Multiphoton electron emission from Cu and W: An angle-resolved study

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The experimental results of multiphoton electron emission from Cu and W induced by 2-eV 100-fs laser pulses with *s* and *p* polarizations at incidence angles between 0° and 85° and different intensities are reported. The data show a third-order nonlinear photoemission process for Cu and a fourth-order behavior for W. For both metals the electron emission is higher for the polarization in the incidence plane, with a maximum value at the pseudo-Brewster angle, while the electron yield as a function of the incidence angle exhibits an unambiguous dependence on the bulk absorption coefficient and it can be accounted for on the basis of the Fresnel equations. [S0163-1829(96)02233-3]

Since the early models developed by Fowler[1] and Dubridge,[2] several theoretical and experimental investigations have been carried out on photoelectron emission from metal surfaces, and nowadays this subject represents an important branch of modern surface science. In particular, the advent of powerful ultrashort laser pulses has allowed the investigation of the nonlinear case on time scales comparable to electron-phonon relaxation times[3–6] and has highlighted several similarities between multiphoton electron emission from a metal surface and the multiphoton ionization of free atoms.[7,8]

Multiphoton electron emission processes have been interpreted by Bechtel, Smith, and Bloembergen[3] (BSB model), extending to the nonlinear case the Fowler-Dubridge theory.[1,2] However, when pulses are shorter than the electron-phonon relaxation time, a decoupling between the electrons and lattice temperatures can take place, generating the so-called anomalous heating effect. This effect, postulated by Bechtel and Bloembergen,[3,9] was observed by Fujimoto and co-workers[5] on a polycrystalline W sample using a 620-nm 75-fs laser source. In alternative, extending the model proposed by Broudy[10] for the linear case to multiphoton processes, a surface-enhanced optical absorption (SEOA) should be expected.[10] This mechanism takes into account the role played by the surface states in favoring the electron emission for the *p*-polarized light and in contrast to what expected by the BB model, the total electron yield *Y* versus the light beam incidence angles and polarization should deviate from that expected on the basis of the bulk absorption coefficient and Fresnel equations. Girardeau-Montaut *et al.*[11] have reported the evidence of a possible SEOA effect, in the single-photon emission case, on a Au sample irradiated by a 248-nm 450-fs laser source at 82° and 86° angles of incidence. Moreover, Srinivasan-Rao *et al.*[12] observed an enhancement of the multiphoton emission for *p*-polarized light up to 75 times larger than for the *s* polarization on Cu mirrors at 72.5° incidence and 10^{11} W/cm^2 intensity, assigning this behavior to optical field effects. With the aim to explain these behaviors, Aeschlimann *et al.*[13] have tried to correlate the surface enhancement with the surface roughness, while Fann *et al.*[14] have suggested that image-potential surface states could give rise to resonant enhancements in the multiphoton photoemission electron distribution.

On the other hand, as reported by Elsayed-Ali *et al.*[15] the electron-phonon transfer time was observed to be 1–4 ps for Cu and is expected to be similar for W. Therefore, operating at 120 fs only *e*-*e* interaction mechanisms should be observed and effects originating from electron-phonon scattering processes should be excluded. Using these experimental conditions, nonlinear photoemission processes on metals, such as W and Cu, should be simplified, the electron gas being decoupled from the lattice.

To clarify the origin of multiphoton electron emission, angle-resolved experiments by *s*- and *p*-polarized subpicosecond laser pulses are required. This paper reports the nonlinear photoemission data obtained on Cu and W polycrystalline samples as a function of incidence angle, light polarization, and beam intensity, using 120-fs pulses at 600 nm with energies up to 100 μJ. It is shown that the changes of the photoemission current as a function of polarization, intensity, and laser beam incidence angle θ are well described for both Cu and W by the bulk absorption coefficient and Fresnel equations, despite the fact that in Cu a third-

order photoemission process is detected, while in W anomalous heating effects seem to be present.

Nonlinear photoelectric effects originate when the energy $h\nu$ of the incident photon is lower than the metal work function Φ. In this case, to extract an electron from the solid, a simultaneous absorption of n photons has to take place according to the condition

$$n=\left\{\left(1\frac{\phi}{h\nu}\right)+1\right\}, \tag{1}$$

$\{x\}$ being the function ''integer part of x.''

Such an effect becomes dominant when an ultrashort high-power laser pulse hits a metal surface. Several models describe the dynamics of the extraction process relating the yield to the intensity of the light incident on the material bulk.[3,10,16–19] Among the proposed theories, the one developed by Bechtel, Smith, and Bloembergen[3] as a generalization of the Fowler-Dubridge model[1,2] attracted interest. Such a model is based on the assumption that the photoemitted current density is a linear combination of many partial contributions, each characterized by its own order of nonlinearity.

$$\mathbf{J}(\mathbf{r},t)=\sum_{n=0}^{\infty}\mathbf{J}_n(\mathbf{r},t), \tag{2}$$

where

$$\mathbf{J}_n(\mathbf{r},t)=a_n\left(\frac{e}{h\nu}\right)^n A(1-R)^n I^n(\mathbf{r},t)T^2(\mathbf{r},t)F\left(\frac{nh\nu-\phi}{kT(\mathbf{r},t)}\right), \tag{3}$$

a_n being an empirical parameter related to the probability that an electron is photoemitted, e the electron charge, A the Richardson coefficient, R the reflectivity, I the incident light intensity, T the sample temperature, and F the Fowler function.[1]

For relatively low light intensities, the dominant contribution to the total current density is in general due to the $\mathbf{J}_n$ term with the lowest order of nonlinearity in Eq. (2). Concerning the electron yield, the model states that it is entirely dependent on the bulk absorption coefficient, which can be expressed in the nonlinear case as $(1-R)^n$, where n is the nonlinearity order and R the reflection coefficient relative to the incident polarization. The ratio between the electron yield for s- and p-polarized beams can be written as

$$\frac{Y_P}{Y_S}=\gamma(\theta)\,\frac{(1-R_P)^n}{(1-R_S)^n}, \tag{4}$$

where θ is the incidence angle. For the BSB model $\gamma(\theta)=1$ and the yield ratio is the ratio of the bulk absorption coefficients. In the case of SEOA, this does no longer hold true and a $\gamma(\theta)>1$ coefficient accounts for the surface effects. In this light an angle-resolved experiment using p- and s-polarized laser beams in the subpicosecond regime will clarify this issue.

The light beam was provided by a Spectra Physics synchronously pumped mode-locked dye laser, producing after compression and further amplification 600-nm 120-fs pulses with energies up to 100 μJ at 30 pulses per second repetition rate. The s or p polarization and the variable attenuation were obtained by a half-wave retarder-polarizer pair. The beam was then focused by a 1-m convex lens on the sample placed in a UHV chamber. The incident pulse energy was measured on line on a portion of the beam immediately before the vacuum chamber. Both Cu and W were polished down to 1 μm, and after degreasing in a tricloroethilene bath and rinsing with ethanol, they were mounted in a Teflon holder inside the vacuum chamber. Before each measurement the samples were laser ablated using the femtosecond laser beam at full power with no focusing lens. This process, as reported by other authors,[20] should provide a satisfactory cleaning of the metal surfaces. The Teflon holder in the vacuum chamber was clamped in a four degrees of freedom manipulator, in such a way that the rotation axis laid in the same plane of the exposed surfaces for each sample. An anode grid was held 2 mm apart from the samples to be analyzed at 20 kV voltage. Finally, the samples were electrically connected to the measurement instrumentation. The entire system was kept in ultrahigh-vacuum conditions at $\approx 10^{-6}$ Pa. When the laser beam hit the sample surface, the photoemitted electrons were drained away by the grid potential, thus avoiding space charge effects. The photoextracted charge induced a photocurrent on the sample which was detected on the charge preamplifier connected to the sample.

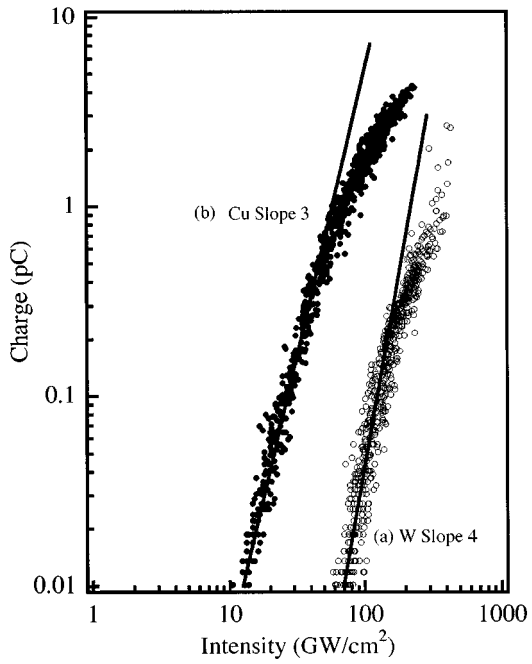

FIG. 1. Charge vs beam intensity curves in bilogarithmic scale for (a) W and (b) Cu at normal incidence.

Figure 1(a) reports, on a logarithmic scale, the integrated photoemitted charge as a function of intensity due to a 120-fs normally incident laser pulse on the W sample. The data show a +4 slope in agreement with data already published.[5] The interpretation of this behavior is based on the hypothesis that a nonequilibrium condition is produced between temperatures of the electron gas and the lattice as suggested in Ref. 5. If the laser pulse duration is comparable or shorter than the electron-phonon energy transfer time, the electrons and lattice will not be in thermal equilibrium and the time evolution of their temperatures can be described by a set of

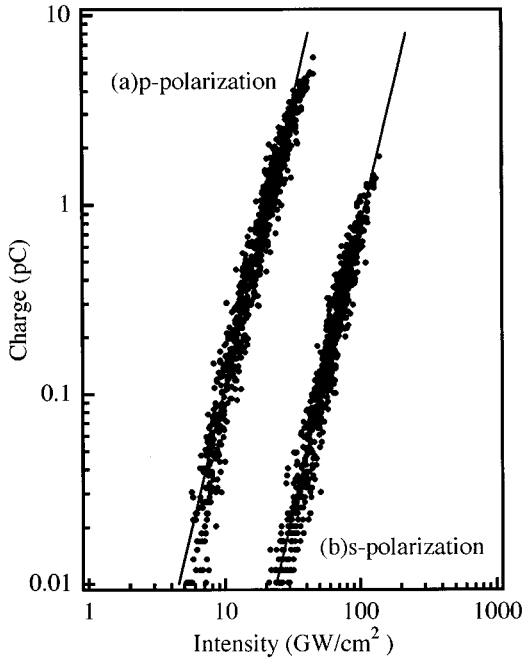

FIG. 2. Charge vs beam intensity curves in bilogarithmic scale for Cu at 75° incidence. (a) *p* polarization and (b) *s* polarization.

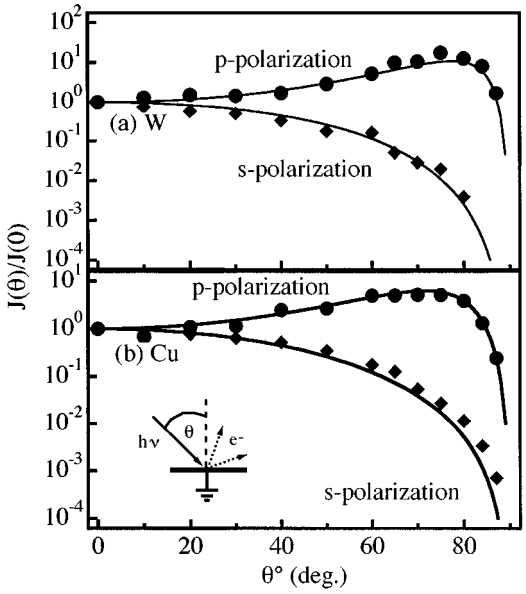

FIG. 3. Photoextracted charge as a function of the incidence angle for a given light intensity. The quantity on the vertical axis has been normalized to the extraction yield at normal incidence. (a) W and (b) Cu. The solid lines represent the theoretical curves calculated using the bulk absorption coefficients and Fresnel equations.

coupled nonlinear differential equations.[21] However, for relatively low laser intensity heating is negligible and the electrons lie in a low-temperature Fermi distribution. Applying these considerations to W, whose work function is approximately 4.55 eV,[22] for 2-eV photons the electron emission will mainly occur via a nonlinear three-photon mechanism. That will result in the logarithmic plot of Y versus I in a line with a $+3$ slope. Instead, the $+4$ slope observed at larger intensities is interpreted as a thermally assisted mechanism where part of the photons arises the Fermi electron gas temperature, favoring an electron emission process involving less than three photons.[5] The decrease in slope taking place at very high intensity is caused by a charge saturation effect arising from a space charge accumulation in the region between the sample and the extraction grid.[5] Such an effect is maximum at normal incidence (Fig. 1) and decreases proportionally to $\cos\theta$, as Fig. 2 shows. Unfortunately, the noise figure of the laser system used in the present experiment did not allow us to extend the investigation at the low-intensity regime where the three-photon electron emission process is expected to be dominant.

At the same experimental conditions used for tungsten, copper exhibits a $+3$ slope [Fig. 1(b)] as expected for a mere multiphoton emission process in the low-temperature Fermi distribution limit [Cu work function 4.65 eV (Ref. 22)]. This result is quite surprising, since the electron and lattice temperatures are coupled through the electron-phonon coupling constant, which is roughly 3 times larger in W than in Cu.[23] This implies an energy transfer time between the electron gas and the lattice shorter for W than for Cu and in both cases on the picosecond time scale. Therefore, a thermally assisted photoelectron emission should be expected also for Cu. A possible explanation of a mere multiphoton emission process in the low-temperature Fermi distribution limit for Cu could arise if the different nature of conduction electrons in Cu and W is considered. While in Cu the dominant s-p character of the conduction electrons leads to more highly dispersed bands and a longer electron mean free path, in W strong electron correlation effects should dominate increasing significantly the e-e interaction processes. As a consequence it is not surprising to observe more pronounced anomalous heating effects in W than in Cu. Actually, a possible relation between anomalous heating and strong electron correlation effects is an interesting subject to be enquired into in detail.

Figure 2 reports on a logaritmic scale the integrated photoemitted current as a function of the incident laser pulse for both the s- and p-polarized beams at 75° incidence angle in the case of the Cu sample. The data show a dependence, not observed at normal incidence, on the laser polarization, indicating that the emission yield is about one order of magnitude larger for the p-polarized light (electric field normal to the surface). This result could apparently suggest, according to the model proposed by Broudy, that the extraction mechanisms are directly related to the component of the electric field normal to the surface (surface enhanced effects); however, this is not the case as is demonstrated in Figs. 3(a) and 3(b). The data report the photoextracted charge as a function of the incidence angle for a given light intensity. The quantity on the vertical axis has been normalized to the extraction yield at normal incidence (equal for both polarizations). For both Cu and W, as the angle varies from normal to grazing incidence, the total yield decreases for the s polarization (diamond dots) and increases for the p polarization (solid dots), up to a maximum value in proximity of the pseudo-Brewster angle, and then rapidly decreases. The solid lines represent the curves calculated by Eq. (4) for both s and p polarizations using $\gamma=1$. The fit is very good, indicating, in agreement with the BSB model, that the multiphoton mecha-

nism responsible for the total electron yield can be explained, in the present case, on the basis of the Fresnel equations and bulk absorption coefficients for both Cu and W, whereas possible SEOA effects are not observed.

The disagreement between the present experiment and others reported in the literature, where SEOA effects are suggested,[11,12] could originate from different experimental conditions, different metals investigated, or even different setups used to collect the extracted charge. Nevertheless, it is important to note that in the present case, the total electron emission yield was measured for the *p* and *s* polarizations at incidence angles ranging from 0° to 85°, allowing a meaningful comparison between Eq. (4) and the experimental data. This comparison unambiguously suggests that the best fitting is obtained for $\gamma(\theta)=1$, thus ruling out any possible SEOA mechanism.

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