

PACS numbers: 81.07.–b; 81.16.Mk; 78.67.–n; 42.65.Re
DOI: 10.1070/QE2013v043n04ABEH015105

Local field enhancement on metallic periodic surface structures produced by femtosecond laser pulses

A.A. Ionin, S.I. Kudryashov, A.E. Ligachev, S.V. Makarov, N.N. Mel'nik, A.A. Rudenko, L.V. Seleznev, D.V. Sinitsyn, R.A. Khmelnitsky

Abstract. **Periodic surface structures on aluminium are produced by femtosecond laser pulses for efficient excitation of surface electromagnetic waves using a strong objective (NA = 0.5). The local electromagnetic field enhancement on the structures is measured using the technique of surface-enhanced Raman scattering from pyridine molecules.**

Keywords: *femtosecond laser pulses, periodic surface nano- and microstructures, local field enhancement, surface-enhanced Raman scattering (SERS).*

1. Introduction

Currently, the technique of nano- and microscale femtosecond laser-induced periodic surface structure (LIPSS or ripples) formation on different materials (metals, semiconductors, insulators, polymers, ceramics, etc.) has been actively developed. A high-efficiency method for fabricating such structures was demonstrated and developed in a number of studies [1 – 10]. Excitation of surface plasmon-polaritons (SPPs) upon scattering of single ultrashort laser pulses from surface inhomogeneities and further laser – SPP interference play a key role in formation of ripples [3, 4, 7, 8].

This method of ripple formation has the following advantages: it does not require additional lithographic equipment (masks, photoresists, etc.) and makes it possible to form, for example, arrays of gratings (ripples) with a density exceeding 1000 lines mm^{-1} for few pulses over the entire laser-beam cross section ($10^2 – 10^6$ μm^2). The main ripple parameters (orientation, period, relief depth) can be varied by choosing the radiation polarisation and wavelength, as well as the laser irradiation dose; hence, one can form complex ripple arrays.

It was shown in a number of studies that the thus obtained ripples exhibit diffraction properties, which are used to colour surfaces [8, 9], while subwavelength ripples have antireflection properties [10]. There are also a number of applications in plasmonics, which can be implemented using this high-efficiency technique of ripple formation. However, the plasmonic properties of ripples have not been experimentally studied.

A.A. Ionin, S.I. Kudryashov, A.E. Ligachev, S.V. Makarov, N.N. Mel'nik, A.A. Rudenko, L.V. Seleznev, D.V. Sinitsyn, R.A. Khmelnitsky P.N. Lebedev Physics Institute, Russian Academy of Sciences, Leninsky prosp. 53, 119991 Moscow, Russia;
e-mail: aion@sci.lebedev.ru, makarov_sergey_vl@mail.ru, sikudr@sci.lebedev.ru

Received 24 December 2012
Kvantovaya Elektronika **43** (4) 304 – 307 (2013)
Translated by Yu.P. Sin'kov

One of important problems of plasmonics is the formation of periodic metal structures for implementing surface-enhanced Raman scattering (SERS) from deposited molecules [11 – 14]. Generally, SERS is the result of joint action of two physical mechanisms: the enhancement of local electromagnetic fields near the metal surface (far-field electromagnetic contribution) and the charge transfer between molecule and metal at their direct contact (near-field 'molecular' contribution).

To solve successfully the problem of preparing high-efficiency substrates for SERS, the following requirements must be satisfied: the ripple formation technique should be maximally efficient and inexpensive and allow one to record Raman scattering (RS) signals at ultralow molecular concentrations. These requirements are well satisfied for the ripple formation technique used in our studies, which is based on the laser – SPP interference. Another problem of modern plasmonics is the generation of superstrong electromagnetic fields on metal surfaces to emit high-energy charged particles and generate ultrashort laser pulses in different frequency ranges (from THz to UV) due to the surface-enhanced nonlinear optical effects.

In this study we used the above-described technique for ripple formation on aluminium to fabricate substrates for studying RS spectra of pyridine molecules with concentrations below 10^{10} cm^{-2}; the ripple relief parameters were chosen so as to reach the maximum SPP excitation efficiency under irradiation by a tightly focused pump laser beam. Comparison of RS signals of individual enhanced pyridine lines on flat and structured surfaces allowed us to measure the local-field enhancement on the ripple surface for the radiation wavelength used.

We chose aluminium because it is much less expensive in comparison with gold or silver (the latter are much more widespread). Another advantage of aluminium is the presence of a natural oxide surface layer (about 3 nm thick), which almost completely excludes overlap of electronic shells of pyridine molecules and metal atoms and suppresses the 'molecular' contribution to the RS signal. As a result, one can select more exactly the contribution to the RS signal due to the local electromagnetic field enhancement near the surface. This estimation of enhancement may help to solve the problem of extreme local field creation, which is planned to investigate in our next studies.

2. Experimental

The experiment was performed using the linearly polarised fundamental mode of a femtosecond Ti : sapphire laser system (Avesta Project) with the following parameters: centre wavelength $\lambda \approx 744$ nm, spectral FWHM ~12 nm, TEM_{00} mode (spot diameter of about 14 mm at the e^{-1} level), pulse duration (in the interaction region) τ_{las}(FWHM) $\approx$ 100 fs, energy E_{inc} up to 6 mJ, and pulse repetition rate of 10 Hz. The laser pulse energy was controlled using a reflective polarisation attenuator (Avesta Project) and monitored by a calibrated DET-210 photodiode (Thorlab), which was exposed to a weak spot using a rotational dielectric mirror. Structures were produced as follows: laser radiation was slightly focused (a sample was placed before the focal plane of the lens) by means of a spherical lens with a focal length of 11.5 cm on the surface of an aluminium sample of optical quality into a spot with a radius of 420 μm at the e^{-1} intensity level. A sample was mounted on a motorised triaxial movable platform and scanned with a velocity of 80 μm s^{-1}. The sample surface was visualised using a JEOL 7001f scanning electron microscope (SEM) and a Nano DST atomic-force microscope.

To analyse RS spectra, we choose pyridine (C_5H_5N), which was first dissolved 10^8 times in isopropyl alcohol, after which the solution was deposited on specially prepared aluminium samples with a flat surface or with ripples produced. The pyridine surface concentration in the vicinity of the pump beam (with a radius of 10 μm) was about 10^8 cm^{-2}. The RS spectra were recorded using an Ar^+ laser (wavelength λ = 514 nm, power 0.1 mW) through an objective with a numerical aperture NA = 0.5.

To study the optical properties of ripples on aluminium, we used the second harmonic (λ = 532 nm) of a cw Nd:YAG laser. The diffracted radiation power was measured by a calibrated DET-110 photodiode (Thorlab). Angular positioning of the sample was performed applying a mechanical rotational table; the positioning error was 0.25°.

3. Results and discussion

With allowance for the dependence of the ripple period and quality on the number of incident pulses, wavelength, and laser fluence, we developed structures demonstrating resonant properties for SPP excitation by cw radiation (λ = 514 nm), which was focused by an objective with NA = 0.5 (the beam convergence angle in the focus $\Delta\theta_{foc} \approx 30°$). Figure 1 shows a SEM image of a ripple formed on an aluminium surface by scanning the latter with an ultrashort-pulse laser beam (peak fluence $F \approx$ 0.48 J cm^{-2}) with a velocity corresponding approximately to 100 pulses per point. The grating period is $\Lambda = 600 \pm 60$ nm (wave number $q = 1/\Lambda \approx 1.67$ μm^{-1}), with an average groove depth of about 30 nm. The oxygen content in the aluminium surface layer in this relief formation regime, as was shown in [8], increases by only 1%–2%.

The resonant properties of the periodic structures formed were previously investigated at the wavelength λ = 532 nm by measuring intensities in the zero and first diffraction orders (Fig. 2). It was found that near the angle of incidence of the laser beam $\theta \approx 10°$ the loss on SPP excitation was maximum and amounted to about 8% of the incident beam intensity; in this case the angular FWHM of the diffraction minimum was $\Delta\theta \approx 13°$.

In the linear approximation of diffraction theory for a metal surface grating the condition for resonant SPP excitation by a beam in the first diffraction order has the form [14]

$$\sin\theta_{res} = \lambda\left(\frac{1}{\lambda_{SPP}} - \frac{1}{\Lambda}\right), \quad (1)$$

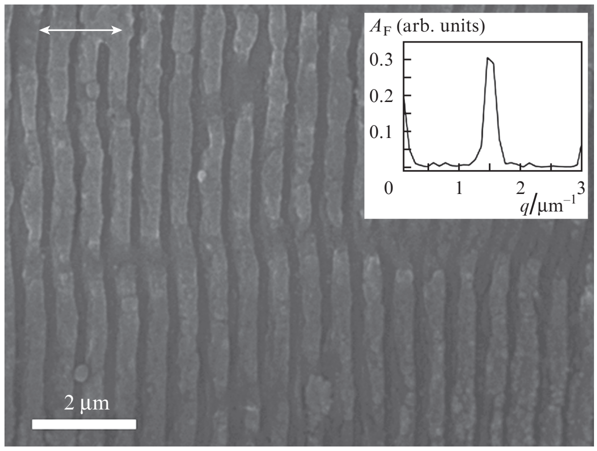

Figure 1. SEM image of a ripple on the aluminium surface. The inset shows a one-dimensional spatial Fourier spectrum of ripple profile. The white arrow indicates the direction of femtosecond laser pulse polarisation.

where λ is the incident radiation wavelength; Λ is the resonant-grating period; λ_{SPP} is the SPP wavelength (for the permittivity $\varepsilon_1 = -42 + i12$ [15] $\lambda_{SPP} \sim \lambda$). It follows from this condition that the resonant angle θ_{res} at $\lambda = \lambda_{SPP}$ = 532 nm and Λ = 600 nm is about 6°, and the angular width $\Delta\theta \sim \theta_{res}(\Delta\Lambda/\Lambda) \sim 1°$.

Our experimental data are described well by the model taking into account the SPP scattering from relatively deep surface inhomogeneities, which leads to a change in the SPP dispersion relation [14, 16]. Within this model the complex SPP wave vector ($k_{SPP} = 1/\lambda_{SPP}$) changes both its real and imaginary parts: Re(k_{SPP}) + Re(Δk) and Im(k_{SPP}) + Im(Δk). For a relief depth of 30 nm and λ = 532 nm, the calculated increase in the real part of the wave vector is Re(Δk) = 0.1 μm^{-1}, which correspond to a change in λ_{SPP} to 505 nm. Having substituted this changed λ_{SPP} value into formula (1), we find the resonant angle to be $\theta_{res} \approx 10°$, which coincides with the experimental value (Fig. 2). We believe the significant increase in the resonant angle width to be related to not only the increase in the relief depth but also to structural defects in the ripples formed.

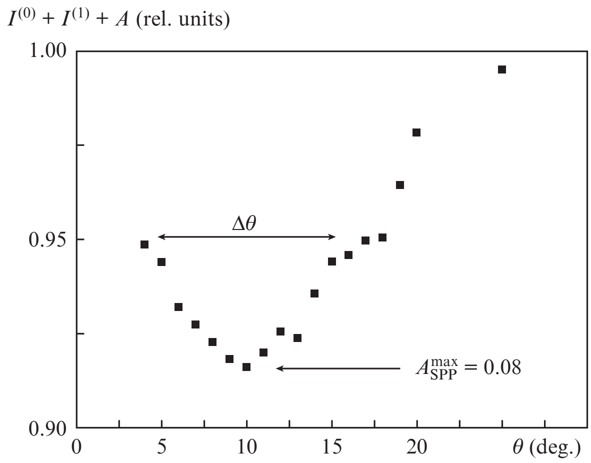

Figure 2. Total normalised intensity of the zero [$I^{(0)}$] and first [$I^{(1)}$] diffraction orders with allowance for the absorption A of aluminium for λ = 532 nm.

If RS spectra are recorded using laser radiation with λ = 514 nm (ε = –39 + i10 [15]), the SPP wavelength on ripples with the same parameters changes due to the scattering [16]: $\lambda_{\rm SPP} = 1/[{\rm Re}(k_{\rm SPP}) + {\rm Re}(\Delta k)] \approx 480$ nm, which corresponds [in accordance with (1)] to $\theta_{\rm res} \approx 12°$. Taking into account that the total angle of convergence of the pump laser beam from the objective is $\Delta\theta_{\rm foc} \approx 30°$ and that SPP excitation is observed at angles of incidence up to 25°–30° (Fig. 2), one can say that the radiation of a tightly focused laser pump beam is practically entirely involved in the SPP excitation in this ripple geometry.

To study the RS signal from pyridine molecules, we used a diluted (approximately 10^8 times) pyridine solution, which was deposited on ripples written on the aluminium surface using femtosecond laser pulses. For comparison, pyridine of the same concentration was deposited on a flat aluminium surface. The RS spectra recorded are shown in Fig. 3.

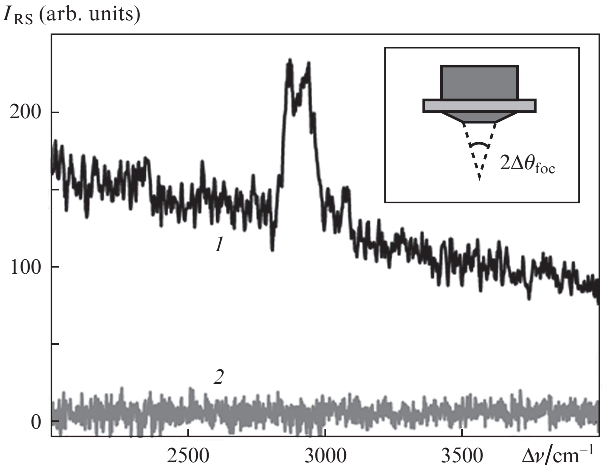

Figure 3. (*1*) Range of the Stokes part of the RS spectrum of pyridine molecules deposited on a ripple in the case of orthogonal orientation of pump polarisation and the groove direction and (*2*) the spectrum of pyridine molecules deposited on a flat aluminium surface. The inset schematically shows the objective focusing laser radiation with a convergence angle $\Delta\theta_{\rm foc}$.

Comparison of the RS spectra of pyridine molecules on ripples and on a flat sample surface (FSS) yielded the electrodynamic contribution of grating to the RS signal $({\rm EF})_{\rm EM} = I_{\rm RS}({\rm PPS})/I_{\rm RS}({\rm FSS})$, which was found to be ~50 near the Stokes shift $\Delta\nu$ ~ 3000 cm^{-1}. Specifically the contribution of the SPP excitation on the grating allowed us to detect an RS signal, because the RS spectrum of a flat surface in the range $\Delta\nu$ = 2000–4000 cm^{-1} is a wide peak near 2000 cm^{-1}, which is hardly distinguishable against the noise background. Note that when the incident pump radiation was polarised along the grating grooves, the RS signal was much weaker than for the field polarisation oriented perpendicular to the grating grooves; in addition, no pronounced peak was observed near the Stokes shift $\Delta\nu$ ~ 3000 cm^{-1}. These facts suggest an important role of excited SPPs when measuring pyridine RS spectra on the ripples.

The obtained enhancement of the RS signal can be estimated from above using the well-known relation for the squared modulus of the ratio of local SPP field $E_{\rm loc}$ on the surface to the incident electromagnetic field E_0 [14]:

$$T^{\rm el} = \left|\frac{E_{\rm loc}}{E_0}\right|^2 = \frac{2|\varepsilon_1|^2\cos\theta_{\rm res}A_{\rm tot}}{\varepsilon_2(|\varepsilon_1| - 1)^{1/2}}, \quad (2)$$

where ε_1 (ε_2) is the real (imaginary) part of aluminium permittivity; and $A_{\rm tot}$ is the total absorption coefficient, including the absorption of light due to SPP excitation and absorption by an aluminium surface. Having substituted the experimental and tabular [15] values, λ = 514 nm, ε_1 = –39 and ε_2 = 10, $A_{\rm tot} = A_{\rm SPP} + A \approx 0.16$, $\theta_{\rm res}$ = 12°, we obtain $T^{\rm el} \approx 7.5$. Thus, since the RS increase due to the local field enhancement is [11]

$$({\rm EF})_{\rm EM} = \left|\frac{E_{\rm loc}}{E_0}\right|^4, \quad (3)$$

the obtained estimate $({\rm EF})_{\rm EM} \sim (7.5)^2 \sim 56$ approximately corresponds to the experimental value ${\rm EF}_{\rm EM} \approx 50$. These estimates show that the ripples on aluminium provide a maximum RS enhancement in the regime of tight focusing of pump laser radiation. According to the data of some theoretical and experimental studies [11, 13], the maximally possible RS gain $({\rm EF})_{\rm EM}$ for molecules on an ideal periodic metal surface grating (provided that $\varepsilon_2 \ll \varepsilon_1$) does not exceed 10^4. However, these values are obtained using time-consuming techniques of forming a relief on the surface of noble metals (Au and Ag), which have no oxide layer; this circumstance hinders separation of the SPP contribution to SERS from the 'molecular' contribution because of the strong interaction of deposited molecules with metal atoms.

4. Conclusions

We proposed an optimal profile for ripples produced by multipulse femtosecond laser irradiation of an aluminium surface as a result of laser–SPP interference; these structures can be used for efficient conversion of tightly focused (NA = 0.5) laser radiation at another wavelength into SPPs. It was demonstrated that the ripples formed make it possible to detect low (less than 10^{10} cm^{-2}) concentrations of pyridine molecules. The use of specifically aluminium allowed us to experimentally estimate the RS signal enhancement, which was found to be ~50; this value is in good agreement with the predictions of the theoretical model considering SPP excitation by pump laser radiation. It is planned to use further this geometry for samples of other materials to obtain an extremely high local electromagnetic field.

Acknowledgements. We are grateful to A.V. Nepomnyashchii (Far East Branch of the Russian Academy of Sciences, Vladivostok) for sample visualisation with an atomic-force microscope.

This work was supported by the Foundation for Assistance to Small Innovative Enterprises (programme 'UMNIK'); the administration of the Teaching and Research Complex of the P.N. Lebedev Physics Institute, Russian Academy of Sciences; the Russian Foundation for Basic Research (Grant Nos 11-02-01202 and 11-08-01165); and the programmes 'Extreme Light Fields and Their Applications' and 'Fundamentals of Technologies for Nanostructures and Materials' of the Presidium of the Russian Academy of Sciences.

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