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Time resolved nonlinear surface plasmon optics

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A new surface-sensitive method of time-resolved optical studies is proposed. The method consists in the independent excitation of several surface electromagnetic waves (SEW) by two laser femtosecond pulse beams with varied time delay $\Delta\tau$ and distance Δr between corresponding excitation regions on surface. To fulfill phase matching condition for plasmon-photon coupling metal grating is used. Due to nonlinear plasmon interaction, the optical radiation with $\omega_1+\omega_2$ and $2\omega_1-\omega_2$ (where ω_1, ω_2 are correspondent laser beam frequency) is generated. The intensity of this nonlinear response *versus* $\Delta\tau$ and Δr are studied. The direct measurements of the SEW temporal properties are presented. Experiments of this type are important for the development of the femtosecond surface plasmon optics.

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The use of surface electromagnetic wave (SEW) is an effective tool for interface studies [1 – 4]. SEW have various applications in matter diagnostics, nonlinear optics and spectroscopy. Many optical effects are difficult to observe, because of a weak nonlinear response or small amount of substance. To avoid this difficulty, one can concentrate laser radiation energy in space and time. The advantage of using SEW is the concentration of light energy near the interface. Special experimental geometry can be used to fulfill phase matching condition for effective SEW excitation [1]. We use metal grating for this purpose. It is essential for nonlinear processes to have high peak intensity, but the average field must be moderated, otherwise the sample will be damaged. Femtosecond laser pulses fit to these requirements.

In the present work we suggest new surface-sensitive method of time-resolved studies based on the use of interacting SEW, excited by two femtosecond laser beams with varying time delay and distance between corresponding excitation regions on the surface. This interaction leads to the generation of optical waves at frequency equal to the second harmonic or the sum frequency of incoming beams. Four waves mixing (FWM) process $2\omega_1-\omega_2$ is also investigated. We are mainly interested in temporal behavior to demonstrate that time-resolved studies on a grating surface can potentially have temporal resolution up to few femtosecond. The sensitivity and selectivity to the properties of the surface are achieved with the second-harmonic (SHG) and sum frequency generation (SFG) processes because these processes are forbidden in the bulk of the isotropic medium [5, 6]. The results show that our method based on the interaction of noncollinear SEW has femtosecond time-resolution and much more possibilities for experimental realizations in comparison with other surface-sensitive optical techniques [7 – 11].

We carry out experiments in different geometry of the incoming beams. Collinear scheme is used in the case of degenerated SFG. We demonstrate the possibility of noncollinear experiments on the example of degenerated and nondegenerated SFG and FWM.

The SEW is generated according to the relation $\mathbf{k}^{\omega}_{t,i}+n_i\mathbf{q}=\mathbf{K}^{\omega}_{\mathrm{SEW},i}$, where $i=1,2$ denote beam number, $\mathbf{q}=2\pi/d$ is reciprocal lattice vector, d is grating period, $\mathbf{k}_{t,i}=\mathbf{k}_i\sin\theta_i$ is laser radiation wave vector projection on a grating plane, θ_i is the angle of incidence of laser beam relative to the normal of the grating, n_i is diffraction order. $\mathbf{K}^{\omega}_{\mathrm{SEW},i}$ is SEW wave vector (see Fig.1).

The generated SEW waves radiate waves at combinational optical frequency if phase matching conditions for optical waves at frequencies ω_1 and ω_2 are satisfied simultaneously with the relation between interacting SEW wave vectors: $\mathbf{K}^{\omega_1}_{\mathrm{SEW},1}+\mathbf{K}^{\omega_2}_{\mathrm{SEW},2}+n_3\mathbf{q}=\mathbf{k}^{\omega_1+\omega_2}_{t,3}$ for nondegenerated SFG and $2\mathbf{K}^{\omega_1}_{\mathrm{SEW},1}-\mathbf{K}^{\omega_2}_{\mathrm{SEW},2}\pm\mathbf{q}=\mathbf{k}^{2\omega_1-\omega_2}_{t,3}$ for FWM process. Fig.1 depicts the vectorial layout for degenerated noncollinear (Fig.1a) and nondegenerate collinear SFG (Fig.1b). Note that in Fig.1 the angle φ represents the angle between the optical wave vector

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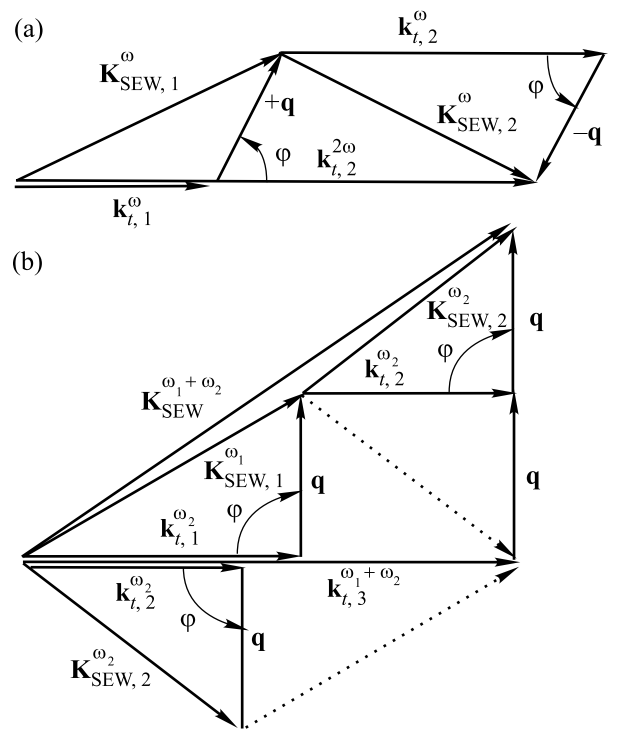

Fig.1. (a) Wave vectors arrangement on grating surface for SFG. Simultaneous excitation of two SEW of one frequency (degenerate) in different directions (noncollinear). The sets of angle are $\varphi = 83^\circ, \theta_1 = 42^\circ, \theta_1 = 59^\circ$. (b) Wave vectors arrangement on grating surface. Simultaneous excitation of several SEW of two frequencies (nondegenerate) in symmetrical geometry in different directions (noncollinear). Angles value are $\varphi = \pm 90^\circ, \theta_1 = 66^\circ, \theta_1 = 52^\circ$

and the reciprocal lattice vector of the grating. Fig. 1b demonstrates that proper choice of angles φ and θ leads to simultaneous satisfaction of phase matching condition of surface plasmon excitation and of the nonlinear process. We highlight that when φ is equal to 90 degree (symmetrical case) excitation of two SEWs with wave vectors $\mathbf{k}_t^{\omega} + \mathbf{q}$ and $\mathbf{k}_t^{\omega} - \mathbf{q}$ respectively takes place simultaneously.

First we describe the case of two collinear plasmon interaction in symmetrical scheme ($\varphi = 90^\circ$) with $\omega_1 = \omega_2 = \omega$. We measure the emission of signal at frequency 2ω and compare it with the autocorrelation function (ACF) of the fundamental beams. The results are presented in Fig.2a. Each beam at fundamental frequency radiates at frequency 2ω via SHG process and as a consequence the recorded signal is nonzero at large delay between pulses. When spatial and temporal overlapping of the pulses occurs degenerated collinear SFG wave is radiated in specular direction. SFG is recorded as function of the delay (plasmon correlation function PCF). This experimental scheme is the same as in an autocorrelator.

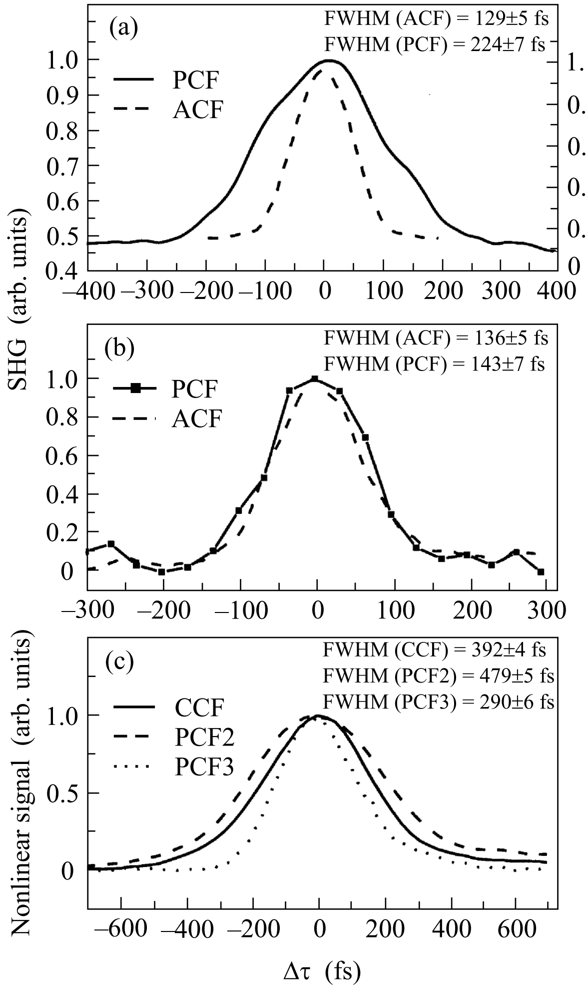

Fig.2. Correlation functions of SFG enhanced by SEW. (a) Autocorrelation function for laser radiation – *ACF* ($\lambda = 760$ nm) and plasmon correlation function *PCF* for degenerate symmetrical case. (b) The same as a) for degenerate noncollinear nonsymmetrical case. (c) Cross-correlation function for laser radiations – *CCF* ($\lambda_1 = 690$ nm and $\lambda_2 = 812$ nm) and plasmon correlation function for SFG – *PCF2* and FWM – *PCF3* non-degenerate symmetrical case: $\varphi = \pm 90^\circ, \theta_1 = 66^\circ, \theta_1 = 52^\circ$

We perform the same experiment in a noncollinear geometry and the results are presented on Fig.2b. In this geometry SHG from each beam and degenerated SFG occurs. SFG wave vector projection on the surface is $\mathbf{k}_{t,3}^{2\omega} = \mathbf{K}^{\omega}_{\mathrm{SEW},1} + \mathbf{K}^{\omega}_{\mathrm{SEW},2}$ and then the SFG signal emission occurs in the direction $\theta_3 \approx (\theta_1 + \theta_2)/2$ [10], different from θ_1 and θ_2. The recorded signal is then background free. The angles of grating grooves orientation are chosen to be the same for both beams

$\varphi_1 = \varphi_2 = 83^\circ$ and all the incident and reflected beams lie in incidence plane. The value of θ_1 and θ_2 are set in such a way to excite simultaneously two SEW according to our grating parameters, see Fig.1a.

We realise also noncollinear nondegenerate SFG and FWM with two synchronised femtosecond laser beams with different frequencies. Symmetrical scheme is used for both beams with frequencies ω_1 and ω_2 like in the degenerate collinear scheme. Beams have different incidence angles as in degenerate noncollinear scheme. To characterize laser pulses we use cross-correlation function (CCF) of beam 1 and beam 2 pulses.

Note that for the described experiments the characteristic length of SEW path is of the same order as radii of excitation spot (15 mkm) on the surface. SEW propagation length l_{pl} and lifetime τ_{pl} are coupled through plasmon velocity $v = 0.9 \cdot c$, where c is the speed of light.

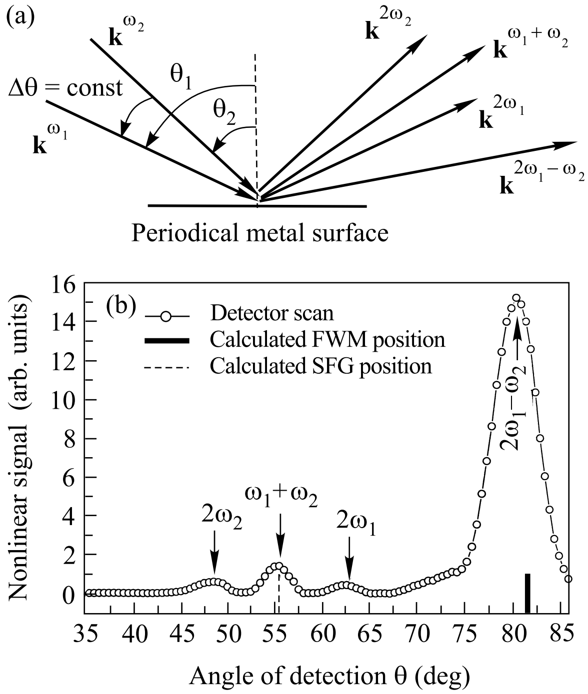

Fig.3. (a) Wave vector arrangement in incidence plane for non-degenerate symmetrical case. (b) Angle distribution of nonlinear signal radiation in incidence plane

At SEW excitation we observe four nonlinear signals $2\omega_1$, $2\omega_2$, $\omega_1 + \omega_2$, $2\omega_1 - \omega_2$ separated in frequencies and in radiation emission angle (see Fig.3). Note that $2\omega_1 - \omega_2$ process has different nature, it is third order nonlinear process and its efficiency is determined by $\chi^{(3)}$ not by $\chi^{(2)}$. Where $\chi^{(2)}$ and $\chi^{(3)}$ are correspondent nonlinear susceptibility tensors. Such properties as spectral width, pulse duration, polarization direction for FWM proved to be different from second order processes – SHG, SFG – for our experimental conditions. Frequencies combination is the same as in well-known CARS (coherent anti-stokes Raman scattering) process. Although we do not have resonance of media on the frequency $\omega_1 - \omega_2$ in our case, signal intensity is rather high. Indeed FWM absolute intensity is higher than SFG or SHG. That can be because $\chi^{(3)}$ electro-dipole tensor has nonzero components in the bulk in contrast to $\chi^{(2)}$. The results of measurements are shown in Fig.2c as PCF 2 for SFG and PCF 3 for FWM process. Note that, the duration of ACF is $\sqrt{2}$ times larger than pulse duration. But for FWM process duration of PCF 3 in $\sqrt{3/2}$ times less then pulse duration because of the difference in the order of the process. The PCF signal is the cross-correlation of SEW_1 and SEW_2 fields. In turn SEW field is the convolution of the plasmon lifetime τ_{pl} and laser pulse duration. From the comparison of ACF and PCF duration it is then possible to obtain the plasmon lifetime. In the symmetrical (collinear and degenerated) SFG case (Fig.2a) we measure the SEW lifetime to be 70 fs. For nonsymmetrical case (noncollinear degenerate) (Fig.2b) this lifetime decreases to 20 fs. For nondegenerate symmetrical noncollinear case SEW lifetime (60 fs) is smaller than in degenerate symmetrical case due to higher SEW absorption on frequency of ω_2. But it is greater then in nonsymmetrical case. As visible from Fig.2b the traces overlap in the case of noncollinear and degenerated SFG demonstrating that the lifetime is much shorter than in the other case of interaction. This increasing of the SEW lifetime in the symmetric case can be connected with SEW properties modification due to Bragg reflection of SEW from the grating grooves.

The nonlinear signal intensity distribution *versus* reflection angle θ is presented on Fig.3b for nondegenerate geometry. All the beams lie in incidence plane. Angle of nonlinear signal radiation defined by phase matching condition agrees well with experimental data.

As plasmon propagates on the metal surface it exponentially decays (in time and in space) through several channels: Ohmic losses, radiation damping and Landau damping.

Besides metal is also in nonequilibrium state after SEW excitation and absorption, and electron relaxation can manifest itself in measured values [11 – 13].

In principle in time resolved SEW experiments it is possible to observe not only SEW lifetime, but also interface relaxation time through processes described above, if a parameter of nonlinear process depends essentially on temperature or metal electrons distribution. For our experimental conditions we did not observed the influence of media temperature on $\chi^{(2)}$ with relative accuracy of 5%.

For wavelength 780 nm in gold the SEW maximal propagation length restricted by Ohmic losses is only 40 mkm, that would correspond to SEW lifetime 130 fs. On the sum frequency the same parameters are accordingly 1.3 mkm and 3 fs. But for difference frequency generation (DFG) (middle and far IR) propagation length can be much large (500 mkm for $\lambda = 10$ mkm). Suggested method allows DFG enhancement by SEW, that could be useful for IR surface time-resolved spectroscopy.

In conclusion, the method of femtosecond surface plasmon spectroscopy is suggested and experimentally demonstrated. It is based on resonance excitation of several surface SEWs by femtosecond synchronised laser beams. These SEWs interact on the surface, allowing us to enhance various nonlinear optical effects, sensitive to the surface properties. That was demonstrated in the present work on the sum-frequency generation and four-wave mixing process. Nonlinear optical response originated from the interacting SEWs reflects the spatial and temporal behaviour of these SEWs. As an example, we measured the SEW lifetime on the surface of the gold grating, which proved to be 60 fs for symmetrical case and less than 20 fs for nonsymmetrical case. For the first time we observed simultaneously SHG, SFG and FWM enhanced by SEW on the grating. The described experiments open practical possibility for the development of time- resolved femtosecond surface plasmon optics and spectroscopy.

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