Femtosecond Field Ion Emission by Surface Optical Rectification

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We show that a model based on the surface optical rectification effect associated with the nonlinear response of free electrons may explain quantitatively, without adjustable parameters, all the observed features of the ultrafast laser-assisted field-ion emission from metal tips. Moreover, the same model provides also a plausible explanation for the low-fluence ultrafast laser ablation recently observed in metal surfaces and nanoparticles. We further test our model with experiments of ultrafast laser-assisted field-ion emission from tungsten tips in the tomographic atom probe.

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Recent experimental evidence from separate fields of laser physics converges into indicating that ultrashort laser pulses, in suitable conditions, may remove atoms from a metal surface within a time as short as few hundreds of femtoseconds. However, the underlying mechanism of this effect is obscure. One example is found in the phenomenon of laser-assisted field-ion emission (LAFIE) from metal tips. In LAFIE, surface atoms are emitted from the tip in the form of ions by the combined action of a high-voltage (HV) electrostatic (dc) field and of a laser pulse, the latter triggering the emission. This phenomenon has been exploited in the tomographic atom probe (TAP), a powerful technique for atomic-scale three-dimensional (3D) imaging of materials [1,2]. In conventional TAP, HV nanosecond pulses are used also for triggering the emission. Nanosecond laser pulses were used in place of HV ones but, for metal samples, only a thermally induced evaporation was observed [3]. In contrast, TAP images obtained with femtosecond laser pulses preserve the atomic resolution (see, e.g., Fig. 1), indicating that thermal effects are probably not dominant in this case [4,5], although this issue is still debated (see, e.g., Refs. [6,7]). In addition, as mentioned above, very recent pump-probe experiments indicate that the ion emission is actually taking place on a femtosecond time scale [8]. Another example was reported recently by Plech *et al.*, who demonstrated a strongly anisotropic ablation of suspended gold nanoparticles induced by 100 fs laser pulses, which stopped completely if the pulse duration was stretched to 1 ps, and whose mechanism was ascribed to some yet unidentified nonlinear optical effect [9]. Finally, at relatively low fluences close to the ablation threshold, a nonthermal ablation regime of planar metal surfaces has been reported, which appears to develop on the femtosecond time scale and whose fundamental mechanism is under discussion [10–13].

In Ref. [7], our group proposed an interpretation of ultrafast LAFIE as resulting from the action of the quasi-dc (THz) electric field generated by the electronic nonlinear optical response of the metal surface: the so-called optical rectification (OR) effect. However, the OR model developed in Ref. [7] neglected the near-field nature of the OR field and therefore was unable to predict its strength and direction. So, the validity of the OR interpretation of LAFIE remained highly uncertain. Here, we present the first quantitative model of the OR electronic surface field and use it to perform a strict verification of its contribution to LAFIE. Moreover, we put forward the working hypothesis that the same effect may be also at the root of the reported ultrafast ablation phenomena.

Optical rectification is a classical second-order nonlinear optical process taking place in noncentrosymmetric materials. It is also predicted to occur at the surfaces of all materials, where inversion symmetry is broken by the strong material gradients. However, a direct detection of surface OR is very difficult and an undisputable evidence of its occurrence is still lacking, although some possible confirmations have been reported [14,15]. Theoretically, the properties of OR on metal surfaces may be calculated by the same methods used for modeling second harmonic generation (SHG) [16–18]. Let us consider a locally flat metal surface element and a local xyz Cartesian coordinate system with the z axis normal to the surface, pointing

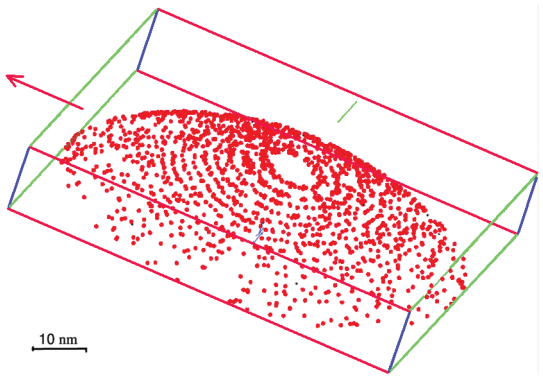

FIG. 1 (color). Atom probe 3D image of the surface of a tungsten tip taken with femtosecond laser emission triggering.

outward, as shown in Fig. 2. Let us also place the origin $z = 0$ in the bulk of the metal, just before all interfacial gradients begin. The surface gradients of electronic density and of all other material properties are then assumed to be comprised between $z = 0$ and $z = l$, where l is the total thickness of the interfacial region, or "selvedge." For an input optical wave of frequency ω and wavelength λ, the resulting surface OR may be characterized by a second-order nonlinear (electrostatic) polarization, formally given by

$$P_{\mathrm{OR},i}(z) = 2\epsilon_0 \chi^{(2)}_{ijk}(z) F_{L,j} F^*_{L,k}, \tag{1}$$

where $F_{L,i}$ with $(i = x, y, z)$ is the local optical-electric-field amplitude at frequency ω, here defined as the field at $z = 0^-$, i.e., just inside the metal bulk, $\chi^{(2)}_{ijk}(z) = \chi^{(2)}_{ijk}(0; \omega, -\omega)(z)$ is the relevant second-order susceptibility tensor for OR at position z (vanishing outside the selvedge), and ϵ_0 is the vacuum permittivity (sum over repeated indices is understood hereafter) [17]. The local field is linearly dependent on the incident optical field, as generally expressed by the relationship $F_{L,i} = L_{ij} F_{0,j} = L_{ij} e_j F_0$, where e_j is a unit vector specifying the input polarization, L_{ij} is the (macroscopic) local-field tensor, and F_0 is the incident optical field amplitude. The tensor L_{ij} depends on the system geometry and on the linear-optical properties of the metal at frequency ω (see, e.g., Refs. [19,20] for its expression in some specific geometries).

Adopting the notations of Refs. [17,18], the OR polarization given in Eq. (1) must be considered to include all the nonlinearly induced electronic displacements and currents taking place in the selvedge (to second order in the input field); i.e., it already takes into account all electronic screening effects. This implies that in order to calculate the generated fields, this polarization may be formally considered as located in a ideal thin vacuum layer replacing the selvedge. Therefore, to first order in the ratio l/λ, the resulting electric field (z component) created within this layer is given by

$$F_{\mathrm{OR}}(z) = -P_{\mathrm{OR},z}(z)/\epsilon_0 = -\chi^{(2)}_{zlk}(z) L_{zl} L^*_{zk} e_l e^*_k I_0/(\epsilon_0 c), \tag{2}$$

where $I_0 = 2\epsilon_0 c |F_0|^2$ is the input light intensity and c is the vacuum speed of light (the x and y field components vanish to first order) [17].

In Eq. (2), the most critical parameter for estimating the generated OR field is the nonlinear susceptibility $\chi^{(2)}_{ijh}(z)$. No direct measurements of this quantity exist, so one should rely on the models alone, increasing the uncertainty of our estimates. However, we may link to experiments by exploiting the fact that, to first approximation (neglecting dispersion), the susceptibility for OR is the same as the susceptibility for SHG, defined as $\chi^{(2)}_{ijk}(2\omega; \omega, \omega)$. The point-by-point value of the latter is also unknown, but SHG experiments provide instead a direct measurement of the integrated *surface* susceptibility $\chi^{(2)}_{S,ijh} = \int_0^l \chi^{(2)}_{ijh}(z) dz$. Thus we may introduce the average susceptibility tensor $\overline{\chi^{(2)}_{ijh}} = \chi^{(2)}_{S,ijh}/l_P$, where $l_P \leq l$ is the characteristic thickness of the interfacial layer in which the second-order surface polarization is nonvanishing. An estimate of the length l_P can be obtained from the density-functional calculations of Ref. [18], where it is found to range from 2 to 3 Å, depending on the metal free-electron density. Moreover, both the models and SHG experiments indicate that the only nonvanishing susceptibility tensor component relevant for our purposes is $\chi^{(2)}_{S,zzz}$. Therefore, we obtain our final expression for the average OR-induced surface electric field (z component):

$$\overline{F_{\mathrm{OR}}} = -\chi^{(2)}_{S,zzz} L^2_{\mathrm{eff}} I_0/(l_P \epsilon_0 c), \tag{3}$$

where $L_{\mathrm{eff}} = (L_{zl} L^*_{zk} e_l e^*_k)^{1/2}$ is an effective local-field factor for the given input polarization. For a pulsed input light, this OR field is also time dependent. Because the electronic response is very fast, we expect the OR field strength to approximately follow in time the laser pulse profile $I_0(t)$, although retardation effects may occur if surface-plasmon optical resonances are involved [they would enter Eq. (3) via the local-field factor L_{eff}]. Equation (3) should replace Eq. (9) of Ref. [7].

From Eq. (3), we note that the direction of this OR field is fixed only by the sign of $\chi^{(2)}_{S,zzz}$, which is negative for most metals, according both to hydrodynamic-model and density-functional calculations [17,18]. Thus, in most metals, the OR electric field is predicted to be pointing out-

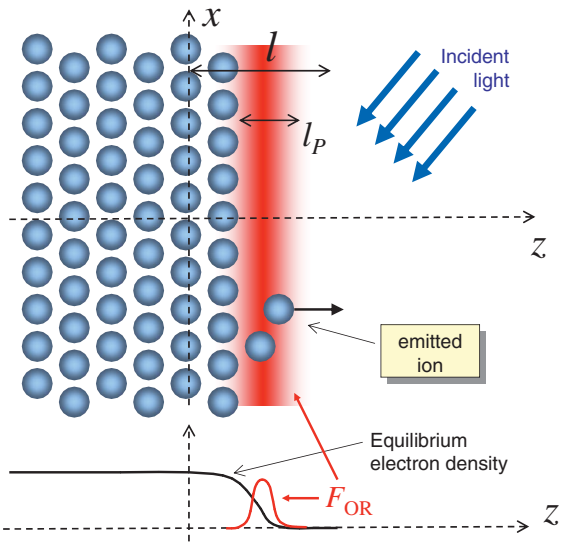

FIG. 2 (color). Pictorial representation of the surface optical rectification process and ensuing LAFIE. The red shaded area is the region where the rectified (OR) field is induced (the red curve shows its qualitative profile, as obtained by density-functional calculations [18]).

ward, i.e., in the right direction for inducing the emission of positive ions. The density-functional calculations reported in Ref. [18] also show that this OR field (as well as the second-order polarization) is located in a interfacial layer (of thickness l_P) which is centered at about 2 Å (i.e., one atomic-plane spacing) outside the outermost surface plane of ions (see Fig. 2). This implies that the OR field will be most effective on the isolated atoms adsorbed on the surface and on the atoms belonging to step edges at the surface terraces, which are also the most weakly bonded ones and therefore the easiest to be emitted. Then, at small-enough light intensities, atoms should be emitted preferentially from the edge of terraces, just as seen in Fig. 1.

Let us now interpret our ultrafast LAFIE experiments in the light of our OR model. Details about our apparatus are given in Ref. [4]. The samples used for the atom probe analysis are metal tips with an apex radius R of 40–60 nm, subject to a dc voltage V of 5–10 kV, corresponding to an electrostatic field $F_0 \propto V/R \sim 15$–50 V/nm at the tip apex. Laser pulses of 130 fs (full width half maximum) and wavelength $\lambda = 780$ nm are weakly focused onto the tip from the side (the spot radius on the tip was 0.3 ± 0.1 mm), with the polarization parallel to the tip axis. A typical example of our pump-probe measurements is shown in Fig. 3, for a tungsten tip. Similar results were obtained in aluminum [8]. We actually measure the decrease in the dc-field evaporation threshold voltage (FETV) as a function of the delay between two identical laser pulses sent on the tip. For sufficiently low laser intensities, only a very fast decay is observed, within about 200 fs. A conventional thermal effect is clearly incompatible with this result, as the electron-lattice thermal equilibration time is much longer (>1 ps) and the lattice temperature decay is even slower ($\gg 100$ ps for our geometry). The OR model is instead fully compatible with this rapid decay.

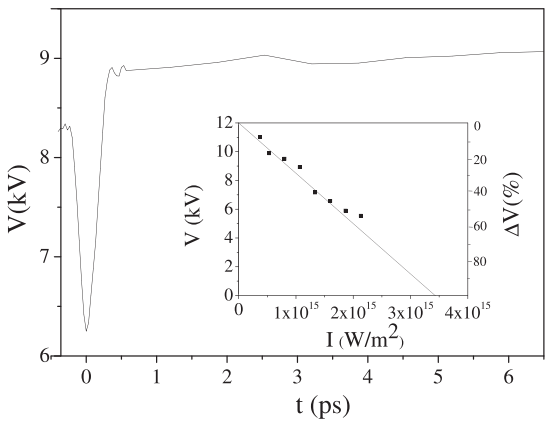

FIG. 3. Pump-probe FETV vs delay time in a tungsten tip for a pulse energy of 15 μJ (peak intensity $I_0 \simeq 7.6 \times 10^{14}$ W/m^2) of both pump and probe. In the inset, FETV vs laser pulse intensity for a single laser pulse; the line slope is obtained from Eq. (3) without adjustable parameters (all values of the quantities appearing in the equation are given in the text).

By Eq. (3), the OR field is proportional to light intensity. Therefore, the OR model predicts a linear decrease of the FETV with increasing light intensity. This is confirmed by our measurements, as shown in the inset of Fig. 3 (these data are for single pulse experiments). Let us now compare the absolute OR field magnitude predicted by Eq. (3) with our FETV measurements. For aluminum, we take $|\chi^{(2)}_{S,zzz}| \simeq 10^{-17}$ m^2/V based on reported measurements [21,22]. For tungsten there are no reported values of $\chi^{(2)}_{S,zzz}$, so we assume the same value as for aluminum. For a strongly prolate tip geometry and a light polarization parallel to the tip axis, the local-field factor is $L_{\text{eff}} \simeq 1$ [20]. Finally, we set $l_P = 2.5$ Å. With these values, the predicted FETV versus light intensity is shown in the inset of Fig. 3 as a solid line (note that no adjustable parameters are used in this plot). The agreement with the data is excellent, actually beyond our expectations, given the many approximations (it might be partly coincidental). A similar comparison can be also made for the peak FETV seen in pump-probe experiments, as that shown in Fig. 3. Here, each pulse (both pump and probe) of peak intensity $I_0 \simeq 7.6 \times 10^{14}$ W/m^2 is predicted to generate a OR field of $\overline{F_{\text{OR}}} \approx 11$ V/nm. This is about 20% of the known threshold dc field F_{th} for ion emission in tungsten ($F_{\text{th}} = 52$ V/nm). Therefore, each pulse is predicted to lead to a FETV reduction of about 20% of the no-light value, i.e., about 2.4 kV. The observed FETV decrease at zero delay with respect to large delays is of 2.7 kV.

The discussion so far was about the combined action of a dc field and of the OR field. Clearly, for large enough light intensities, the OR field alone can reach the field-effect threshold F_{th} for single atom desorption. The threshold values considered in our LAFIE experiments correspond to the desorption of about 0.05 atom per pulse, i.e., a fraction of about 3×10^{-6} of all the atoms belonging to the illuminated surface monolayer of the metal. However, owing to the strong exponential dependence of the ion emission yield on laser intensity [7], this isolated desorption process is expected to turn into the ablation of a whole atomic surface monolayer just by increasing the laser intensity by a relatively small factor (≈ 1.7, in the case of tungsten).

Let us now see if our OR model can explain the main features of the experiment of ultrafast ablation of gold nanoparticles mentioned in the introduction [9]. Perhaps the most puzzling feature here is that the ablation was observed to take place preferentially close to the two opposite "poles" of the spherical particle, where the polar axis is defined by the direction of the input (linear) laser polarization. The OR model nicely explains this feature by the fact that L_{eff} is expected to be large only near the poles and to vanish at the "equator" of the particle. At the employed wavelength of 400 nm, we have $L_{\text{eff}} \approx 7$ at the poles. For a 100 fs pulse having a fluence of 10 mJ/cm^2 (which is the minimum fluence at which bubble nucleation allowed material separation and hence detection of the

ablation, since the particles are suspended in water) the predicted OR field at the poles is of about 100 V/nm, about 3 times the threshold for field-ion emission and almost twice the value needed for monolayer ablation. Therefore, several atomic layers are predicted to be removed, as observed. The stretched pulse of 1 ps should lead to an OR field of 10 V/nm, below the threshold for ion emission, thus explaining the stopped anisotropic ablation.

Let us finally discuss the pump-probe ablation of planar metal surfaces reported in Refs. [10,12,13]. These experiments are performed at fluences of 100–150 mJ/cm^2 in 30 fs pulses (i.e., a light intensity of $I_0 \approx 3$–5×10^{16} W/m^2), somewhat smaller than the ablation threshold (200–300 mJ/cm^2). The results show a decay of the ablation yield taking place within 100–200 fs, similar to what we see in LAFIE. To explain this result, Dachraoui *et al.* proposed the occurrence of the so-called ''Coulomb explosion,'' arising after a laser-induced sudden depletion of electronic density [12,13]. However, detailed calculations show that in metals the electronic screening should make this effect negligible [23]. Although other electron-based effects could be conceived, thus far no proposal was translated into a quantitative model capable of explaining the known evidence. Let us now consider the OR model. The ablation thresholds reported in Refs. [10,12,13] can be explained by our OR model by taking $L_{\text{eff}} \approx 0.1$–$0.3$. If the surface were perfectly flat, which is not common in surface ablation experiments, the local-field factor L_{eff} for p-polarized incident light at the employed wavelength of 810 nm would be of 10^{-2}–10^{-1}, depending on the metal, thus marginally compatible with the observations. Even a small degree of surface roughness will introduce asperities where the field will be enhanced [20], increasing L_{eff} and improving the agreement. The OR model of course explains well the observed ultrafast decay. The predicted maximum energy of the emitted ions is of the order of $e[\overline{F_{\text{OR}}} - F_{\text{th}}]l_P$ that is of several eVs, in agreement with the typical values reported in the literature [11]. We note here that our interpretation is based on the assumption that the light polarization used in the ablation experiments is p (for both pump and probe pulses), while the ultrafast effects should disappear for s polarization (or for normal incidence), because L_{eff} vanishes [24]. Unfortunately this check is not reported in Refs. [10,12,13], but a strong polarization dependence of laser ablation, with p polarization more effective than s well beyond what expected from the polarization dependence of light absorbance, has been actually reported, although not in pump-probe measurements [25].

In summary, we have shown that the nonlinear optical phenomenon of surface optical rectification quantitatively explains the observed light-induced field-ion emission from metals. We also proposed that the same effect could explain the ultrafast laser ablation of metals in certain regimes, although more experiments will be needed for confirming this idea. Reversing the point of view, these effects also provide the first direct verification of the actual occurrence of this long-predicted, but quite elusive, nonlinear optical phenomenon.

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