STRONG PHOTOELECTRON EMISSION FROM SILVER NANOSTRUCTURES

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ABSTRACT

Localized optically-nonlinear photoelectron emission from metal (silver) nanostructures under two-pulse emission has been developed for relatively low energy. For two-photon emission from random metal nanostructures, it has been shown that the coherent control allows one to move nanosize hot spots whose positions are controllable on a nanometer scale. It is proposed to use silver random planer composite and introduce this photoemission process as an ultrafast process, on femtosecond or subfemtosecond scale.

INTRODUCTION

Using the adiabatic transformation, it is possible to transfer the optical excitation energy to the nanoscale (Stockman, 2004). However, such a concentration and the photoelectron emission caused by it are static in space. Recently it has been proposed to use the coherent control to dynamically concentrate the optical excitation energy in space and time on the nanometer-femtosecond scale (Stockman *et al*., 2002; Stockman *et al.*, 2004). However, for nonlinear photoprocesses, not only such a concentration is possible, but also the time-integral is coherently controllable (Stockman, 2004). This phenomenon has been later observed for two-photon electron emission from random nanostructured metal systems (Kubo *et al.*, 2005) using two-pulse, interferometric coherent control in combination with the electron microscopy. On the other hand, in various fields of nanoscience and nanotechnology, one of the key processes to achieve is the controlled photoinduced injection of charges into nanoscopic regions of semiconductor or metal systems, or vacuum. It is very important to perform this injection as an ultrafast process, on femtosecond or subfemtosecond scale and have a possibility to choose the injection nanosite dynamically with a nanometer-scale resolution. Such processes can be used, for instance, in site-specific, time-resolved electron-excitation spectroscopy of molecules and

nano-objects; its technological applications are possible in superfast nano-optoelectronics to transfer signals from optical to electronic components. There are, however, major obstacles to implement such processes. One of them is the difficulty in directly focusing light to nanoscopic regions. The physical reason for this is that the exchange of energy between the electric and magnetic fields takes a quarter of wavelength in space. This is a relatively slow, long-range process (compared to a nanoscale), which is due to the large term, speed of light, c in the Maxwell equations,

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} \text{ and}$$

$$\nabla \times \mathbf{E} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi}{c}j_{ext}.$$

The following goal has been considered in this theoretical work, namely possibility of using the two-photon pulse to dynamically control electron emission from randomly rough metal surfaces as an ultrafast process, on femtosecond or subfemtosecond scale, which is localized within a few nanometers. The contrast of this control depends on the relaxation polarization time t_{rp} with respect to the typical delay δt which is on order of or greater than the pulse length t_p. Before introducing the relaxation polarization time $t_{rp}(\omega)$, let us first consider the related parameter: the relaxation rate $\gamma(\omega)$ which describes the relaxation due to the dielectric losses in metal. In other words, this is the dephasing of eigenmodes and it also defines their population life time or the relaxation polarization time through the following relation

$$t_{rp}(\omega) = \frac{1}{\gamma(\omega)}$$

Since, $1/\gamma$ is amplitude of the relaxation or dephasing time of the eigenmodes, the factor of 2 in the denominator has been taken into account. Therefore, the proper term for the lifetime would be: the relaxation polarization time of the eigenmodes.

The relaxation polarization time $t_{rp}(\omega)$ for silver, computed from the experimental data (Johnson & Christy, 1972) is shown in Figure 1. The relaxation polarization time for silver is much longer, in particular between 1 and 2 eV, which is near-IR to red region. For silver $t_{rp}(\omega) \sim 60\,\text{fs}$. One of the interesting aspects is the cutoff of the plasmonic region around 4 eV, which is not shown in the graph. These highly localized electrons in the d band are contributing to the absorption and decay of the eigenmodes. The minimum difference $\delta\omega$ in eigenfrequencies that can be resolved (discriminated between) by this coherent control is $\delta\omega \geq (\delta t)^{-1} \sim (t_{rp})^{-1}$. Time t_{rp} depends on frequency ω and ranges

from several femtoseconds in the blue region to ~100 fs in the near infrared (ir) (Stietz *et al*., 2000; Bosbach *et al*., 2002; Zentgraf *et al*., 2004).
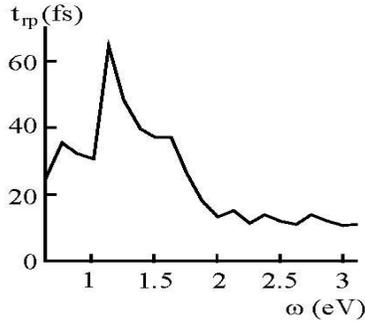
Figure 1:   Lifetime of eigenmodes t_{rp} for silver, computed from the experimental data of Johnson & Christy (1972).

METHOD

Consider a specific variant of the coherent control where a femtosecond excitation pulse consists of two identical laser subpulses with a controllable temporal delay δt between them, as shown in Figure 2, which excite a nanosystem of the type shown in Figure 3. Such an excitation directly models the interferometric coherent control of experiments (Kubo *et al*., 2005). The physics of the coherent control in this case is very clear. The first subpulse excites an oscillating polarization in the nanostructured system. Because different sites of a nanostructure have different eigenmodes localized at them (Stockman *et al.*, 2001), and these eigenmodes generally have different frequencies, there will be phase shifts accumulated between them during the first subpulse and subsequent delay δt. When the second subpulse arrives, it will do a positive work on those oscillations that are in phase with it enhancing them and depleting energy of the out-of-phase oscillations. By a proper choice of δt, any given *hot spot* of the polarization can be enhanced to its maximum or, to the opposite, suppressed.
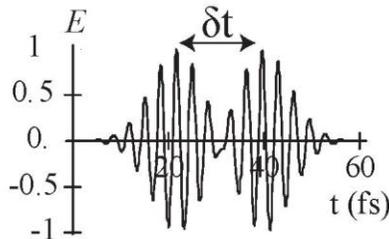
Figure 2 :   Example of electric field of excitation pulse ($\delta t = 5$ fs, $t_p = 10$ fs).

Consider an excitation pulse not too intense, so the response of the nanosystem to it is linear and the quasi-stationary approximation can be used. The term *quasi-stationary* is used here instead of the usual one in the physics *quasi-static* because all sizes of the system are much less than the excitation light wavelength.

Then the local field potential $\varphi(\mathbf{r},t)$, induced by the external (excitation) potential $\varphi_0(\mathbf{r},t)$, is determined by the retarded Green's function $G(\mathbf{r},\mathbf{r}';t)$, of the system (Stockman *et al.*, 2002; Stockman *et al.*, 2004)

$$\varphi(\mathbf{r},t)=\varphi_0(\mathbf{r},t)-\int\varphi_0(\mathbf{r}',t')\frac{\partial^2}{\partial r'^2}G(\mathbf{r},\mathbf{r}';t-t')d^3r'dt' \tag{1}$$

It has been considered that each of the two subpulses to have a Gaussian envelope with carrier frequency ω_0, duration t, linear polarization in the z direction, and amplitude E_0, i.e,

$$\varphi_0(\mathbf{r},t)=-zE_0\exp\left[-\left(\frac{t}{t_{rp}}\right)^2\right]\cos(\omega_0 t) \tag{2}$$

Then the local electric field in the nanosystem is given by
$$\mathbf{E}(\mathbf{r},t)=-\nabla[\varphi(\mathbf{r},t-\delta\tau)+\varphi(\mathbf{r},t)] \tag{3}$$
where $\varphi(\mathbf{r},t)$ is computed from Eq. (1) with $\varphi_0(\mathbf{r},t)$ given by Eq. (2).

It has been assumed that $\Phi>\hbar\omega_0>\frac{1}{2}\Phi$, where Φ is the metal work function. Then the electron emission is predominantly two-photon. It has been considered that the nanosystems that are planar in the xy plane with some small thickness of 4 nm in the z direction. It has been assumed that only the electrons emitted in the positive z direction are detected. Under these conditions, the electron current density $j(x,y)$ in the (xy) plane of the nanostructure, integrated over time, is proportional to

$$j(x,y,\delta t)\propto\int_{-\infty}^{\infty}dt\int_{-\infty}^{\infty}\Theta(r)\left(\nabla[\varphi(\mathbf{r},t-\delta\tau)+\varphi(\mathbf{r},t)]^2\right)dz \tag{3}$$

where $\Theta(r)$ is a characteristic function equal to 1 inside the metal nanostructure and zero otherwise. Note that the time-integrated current $j(x,y,\delta t)$ depends on the delay time, δt, between the subpulses as a parameter.

RESULTS AND DISCUSSION
Numerical computations have been performed for an example of the random planar nanostructure shown in Figure 3 using Equations (1)-(4). Silver was chosen as the metal

because it has the smallest optical losses of any natural metal in the visible and IR spectrum [see Figure 4]. This is due to the fact that in the optical spectral region, real part of the dielectric permittivity ε of a metal like silver is very large and negative, i.e., $\text{Re}[\varepsilon(\omega)] << -1$ (Johnson & Christy, 1972).
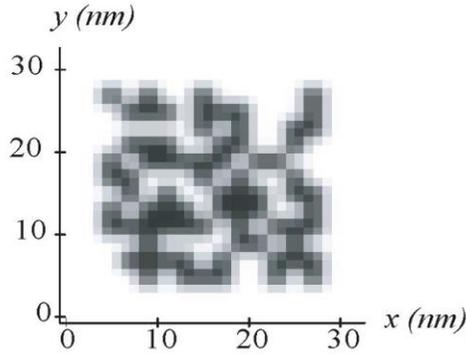
Figure 3: Geometry of nanosystem in the cross section through the *xy* plane of symmetry. The units in *x* and *y* axes are nm; the thickness of the system in the *z* direction is 4 nm.
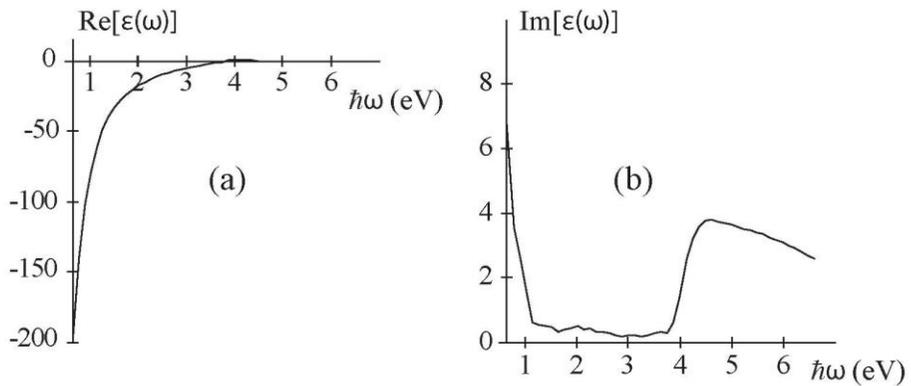
Figure 4: Real part (a) and imaginary part (b) of dielectric permittivity for silver as a function of excitation frequency $\hbar\omega$. Curves display the experimental data from (Johnson & Christy, 1972).

Theoretical calculations are shown in Figure 5. As one can see, for two delay times, $t = 5.90\,\text{fs}$ and $t = 6.29\,\text{fs}$, that differ only by 0.39 fs (approximately quarter of optical period), the hot spot of electron emission (shown by the spike in gray scale) moves within 2 nm to the neighboring position [panels (a) and (b)], and then returns back in a fraction of the optical period [panel (c)]. For a longer delay [panel(d)], this hot spot moves by $\sim 10\,\text{nm}$ to a new position. Thus, it is possible to coherently control the position of the two-photon excitation of the electron emission within the entire nanostructure with a resolution of just a few nm. Note that these kinetics of hot spots with the delay time, shown in Figure 5, are in an excellent qualitative agreement with the experimental data (Kubo *et al.*, 2005).
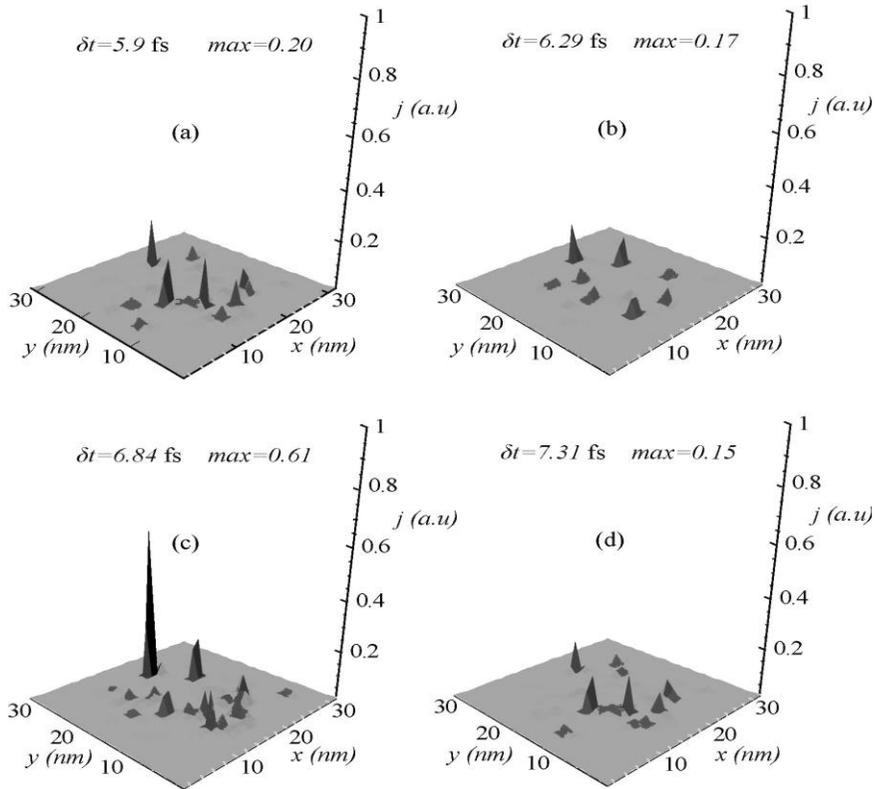
Figure 5: Integrated photoemission current in the plane of the nanosystem shown in Fig. 3, made of silver, for $\hbar\omega = 2.5$ eV. Scales are in nm, the maximum current (in relative but consistent units) and the delay are shown above the corresponding plots.

Comparison to the experiment (Kubo *et al*., 2005), there are two main similarities in these results. First, this is a random nanostructure, and the position of any hot spot is completely random, which may be desirable for various applications. Second, the contrast of the coherent control is high: the ratio of the maximum to minimum intensity of any hot spot as a function of *t* in the range of 10:1, which may be suitable for many applications. The cause of a moderate contrast is certainly insufficiently long polarization relaxation time in the visible or near-UV region. However, if the photon energy is significantly decreased to increase t_{rp}, then the two-photon electron emission from clean silver is impossible. This can be remedied by using a coverage with a thin layer of an alkali metal to decrease Φ, as is used industrially in photomultipliers. Also, one can use the photoemission not into vacuum, but into a semiconductor, with the corresponding electric bias.

CONCLUSION

Finally to summarize the major results of this work, theory of localized optically-nonlinear photoelectron emission from metal nanostructures under two-pulse control has been developed for relatively low energy. For two-photon emission from random metal nanostructures, it has been shown that the coherent control allows one to move the hot spots of the electron emission within distances of 1-10 nm. However, the contrast of the dependence on the control parameter (delay between the pulses) is not extremely high and the positions of the hot spots are quasirandom. These findings are in a good qualitative agreement with experiments (Kubo *et al*., 2005).

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