Time of flight-photoemission electron microscope for ultrahigh spatiotemporal probing of nanoplasmonic optical fields

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Abstract
Nanoplasmonic excitations as generated by few-cycle laser pulses on metal nanostructures
undergo ultrafast dynamics with timescales as short as a few hundred attoseconds
$(1 \text{ as} = 10^{-18} \text{ s})$. So far, the spatiotemporal dynamics of optical fields localized on the
nanoscale (nanoplasmonic field) have been hidden from direct access in the real space and time
domain. An approach which combines photoelectron emission microscopy and attosecond
streaking spectroscopy and which provides direct and non-invasive access to the nanoplasmonic
field with nanometer-scale spatial resolution and temporal resolution of the order of 100 as has
been proposed (Stockman *et al* 2007 *Nat. Photon.* **1** 539). To implement this approach, a time
of flight-photoemission electron microscope (TOF-PEEM) with ∼25 nm spatial and ∼50 meV
energy resolution, which has the potential to detect a nanoplasmonic field with nanometer
spatial and attosecond temporal resolution, has been developed and characterized using a
400 nm/60 ps pulsed diode laser. The first experimental results obtained using this newly
developed TOF-PEEM in a two-photon photoemission mode with a polycrystalline Cu sample
and an Ag microstructure film show that the yield and the kinetic energy of the emitted
photoelectrons are strongly affected by the nanolocalized plasmonic field.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Surface plasmons are of interest to a wide spectrum of scientists, ranging from physicists, chemists and materials scientists to biologists. Renewed interest in surface plasmons comes from recent advances that allow metals to be structured and characterized on the nanometer scale. Nanosized metal structures allow us to trap and confine light on a nanoscale, which in turn enables us to control surface plasmon properties to reveal new aspects of their underlying science and to tailor them for specific applications. For instance, surface plasmons are being explored with regard to their potential in optics, magneto-optical data storage, microscopy and solar cells, as well as being used to construct sensors to detect biologically relevant molecules [2–4].

When few-cycle laser pulses illuminate the metal nanostructure, ultrafast nanoplasmonic field dynamics can be initiated. Photoelectron emission microscopy (PEEM) using femtosecond laser pulses in a pump–probe arrangement and a plasmon-enhanced two-photon photoemission (2PPE) process have been developed and extensively applied by several groups to study the spatial and temporal dynamics of surface plasmon

polariton (SPP) waves, mainly on Ag and Au surfaces [5–9]. The dephasing time of a nanolocalized plasmon is in the range of 5–100 fs across the plasmonic spectrum, allowing coherent control of nanoscale energy localization with femtosecond laser light. In addition, the nanolocalized plasmons can lead to the formation of 'hot spots', where the electrical field and photoemission is enhanced by a factor of several hundred [10]. More importantly, collective electron motion in a nanoplasmonic system unfolds on a much shorter attosecond timescale, as defined by the inverse spectral bandwidth of the plasmonic resonant region [1]. Theoretical results have predicted that local optical fields in disordered nanostructured systems (clusters, composites and rough surfaces) will experience giant fluctuations on attosecond temporal and nanometer spatial scales [11]. Recent simulation results show that those attosecond fluctuations are strong enough to cause a pronounced energy shift of the passing photoelectron emitted by a synchronized XUV attosecond pulse [1]. So far the attosecond dynamics of the nanoplasmonic field has not been directly experimentally disclosed on an attosecond timescale and nanometer spatial resolution. Hence an experimental study of those ultrafast and nanolocalized plasmonic field dynamics is of particular importance and requires an instrument which combines ultrahigh spatial and temporal resolution.

In this paper we characterize a time of flight-photoemission electron microscope (TOF-PEEM), which has the potential to reveal nanoplasmonic fields on nanometer spatial and attosecond temporal scales. The temporal resolution will be achieved by using a pump–probe scheme with synchronized isolated attosecond XUV pulses and few-cycle optical pulses, which is known as the attosecond streaking technique [12]. The setup of this newly developed TOF-PEEM is described and the spatial and energy resolution are determined. As a first application, the 2PPE process from a polycrystalline Cu and Ag film has been investigated by using a 400 nm/60 ps pulsed diode laser.

2. Approach to detecting attosecond dynamics of nanoplasmonic fields and its experimental setup

The approach to detecting the attosecond dynamics of a nanoplasmonic field is schematically illustrated in figure 1. This approach combines two modern techniques: photo-electron emission microscopy and attosecond streaking spectroscopy [12].

A plasmonic metal nanosystem is driven by an intense and waveform-controlled femtosecond laser pulse with frequencies within the range of the plasmonic resonances (from near UV to near infrared (NIR)). This generates optical fields localized on the nanometer scale, which are referred to as nanolocalized optical fields. The local fields are enhanced with respect to the excitation field by a factor that depends on the quality of the localized surface plasmon resonances and can be as high as a few hundred-fold for a silver nanosystem. These field 'hot spots' are represented by high peaks of the enhanced local fields, as shown in the three-dimensional plot in figure 1. An attosecond XUV pulse at 90 eV, for example, produced through high harmonic generation (HHG), is synchronized with the driving optical field and sent to the
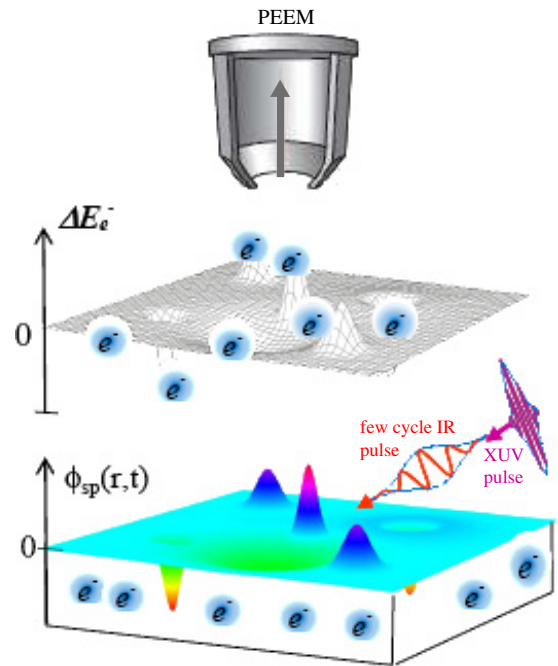

Figure 1. Approach of probing the attosecond dynamics of nanoplasmonic fields. The instantaneous local fields, which are excited by the few-cycle IR laser pulse, are shown as a three-dimensional plot, where the vertical axis $\phi_{sp}(r, t)$ represents the nanoplasmonic field potential. The application of an XUV pulse is shown by a violet waveform that is temporally delayed with the excitation field. The XUV excitation causes the emission of photoelectrons, which are accelerated or decelerated by the local plasmonic potential at the instance of escape, where the vertical axis stands for the electron energy shift, ΔE_e^-. Photoelectrons with or without an energy shift are distinguished by a PEEM with high energy resolution. Note that the drawing is not in scale.

nanosystem. The XUV-emitted valence band photoelectrons, owing to their large kinetic energy and short emission time (determined by the attosecond pulse duration), escape from the nanosized regions of local electric field enhanced by the plasmonic resonances within a fraction of the oscillation period of the driven plasmonic field. The ultrashort escape time implies a final energy change of the emitted photoelectrons that is proportional to the quasi frozen local electric potential at the surface at the instance of electron release. These photoelectrons are accelerated or decelerated by the local plasmonic field as shown in figure 1, which defines their energy. The imaging of the emitted XUV photoelectrons by an energy-resolving PEEM probes the electrical field potential at the surface as a function of the XUV-pulse incidence time and the position at the surface with an attosecond temporal and nanometer-scale spatial resolution. As the emission instance is defined by the XUV pulse, this would allow one to measure the complete spatiotemporal dynamics of the local fields. The corresponding spatial resolution is defined solely by the aberrations of the PEEM electron optics, which can realistically be of the order of ~10 nm. The temporal resolution is determined by the duration of the attosecond pulse and the time of flight of the photoelectrons through the local field region, which can be of the order of (a few) hundred attoseconds.
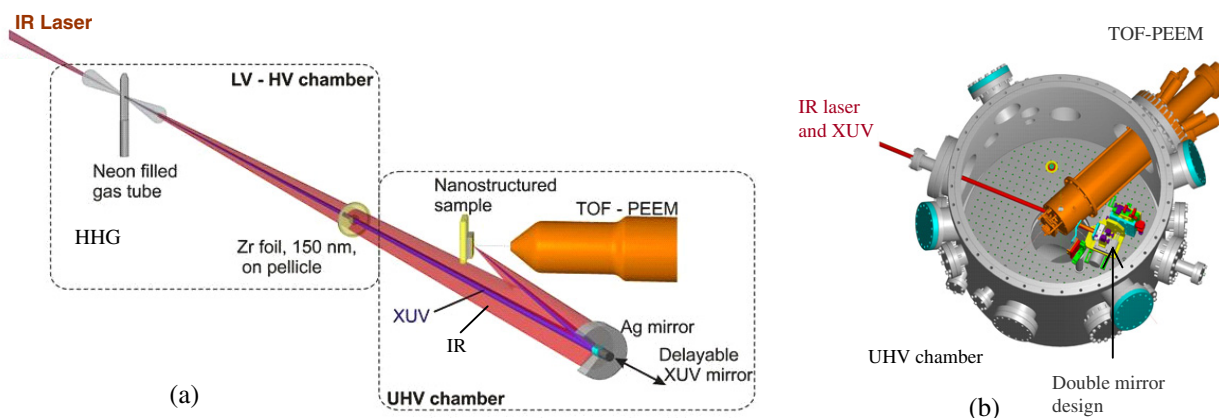
Figure 2. (a) Illustration of the experimental setup of attosecond nanoplasmonic field microscope. Few-cycle VIS/IR laser pulses from Ti:Sa laser amplifier enter the chamber for high harmonic generation (HHG). Both XUV and IR laser pulse are directed into a UHV chamber which hosts an interferometric double mirror setup and the TOF-PEEM. (b) Shows a 3D drawing of the UHV experimental chamber together with the double mirror assembly and the inserted TOF-PEEM.

The experimental realization of an attosecond nanoplasmonic field microscope, which will measure the time evolution of excited optical fields on plasmonic nanostructures with nanometer spatial and attosecond time resolution, is based on probing the response of photoelectrons excited by an isolated attosecond XUV pulse (photon energy 90 eV, pulse duration 80 as). The photoelectron, emitted from the outer surface regions of the nanoplasmonic structures in locally enhanced plasmonics fields that were excited by few-cycle infrared (750 nm, 4 fs) and carrier envelope phase-stabilized laser pulses, are then detected by the TOF-PEEM. The experimental setup of the attosecond nanoplasmonic microscope is shown in figure 2. Ultrashort pulsed XUV radiation ranging up to photon energies exceeding 100 eV is generated by a HHG driven by a few-cycle phase-stabilized Ti:Sa laser pulse (750 nm, 4 fs) in a Ne gas jet target [13]. By selecting a broadband (bandwidth 28 eV FWHM, center photon energy 80 eV) spectrum of the harmonic plateau range close to the cut-off of the harmonic spectrum via a Mo/Si multilayer XUV mirror, an isolated attosecond XUV pulse can be extracted and pulse durations ranging down to 80 as FWHM have been experimentally verified [14]. The NIR laser pulse for exciting the plasmonic field oscillations and the photoelectron-produced XUV pulse for probing the plasmonic field are refocused to the sample by means of an interferometric double mirror configuration (a Ag outer mirror and delayable XUV inner mirror as shown in figure 2(b)) allowing for a controlled and variable time delay between both pulses (step size <50 as). Spatial and energy-resolved detection of the emitted photoelectrons from nanoplasmonic structures is carried out by employing the TOF-PEEM. The sample is positioned on an integrated xy-stage in the PEEM, and the sample part of the PEEM is enclosed in an UHV chamber (base pressure 10^{-8} Pa).

3. Experimental characterization of a TOF-PEEM for attosecond nanoplasmonic field microscopy

To map nanoplasmonic fields with ultrahigh spatial and temporal resolution, a TOF-PEEM was constructed and its
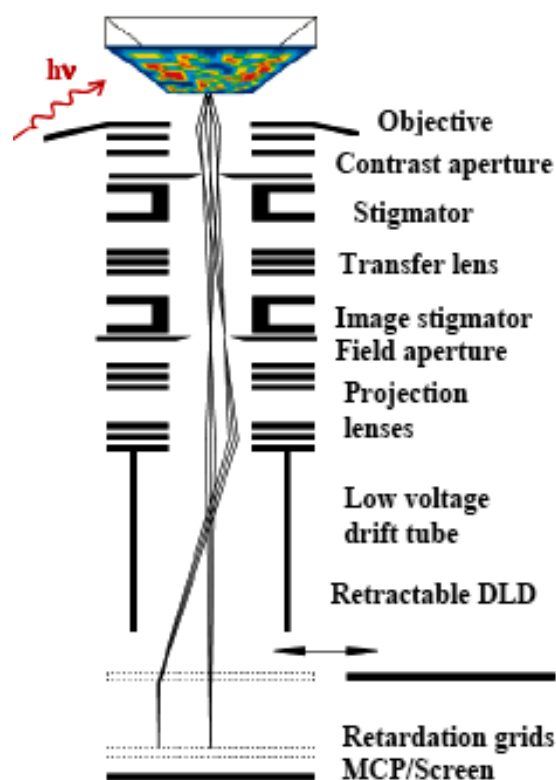
Figure 3. Electron-optical scheme of the new TOF-PEEM, which combines an electrostatic lens setup, a time of flight drift tube and two alternative detection units (a retractable delay line detector or an imaging unit with retarding field analyzer).

schematic is shown in figure 3. It combines a TOF detector, a high pass retarding field analyzer filter, also called an imaging energy filter (IEF) as well as an imaging unit (MCP and screen) in one PEEM, which enables one to gather electron-energy-filtered information from the same sample with different filter methods. Both the high pass filter (retardation grids) and the TOF detection are integrated in a straight column and are easy to handle. The design is kept strictly electrostatic.
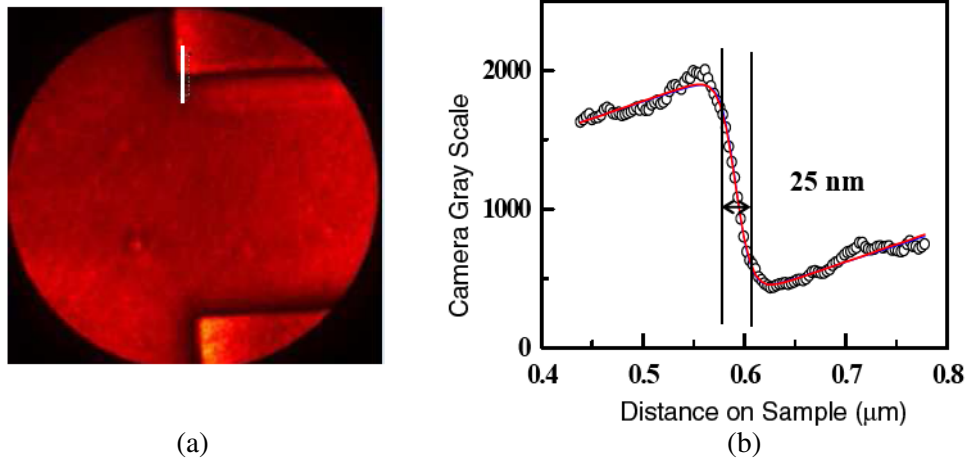
(a)   (b)

Figure 4. (a) A PEEM image for the spatial resolution test is obtained using a microstructured Cu sample illuminated by a mercury discharge lamp. (b) A quantitative analysis of the spatial resolution of the PEEM. A white line across the edge of the structure in the PEEM image is used as a position marker to indicate where the linescan has been performed on the sample to obtain the profile in (b).

The TOF-PEEM is equipped with a time of flight drift tube followed by a 2D delay line detector (DLD) and it thus allows for the acquisition of three-dimensional datasets, the energy distribution of the measured photoelectrons via measurement of the flight time of the electrons as well as the lateral distribution via spatial resolution of the DLD [15]. A particular strength of the TOF detection is that each incoming electron is counted. Therefore the advantage in acquisition time over a band pass is the number of data points in the spectrum. The DLD is a counting system and is therefore limited in the count rate by the dead time of the system (~1 MHz). Therefore it is an excellent system for low count rate/laser shot and high repetition rate experiments.

The lateral size of a nanoplasmonic field generated at metal nanoparticles or other forms of nanostructures is usually in the range of several to hundreds of nanometers. The current state-of-the-art TOF-PEEM can reach a spatial resolution of down to ~20 nm [16]. A spatial resolution test of the PEEM was conducted with a Cu-coated microstructured Si test sample. A linescan was performed across one edge of the microstructure as marked in the PEEM image of figure 4(a). The obtained profile in figure 4(b) from the linescan in the PEEM image shows that the measured edge slope width is about 25 nm (following a 16%–84% criterion). Thus spatial resolution of the PEEM is estimated to be at least 25 nm based on the obtained edge width of the Cu structure. The transmission of the PEEM in this measurement is about 20%.

The characterization of the TOF energy resolution is realized with the drift tube operated at a low column voltage and a DLD in the PEEM. The low column voltage enables a conversion of the energy dispersion into time dispersion of the electronics. The DLD can detect the time of arrival and the position of the electrons. Figure 5 shows a result of a TOF spectrum obtained by illuminating a Mo(110) single crystal with a 400 nm/60 ps pulsed diode laser. The acquisition time was about 12 min for the full spectrum. The spectrum of the molybdenum surface shows a Fermi edge with a width of $\Delta E_{\text{FD measured}} = 96$ meV (16%–84% criterion) at room temperature.
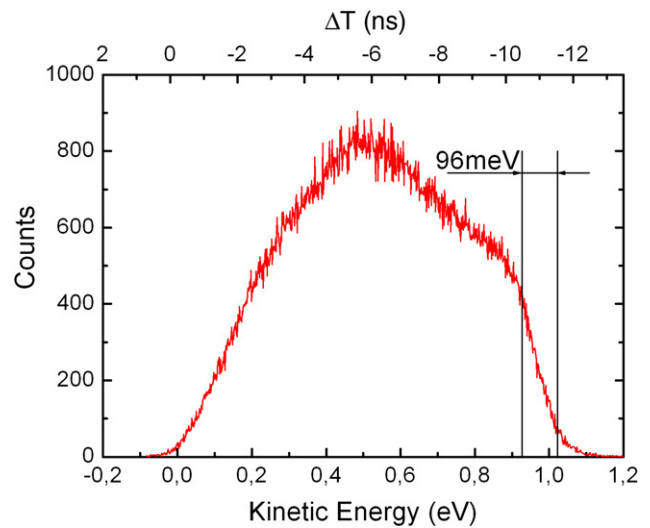

Figure 5. Measurement of the TOF photoelectron energy spectrum of Mo(110) near the Fermi edge at a room temperature of 295 K gives about ~96 meV energy width.

A straightforward theoretical estimation of the Fermi edge width at a room temperature of $T = 295$ K allows the determination of the energy resolution of the PEEM. The thermal broadening at temperature T due to the Fermi–Dirac distribution can be described by [17]

$$f(E) = \frac{1}{e^{(E-E_{\text{F}})/k_{\text{B}}T} - 1}. \tag{1}$$

For the 16%–84% criterion the width of the Fermi–Dirac edge can be calculated as

$$\Delta E_{\text{FD}} = 3.32 k_{\text{B}} T \tag{2}$$

where k_{B} is the Boltzmann constant. At a room temperature $T_{\text{room}} = 295$ K, $k_{\text{B}}T = 25.42$ meV, then the width of the Fermi–Dirac edge becomes $\Delta E_{\text{FD}} = 84.4$ meV. A simple
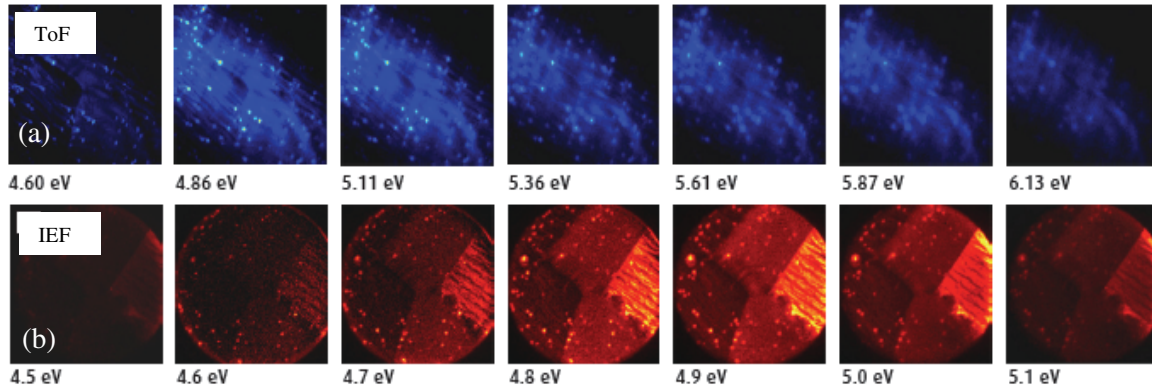
Figure 6. Series of energy slices of a polycrystalline copper sample (field of view 9 μm): (a) excited with 400 nm/60 ps diode laser and measured by the TOF; (b) illuminated with a Hg lamp and measured with the IEF. The slices are scaled to the final state energy.

deconvolution by

$$\Delta E_{\text{TOF}} = \sqrt{(\Delta E_{\text{FD measured}}^2 - \Delta E_{\text{FD}}^2)} \qquad (3)$$

yields a TOF analyzer resolution of $\Delta E_{\text{TOF}} = 46$ meV.

The feasibility of using the TOF-PEEM characterized here to resolve the attosecond dynamics of nanoplasmonic fields can be evaluated. The approach of attosecond nanoplasmonic field microscopy was described in section 2 and shows that the quasi frozen potential of a nanoplasmonic field yields an energy shift of the photoelectrons. This energy shift is proportional to the instant field potential which evolves on an attosecond timescale. Therefore an energy-resolving measurement of photoelectrons in an optical-pump/XUV-probe experiment allows the temporal-resolving measurement of nanoplasmonic fields. The energy shift can reach up to 12 eV during half a cycle of the local oscillation (∼1 fs) and may change by several eV within time steps of 400 as [1]. Therefore the ∼50 meV energy resolution of the TOF-PEEM is well sufficient to resolve the shifts of the photoelectron energies, and thus the attosecond dynamics of the nanoplasmonic field is expected to fully unfolded using the TOF-PEEM.

4. First experimental results using static 2PPE TOF-PEEM on Ag and Cu film samples

First results using the TOF-PEEM in a 2PPE experiment without time delay are given in figure 6(a). A polycrystalline Cu sample was prepared by cycles of sputtering and annealing. In the TOF operation mode, the sample was irradiated with 400 nm/60 ps optical pulses from a pulsed diode laser. The emission of electrons is facilitated through two-photon emission without time delay between the incident photons. A series of energy slices by TOF-PEEM are shown in this figure. At the same time, a series of energy slices obtained with IEF and Hg lamp excitation (Hg lamp, $\lambda \sim 250$ nm) of the same sample area are given in figure 6(b) for comparison. The electron energy discrimination was performed by TOF in the case of laser excitation, whereas the electron energy discrimination was conducted by the IEF for the case of Hg lamp excitation. The drift energy of the tube in the PEEM was

20 eV and the laser signal was used as a time marker for DLD. The slices are extracted from the full 3D (x, y, t) data stack by setting a condition for the arrival time of the photoelectrons in the TOF operation mode. Photoelectron generation with a 400 nm laser is a 2PPE process. This can be seen in the spectra (figure 7), which end at a final state energy of $2h\nu = 6.2$ eV. As a consequence of the part of the spectrum closest to the work function cut-off, there are many more secondary electrons located than the spectra obtained with Hg lamp excitation. Therefore the contrast change becomes weaker in this case as compared to the image series obtained with the IEF mode. Furthermore, it is interesting to note that we observe some bright spots in the PEEM images under 400 nm/60 ps laser excitation.

Four prominent crystallites can be distinguished within the field of view in figure 6(b) under Hg lamp excitation. As can be seen from the energy slices, the left crystallite has a higher work function than the others. The intensity differences in the other three crystallites, which can be seen in the IEF measurement, are due to polarization effects or different electron densities at the Fermi edge. This indicates that these three crystallites are either crystallites with different surface normals or a similar work function, or, much more likely, these three crystallites have the same crystallographic orientation to the surface normal but a different orientation in the plane.

The sum image shown in figure 7(a) is an integrated image over the time coordinate t of the TOF image series and the IEF energy slices (both are from figure 6). TOF spectra in figure 7(b) are taken for a smooth area of the Cu sample (marked by the larger square in the sum image) and a single bright spot, i.e. a point of high intensity (marked by the smaller square). The intensity in this bright spot is enhanced by a factor of ∼6 relative to the smooth area.

We also investigated microstructured Ag film on Si substrate by use of the TOF-PEEM. Figure 8(a) shows the PEEM image (an integrated image over the time coordinate t of the TOF images) from the Ag microstructure on Si substrate excited by 400 nm/60 ps laser. Figure 8(a) shows the microstructures and, more interestingly, a number of nanosized 'hot spots' as previously observed using the femtosecond pulse
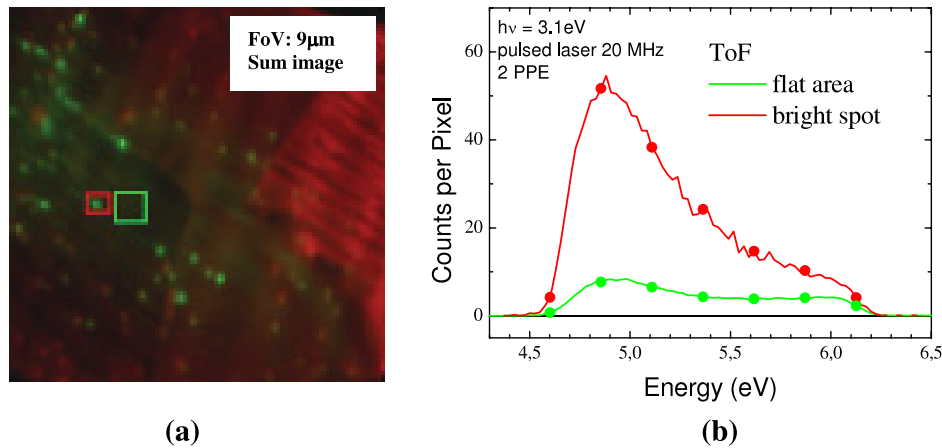
Figure 7. (a) Sum image of the slices in figure 6 over all energies for TOF (laser excitation) and IEF (Hg excitation). (b) The TOF spectra were taken from the smaller square marked region for the 'bright spot' and the larger square marked region for the flat area, as indicated in the sum image. The dots in (b) correspond to the energy slices in figure 6.
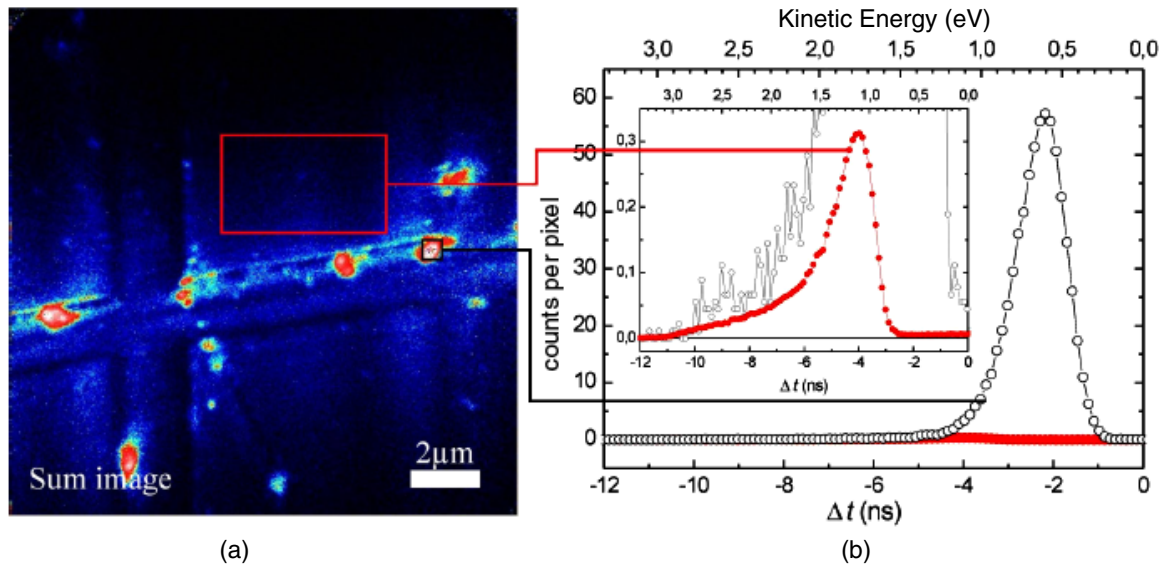

Figure 8. (a) PEEM image of the Ag microstructure on a Si substrate and (b) local TOF spectra, taken with 400 nm/60 ps laser excitation. Note that the intensity in the nanosized 'hot spot' is enhanced by a factor of 200 and kinetic energy of the electrons from 'hot spot' area is about 0.6 eV lower than that from the smooth area.

irradiation from a femtosecond Ti:S laser [18]. Similarly, TOF spectra shown in figure 8(b) are taken from a smooth area of the Ag structure (marked by a larger square) and a single 'hot spot' (marked by a smaller square) on the structure to evaluate the result. The intensity in this hot spot relative to the smooth area is enhanced by a factor of ∼200. Furthermore, the peak energy of the photoelectrons emitted from the hot spot is about 0.6 eV lower than that of photoelectrons from the smooth area.

It is very interesting to note that there are two obvious differences in hot spot 'behavior' between the Cu and Ag samples. The most prominent one is that electron yield from hot spots relative to a smooth area on the Ag sample shows a much higher enhancement (∼200-fold) than that of the Cu sample (∼6-fold). The other one is that the kinetic energy of electrons from the hot spot area shows a lower

energy than that of the smooth area on the Ag sample, while the Cu sample does not obviously show this kind of energy shift between hot spots and smooth area. This cannot be explained in terms of the electronic valence band structure of both materials (Ag and Cu), which is qualitatively very similar: both materials show a low density of state sp-band close to the Fermi energy and a high density of state d-band 3–6 eV below the Fermi level [19, 20]. However, both elements exhibit a different surface plasmon resonant wavelength, which is ∼400 nm in Ag [9] and ∼570 nm in Cu [21], respectively. Due to the experimental excitation wavelength of 400 nm, surface plasmons are resonantly excited in Ag, but they are not resonantly excited in Cu. The large localized optical field of the resonant surface plasmons may cause the d-band electrons of Ag to get field-emitted, while this effect cannot be observed in the Cu sample, where the optical field enhancement is much

weaker. This explains the observed high electron yield (due to high density of state in the Ag d-band) as well as the measured energy shift (due to the high binding energy of the d-band electrons) in the Ag sample.

5. Summary

The experimental feasibility of probing attosecond nanoplasmonic field dynamics with a TOF-PEEM is analyzed in this paper. A newly developed TOF-PEEM is presented, and characterization results of the TOF-PEEM show that ~25 nm spatial and ~50 meV energy resolution can be achieved. The attainable temporal and energy resolution of the TOF-PEEM make it sufficient for unfolding the dynamic processes of a nanoplasmonic field with attosecond temporal and nanometer spatial resolution. A first application of the TOF-PEEM in 2PPE mode shows that nanolocalized optical fields give a locally enhanced photoelectron yield and appear as 'hot spots' in the PEEM image. TOF-PEEM has thus been proven to be a powerful tool to investigate the effect of nanolocalized optical fields on the sample surface, as they are created by resonant surface plasmons. An experiment of VIS-pump/XUV-probe attosecond microscopy to measure the temporal evolution of localized optical fields will be the next experimental step, which will reveal nanolocalized optical fields with unprecedented temporal resolution.

Acknowledgments

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