [11] K. Katayama, T. Sawada, Q. Shen, A. Harata, Phys. Rev. B 58 (1998) 8428.
- [12] S.I. Anisimov, B.L. Kapeliovich, T.L. Perlman, Sov. Phys. JETP 39 (1975) 375.
- [13] T. Morishita, A. Hibara, T. Sawada, I. Tsuyumoto, J. Phys. Chem. B 103 (1999) 5984.