Linear and nonlinear total-yield photoemission observed in the subpicosecond regime in Mo

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(Received 27 April 1998; revised manuscript received 11 January 1999)

The total charge emitted from a polycrystalline Mo sample by 500 fs laser pulses at normal incidence is measured as a function of the laser peak intensity. Total yield data are taken at wavelengths of 527 and 264 nm. In both cases, a nonlinearity higher than expected is measured. A thermally enhanced regime is clearly observed when using 264 nm pulses for laser peak intensity larger than 0.1–0.2 GW/cm^2. This effect is interpreted on the basis of the nonequilibrium heating of the conduction electrons. Pump and probe photoemission data at 527 nm show a significant enhancement of the photoelectric sensitivity when the probe pulse is delayed by 1 ps from the pump. This enhancement is related to the growth of the available electron density induced by the nonequilibrium heating. Single pulse photoemission at this wavelength is not properly explained by a thermally assisted photoemission regime. This may indicate that other processes have a role in determining the photoemission yield. [S0163-1829(99)10527-7]

I. INTRODUCTION

The study of conduction electrons excited by ultrashort and intense coherent light pulses is relevant to the physics of nonequilibrium heating and electron-electron (e-e) scattering processes in the condensed matter. In particular, linear and nonlinear photoemission induced on metals by short laser pulses have been used to investigate the influence of nonequilibrium heating processes.[1]

The excitation of a metal by intense laser pulses can lead to the emission of electrons through multiphoton photoemission (MPE), thermionic emission, or a combination of these two processes. In the ns range it has been observed that MPE dominates thermionic emission for incident fluences less than 40–100 mJ/cm^2. Instead, in the ps regime, the damage threshold of most materials is reached before a significant contribution from a purely thermal current is observed.[2] In this regime, a thermally enhanced MPE has been reported for *W*, just below the damage threshold.[3] Laser pulses in the sub-ps regime allow the excitation of the conduction electrons in a metal and to measure the photoelectric yield before appreciable energy is transferred to the lattice vibrational states. The uncoupling between the electron gas and the ion lattice allows the electron temperature T_e to become larger than T_l.[4] Since the heat capacity of the electron gas (at room temperature) is generally two orders of magnitude smaller than the lattice heat capacity, $T_e - T_l$ can be thousands of degrees during the interaction time. As a consequence, the photoelectric yield induced by ultrashort laser pulses is influenced by the instantaneous electron-gas peak temperature, a regime called ''thermally assisted photoemission.'' [3] This paper reports the effects of nonequilibrium heating on the total yield photoemission from a Mo sample.

The emitted total charge is measured as a function of laser-pulse peak intensity at the wavelengths of 264 and 527 nm, with a temporal pulse width of 500 fs. The photoemission data obtained using UV laser pulses ($\lambda = 264$ nm, $h\nu = 4.7$ eV), with a photon energy $h\nu$ higher than the Mo work function Φ (≈ 4.6 eV), has shown a thermally assisted photoemission contribution on an otherwise linear photoemission process. It is found that the predictions of the classical Fowler-DuBridge theory,[5] extended by Bechtel to the nonequilibrium, high intensity regime (extended Fowler-DuBridge theory),[3] are consistent with our UV experimental data.

Instead, the total yield measurements at 527 nm ($h\nu = 2.35$ eV) has revealed a nonlinearity higher than that expected for a two photon thermally assisted photoemission. Pump and probe measurements, with the pulses not overlapped in time, evidences the effects of the nonequilibrium electron heating induced by the pump pulse on the delayed probe. In this case, it is found that the photoelectric sensitivity of the probe pulse is significantly enhanced when the pump-probe delay time is reduced to ≈ 1 ps. This enhancement is related to the growth of the available electron density induced by the nonequilibrium heating.

II. EXPERIMENT

The radiation source is based on a passively mode locked, feedback controlled Nd:glass oscillator and a Nd:glass regenerative amplifier with stretcher and compressor stages, yielding 1.3 ps laser pulses at 1054 nm with a maximum energy of 6–8 mJ after the amplification stage. These infrared pulses

are frequency doubled in a second harmonic compressor, capable of yielding green laser pulses at 527 nm with a temporal compression, with respect to the infrared pump pulses, of a factor between 2.5 and 4, according to pump intensity.[6] Typical laser-pulse temporal width after the second harmonic compressor are ~500 fs, with a maximum energy of 0.8–1 mJ and a repetition rate of 10 Hz. A subsequent frequency doubling in a potassium dihydrogen phosphate (KDP) crystal of the green pulses permit us to obtain UV pulses at 264 nm ($h\nu=4.7$ eV), with a comparable temporal width and a maximum energy of 300 μJ. The temporal width of the 264 nm laser pulses is measured using self-diffraction in a quartz slab.[7] The pulse spectrum is monitored continuously during the experiments.

The polycrystalline Mo sample is polished with a micrometer compound to a mirror finish, cleared in ultrasonic baths of acetone and ethyl alcohol and dried with N_2. After the insertion in an ultrahigh vacuum system (base pressure of 4×10^{-9} mbar during the experiments) the emitting area is activated by irradiating it *in situ* with 264 nm laser pulses at high fluence. As reported by other authors,[8] the action of UV pulses provides a satisfactory cleaning action, removing a significant portion of the oxide at the surface, as demonstrated by the observed increase in photoemission yield with laser irradiation.

An anode wire in front of the sample surface is biased to 11 kV to collect the extracted charge and avoid space-charge effects. The emitted charge is measured directly from the cathode with a fast (500 MHz) sampling oscilloscope. An absolute calibration is made with a calibrated, charge-sensitive amplifier. The transmission of the optics and fused-quartz viewport of the vacuum chamber is taken into account in calculating the pulse energy on the cathode.

III. RESULTS AND DISCUSSION

Figure 1 reports a log-log plot of the photoelectric sensitivity dependence on intensity for a Mo sample at two wavelengths [$\lambda=264$ nm ($h\nu=4.7$ eV) and $\lambda=527$ nm ($h\nu=2.35$ eV)]. The sensitivity S is measured in amperes per watt (A/W) and is defined as J/I, where J is the peak current density and I is the laser peak intensity. According to multiphoton photoemission theory, the expected logarithmic slope (N) for Mo [work function $\Phi\cong4.6$ eV (Ref. 15)], is $N=0$ for $h\nu=4.7$ eV (one photon process) and $N=1$ for $h\nu=2.35$ eV (two photon process). Nevertheless, as clearly evidenced in Fig. 1, stronger nonlinearities are found at both wavelengths, indicating that the single photon and two photon processes have been distorted.

In the present experiment, the laser pulse temporal width ($\tau\cong0.5$ ps) is shorter than the typical relaxation time between electron and phonons, which is of the order of 1 ps for most metals.[9] The consequent distortion of the Fermi distribution by the induced nonequilibrium heating modifies the photoemission process. To account for this effect, the experimental data are compared to the predictions of the extended Fowler DuBridge theory (EFD).

According to EFD, the total current density J is expressed as a sum of partial current densities J_n

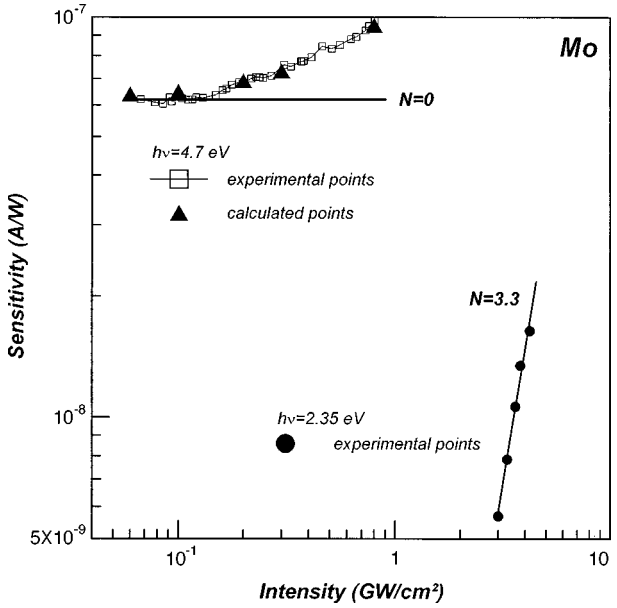

FIG. 1. Single pulse sensitivity versus peak intensity from a Mo sample using 0.5 ps laser pulses at 527 nm ($h\nu=2.35$ eV) and 264 nm ($h\nu=4.7$ eV), normal incidence. N indicates the logarithmic slope.

$$J=\sum_{n=0}^{\infty}J_n, \tag{1}$$

where the partial current density can be expressed as a function of the laser peak intensity and electron temperature,

$$J_n=a_n\left[\frac{e}{h\nu}(1-R)I\right]^n AT_e^2F(X_n),$$

$$X_n=\frac{nh\nu-\Phi}{k_BT_e}, \tag{2}$$

a_n being a constant proportional to the transition probability of an electron from the conduction band to vacuum for the n-photon process ($nh\nu-\Phi>0$), A the Richardson constant, F the Fowler function, and T_e the electron temperature.

In the case of a linear photoemission process, only J_0 and J_1 can contribute to the total photocurrent, while higher-order terms are disregarded since they correspond to the absorption of a number of photons larger than that needed to overcome the surface-potential barrier. The surface electron temperature profiles have been calculated using the two temperature model (TTM).[4] The calculated electron peak temperatures, in the intensity range investigated here, do not exceed 600 K. That excludes thermionic emission contribution to the measured current density. Therefore only J_1 is contributing to the photoemitted charge.

The Fowler function, for $h\nu-\Phi>0$, can be written as

$$F=F_0-F_S, \tag{3}$$

where

$$F_0=\frac{\pi^2}{6}+\frac{X_1^2}{2},$$

TABLE I. Physical parameters of Mo.

λ: wavelength (nm)	264	527
R: reflectivity[a]	0.66	0.58
α: absorptivity[b] (m^{-1})	18×10^{7}	8.8×10^{7}
K: thermal conductivity[c] (W/m K)	142	
C_1: lattice heat capacity[d] ($J/m^3 K$)	2.65×10^{6}	
γ: electronic heat capacity[e] ($J/m^3 K^2$)	212	
g: electron-phonon coupling[f] ($W/m^3 K$)	1×10^{17}	

[a]Measured at normal incidence.
[b]Reference 10.
[c]Reference 11.
[d]Reference 12.
[e]Reference 13.
[f]References 9 and 14.

$$F_S=\sum_{h=1}^{\infty}(-1)^{h+1}\frac{e^{-hX_1}}{h^2}. \tag{4}$$

These expressions can be simplified by considering that, in the same intensity range, the condition $k_B T_e < h\nu-\Phi$ is satisfied and, as a consequence, F_S is small with respect to F_0 and it can be neglected, i.e., $F\approx F_0$. Under these circumstances, a_1 results in

$$a_1=\frac{S_0}{\frac{e}{h\nu}(1-R)AT_0^2F_0(T_0)}, \tag{5}$$

with S_0 and T_0 being the sensitivity and the electron temperature relative to the linear photoemission zone. Using the parameters reported in Table I and considering T_0 equal to room temperature, the single-photon emission cross section a_1 for Mo at 264 nm is estimated to be $8\times10^{-15}\,cm^2/A$. From Eqs. (2)–(5), it follows that the ratio between the nonlinear sensitivity (S) at high intensity levels and the linear sensitivity (S_0) in the low intensity regime is given by

$$\frac{S}{S_0}=\frac{T_e^2+\frac{3}{\pi^2}\left(\frac{\Delta}{k_B}\right)^2}{T_0^2+\frac{3}{\pi^2}\left(\frac{\Delta}{k_B}\right)^2}, \tag{6}$$

where $\Delta=h\nu-\Phi$.

According to the present model, the measured sensibilities ratio S/S_0 is derived only from the (mean) surface electron temperature and the photon excess energy with respect to the work function (Δ). In this respect, the total yield photoemission data constitute a direct probe of the nonequilibrium heating of the electron gas while Eq. (6) estimates directly the electron-gas (nonequilibrium) temperature.

The consistency of this model can be verified by calculating, on the basis of the TTM equations and Eq. (6), the sensitivity enhancement measured in the experiment. The temporal profile of the surface electron temperature induced by a 0.5 ps Gaussian laser pulse has been calculated using the TTM model with the parameters reported in Table I. It must be recalled that the measured sensitivity corresponds to an integrated charge, so it depends on the mean temperature $\langle T_e^2\rangle^{1/2}$ of the electron gas, obtained by averaging the temperature profile in the full width at half maximum (FWHM) temporal width of the laser pulse. In Fig. 1 the values of the calculated sensitivity (black triangles) and the experimental values (open squares) are reported. A good agreement is found for $\Delta=80$ meV, which implies a work function of $\Phi\approx4.61$ eV. This value is close to that reported in the literature[15] for polycrystalline Mo.

Using photons of energy $h\nu=2.35$ eV it is possible to study the nonequilibrium heating effect on an intrinsically nonlinear two photon electron emission process. In this case, the Mo sensitivity should exhibit a linear dependence on the laser intensity. Figure 1 shows that the measured sensitivity trace has a logarithmic slope close to 3.3, indicating a strong nonlinear behavior. In this case, according to EFD theory, the total current is given by the sum of the partial currents contributions up to the second order,

$$J=J_0+J_1+J_2. \tag{7}$$

Using the TTM equations to calculate surface temperatures, it is possible to calculate the logarithmic slope of the sensitivity relevant to J_2, which gives the dominant contribution. It is found that, in the present intensity range, the calculated logarithmic slope (~2) is significantly lower than the experimental value. This discrepancy could be explained by a two photon process modified by a variation of the material parameters under the action of the laser pulses, or by a contribution from lower order thermally assisted processes. In the first case it is not possible to estimate the variation of the material parameters, like the work function, the electron-phonon coupling, and the absorption constant. In the second case the coefficients a_n, that express the transition probabilities, are unknown and therefore it is impossible to sum the partial currents with the proper weights. However, a slope higher than that expected is in agreement with previous experimental data and qualitatively justified by the considerations of Girardeau-Montaut.[16]

The effects of nonequilibrium heating of the electron gas on the total yield emission can be directly observed when a pump pulse precedes the probe and the pulses are not temporally overlapped. In this case, the coherent effects between the pulse peak intensities are suppressed and the possible photoemission enhancement can be assigned to the nonequilibrium electron heating.

Figure 2 shows the pump and probe experimental setup. The laser pulse is split by a 50/50 beam splitter (BS1 in Fig. 2). One beam is sent through a variable delay line, the other through a half wave plate and a linear polarizer (HW and P1 in Fig. 2). The transmission axis of the polarizer is orthogonal to the polarization plane of the beam in the delay line. Rotating the half wave plate it is possible to adjust the en-

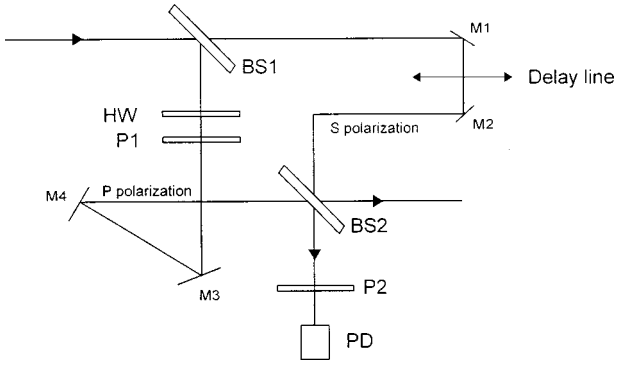

FIG. 2. Scheme of the experimental setup. BS1, BS2: beam splitters; HW: half wave plate; P1 and P2: linear polarizers; PD: photodiode; M: mirrors. See text for a description.

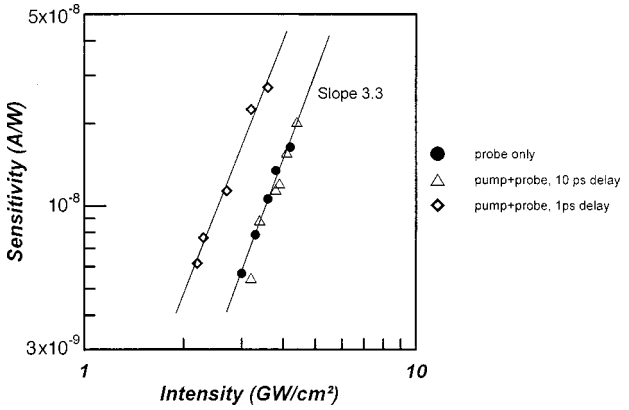

FIG. 3. Sensitivity versus peak intensity from Mo, using 0.5 ps–527 nm laser pulses at normal incidence. Filled symbols refer to single laser pulses, empty symbols to a probe pulse delayed from a pump pulse. The sensitivity of the probe pulse is measured for two time delays, 10 ps (triangles) and 1 ps (diamonds).

ergy of the laser pulses without affecting the polarization plane. This scheme allows to have two beams with crossed polarizations and to control the intensity of one of them. The two beams are then overlapped onto a second beam splitter (BS2), that preserves the incoming polarization, and form two outgoing beams of collinearly superposed, orthogonally polarized, and delayed pulses. The linear polarizer P2 has the transmission axis orthogonal to the beam coming from the delay line. Under these conditions the photodiode measures a signal proportional to the energy of the pulse from the half wave plate polarizer (HW-P1) stage. The delayed pulses are then focused at normal incidence onto the sample surface, from which the extracted charge is measured.

With the described setup, it is possible to measure the intensity dependence of the total yield as a function of the delay between a first, constant energy pulse (the pump pulse) and a second pulse (the probe pulse) whose energy can be varied continuously.

Figure 3 reports the photoemission yield versus peak intensity due to a probe pulse when a $3\mathrm{GW/cm}^2$-0.5 ps pump precedes the probe for time delays of 10 and 1 ps. The energy of the pump pulse is subtracted from the total energy measured by the photodiode. Also the charge extracted by the pump pulse alone is subtracted from the total charge measured from the cathode when both pulses are present.

The pump pulse induces a transient nonequilibrium electron heating that is completely relaxed to lattice temperature after 10 ps. This effect is evidenced by the fact that the probe pulse sensitivity coincides with the single pulse sensitivity, in the 10 ps delay pump and probe experiment, indicating that the probe pulse interacts with a cold electron gas. For a delay time of 1 ps, a clear enhancement of the sensitivity of the probe pulse is observed. The enhancement in the sensitivity is about a factor 3 with respect to single pulse. This enhancement is attributed to the transient nonequilibrium heating induced by the pump pulse. It would be interesting to follow the evolution of the sensitivity continuously as a function of the delay from the pump pulse, but to obtain reasonable results a laser pulse duration much shorter than the electron-phonon relaxation time is required.

To make a qualitative analysis, recall that $T_e F(X_n)$ is an estimate of the number of electrons that are available to the n-photon emission process in the case that the electron gas can be described by a Fermi distribution at temperature T_e.[5] The leading edge of the probe pulse interacts with an electron gas that is at high temperature, while the trailing edge interacts with a much colder electron gas. As a first approximation it is possible to calculate the ratio of available electrons between room temperature and the high temperature seen by the leading edge of the probe pulse with the relation

$$R=\frac{T_e^2 F_e(X_2)}{T_0^2 F_0(X_2)}, \tag{8}$$

where the subscript ''0'' refers to room temperature and the subscript ''e'' to the electron-gas temperature induced by the pump pulse.

The mean electron temperature seen by the leading edge of the probe pulse is estimated around 1000 K using the TTM equations. In this case, the ratio of available electrons is $R\approx 2.5$, to be compared with an experimental enhancement ratio between 2.7 and 2.8. Even allowing for an incertitude in electron temperature of some hundreds of degrees, the values of the estimated ratios R are of the same order of the experimental enhancement.

This analysis indicate that, even if the logarithmic slope of the single pulse photoemission is not explained considering the intensity dependence of J_2 as calculated from EFD theory, the measured enhancement in the two pulse experiment is indeed directly related to a nonequilibrium electron heating effect.

It must be noticed that the electron gas of a metal heated by a sub-ps laser pulse cannot be considered a thermalized distribution during the interaction time and consequently the electrons are not described by a Fermi-Dirac distribution at temperature T_e. According to the thermalization times measured in Au of about 700 fs for electrons at temperatures of 0.1 eV (Ref. 17) and assuming, as a rough estimate, a similar thermalization time in Mo, the probe pulse in the present experiment interacts with a hot and thermalized electron distribution. Since the EFD theory assumes a thermalized electron distribution, this is consistent with the fact that the sensitivity enhancement of the probe pulse due to a nonequilibrium heating induced by a pump pulse is qualitatively explained in the framework of the EFD model. However, the single pulse logarithmic slope is not properly ex-

plained by this model. This may indicate that contributions from other processes have a role in determining the photoemission process (for example e-e scattering). More experimental work is needed to address this question.

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