OPTICS
AND LASER PHYSICS

Metastructures for the Giant Enhancement of Raman Scattering in the Near Infrared Spectral Range

**V. I. Kukushkin[a], *, V. E. Kirpichev[a], E. N. Morozova[a], V. V. Solov'ev[a],
Ya. V. Fedotova[a], and I. V. Kukushkin[a]**

[a] *Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432 Russia*
*e-mail: kukush@issp.ac.ru

The properties of periodic dielectric structures coated with a thick metal layer, which allow enhancing an inelastic light scattering signal by more than eight orders of magnitude at a laser pump wavelength of 1064 nm, have been studied. It has been shown that the giant resonance enhancement of the Raman signal in the near infrared range is ensured by additionally enhanced plasma resonance and by geometrical resonance between the sizes of the dielectric structure and the wavelength of laser radiation. The dependence of the enhancement factor of the Raman scattering on the height of columns in periodic dielectric structures, as well as the dependence of the enhancement factor on the thickness of the metallic coating, has been studied. New resonance modes have been revealed, for which the height of dielectric columns is 1/4, 1/2, and 3/4 of the wavelength of laser radiation. It has been shown that record high enhancement factors of the Raman scattering can be reached in the near infrared range, which is also due to a high Q factor of plasma waves in metals at these frequencies.

One of the most important problems of modern solid state physics and microelectronics is the problem of enhancement of a local electromagnetic field near metasurfaces, which are combinations of nanostructured metallic and dielectric resonators. The solution of this fundamentally important problem can improve the sensitivity of electromagnetic detectors by orders of magnitude. This is particularly urgent for the far infrared and terahertz ranges, where the sensitivity of detectors is still insufficiently high. It is noteworthy that, for surface enhanced Raman scattering (SERS) resulting in the giant increase in the intensity of the Raman scattering owing to plasmon effects by factors more than 10^9 in the visible spectral range, there is a well-established example of the giant enhancement of the local field. The aim of this work is to develop combined plasmon–dielectric metastructures and to study their properties allowing the giant enhancement of the local field in the infrared range. The enhancement factor of the local field in the infrared range is measured by analyzing the Raman SERS effect.

Raman spectroscopy with the giant enhancement of scattered light caused by plasmon effects (SERS effect) [1–3] is traditionally applied at quite short laser excitation wavelengths (450–750 nm) because inelastic light scattering is stronger for shorter laser excitation wavelengths. However, the problem with strong background luminescence usually appears in this wavelength range and the degradation of organic molecules occurs because of the strong absorption of light. Furthermore, an increase in the frequency of radiation is accompanied by a strong decrease in the Q factor of plasma waves (ratio of the square of the real part of the permittivity to its imaginary part) in almost all metals (particularly in gold) and, as a result, by a strong increase in their damping [4, 5]. To solve the listed problems, longer wavelength infrared laser excitation can be used because the damping of plasma waves is much lower in this wavelength range [5] and, in addition, problems with intense luminescence and degradation of molecules almost disappear.

We emphasize that the intensity of the Raman scattering is proportional to the fourth power of the excitation frequency only for the case of nonresonant "bulk" inelastic light scattering. The situation can be opposite for scattering with the giant enhancement of the Raman signal on nanostructured metallic SERS substrates. The reason is that the frequency dependence of the enhancement factor, which is specified by the square of the Q factor of plasma waves in a metal, is more important in this case. This Q factor is the ratio of the square of the real part of the permittivity (ϵ_1) to its imaginary part (ϵ_2): $Q = \epsilon_1^2/\epsilon_2$. It is well known [5] that an increase in the wavelength from 500 to 1500 nm is accompanied by change in the Q factor of plasma waves in silver and gold by orders of magnitude, which compensates losses of the scattering intensity associ-

ated with the mentioned biquadratic frequency dependence of the intensity of light scattering. Thus, SERS enhancement in the near infrared spectral range can be much larger than that in the visible spectral range. Moreover, as the laser excitation wavelength increases in the case of SERS substrates, the signal can be enhanced at a much larger distance from a substrate, allowing the study of larger molecules [6]. It is also noteworthy that SERS substrates operating at wavelengths above 1000 nm can be fabricated using photolithography rather than electron lithography, which significantly reduces the cost of production of such structures.

Thus, one of the most important goals of bionanotechnology is to develop stable and inexpensive SERS-active nanostructures for the near infrared range (wavelengths of 1000−1500 nm) providing the maximum enhancement of the Raman signal [7−9].

In [10, 11], we developed and studied combined dielectric and metallic resonators for the giant enhancement of the inelastic light scattering signal. In this case, dielectric resonators were fabricated on Si/SiO$_2$ substrates, where periodic structures (dielectric square columns 10−400 nm in height) with the planar size a (and period $p = 2a$), which varied from 50 to 1500 nm, were fabricated by means of electron lithography and plasma etching. To produce a combined dielectric−metallic resonator, a thick metal layer was deposited on this periodic dielectric structure by the method of thermal spraying. In [11, 12], we detected oscillations in the enhancement factor of the Raman signal as a function of the period (and the planar size) of dielectric columns with various fixed heights. The detected oscillations of the enhancement factor of the Raman signal are determined by modes of the combined resonator, and the enhancement is maximal when the parameter a is equal to half the wavelength of laser radiation.

In this work, the dependences of the enhancement factor of the Raman scattering on the height of columns in periodic dielectric structures and on the thickness of the metallic coating layer are studied for the case of 1064-nm laser radiation. New resonance modes are detected at the heights of dielectric columns of 1/4, 1/2, and 3/4 of the wavelength of laser radiation. It is shown that record-high enhancement factors of the Raman scattering can be reached in the near infrared spectral range because of the high Q factor of plasma waves in metals at these frequencies.

We studied the structures fabricated by the method described in detail in [10−12]: 2 × 2-mm active (with dielectric columns) regions were prepared on a 5 × 5-mm thermally oxidized silicon substrate with an oxide thickness of 1200 nm. Active regions contained square columns with the height h, side $a = 500$ nm, and period $p = 1000$ nm, which corresponded to the maximum enhancement of the Raman signal at a laser radiation wavelength of 1064 nm [12]. The height of dielectric columns h was varied in various structures from 10 to 1000 nm. The entire structure (all active and inactive regions) was coated with a thick metallic layer (silver with the thickness t from 10 to 160 nm) by the method of thermal spraying. The spatial distribution of the intensity of the Raman scattering on such structures was studied using a Raman microscope, which ensured a spatial resolution to 1 μm, but we chose an optimal diameter of 10 μm for the spot of the focused laser beam (the scanning step in this case was also 10 μm). The Raman microscope used in our work allowed measurements at a wavelength of 1064 nm and (for comparison) at wavelengths of 488, 532, and 568 nm. It was found that an almost identical Raman spectrum was observed on the 2 × 2-mm region containing 2000 × 2000 columns after the drying of the analyte (thiophenol) aqueous solution drop with a very low concentration (down to 10^{-8}). We note that the intensities of all lines of this spectrum remained the same (with an accuracy to 10%) at the scanning of the large area of the SERS substrate.

It was found that the suppression of luminescence and inelastic scattering signals was observed in places with a smooth metallic coating, which were located between regions with periodically modulated structures, instead of the enhancement of the Raman scattering. On the contrary, the giant (more than eight orders of magnitude) enhancement of the Raman scattering signal was observed in places where periodic dielectric structures with the thick metallic coating were located. In this case, the enhancement factor depended both on the height of dielectric columns of the periodic structure and on the thickness of the metallic coating. It was shown that the observed resonance enhancement of the Raman signal is due to the transformation of electromagnetic radiation to localized plasmon-polariton modes, and the efficiency of such transformation is determined by the commensurability of the wavelength of a plasmon-polariton mode and the height of dielectric columns of the periodic structure.

When studying the SERS effect at a laser excitation wavelength of 1064 nm, we used various organic analytes (4-aminobenzenethiol, thiophenol, etc.) and found that the enhancement factors obtained for the Raman scattering were almost the same for all used analytes. Below, we present the results obtained for thiophenol, because the Raman spectra measured on the SERS substrate and in bulk contained many identical lines at almost identical spectral positions. This fact allowed the most direct comparison of the scattering intensities and obtaining reliable results for the giant enhancement of the Raman signal. Figure 1 shows the Raman spectra of thiophenol (C$_6$H$_6$S) measured for laser photoexcitation at a wavelength of 1064 nm in the case of bulk liquid thiophenol (concentration of 100%) and in the case where the thiophenol solution drop with a concentration of 3×10^{-7}
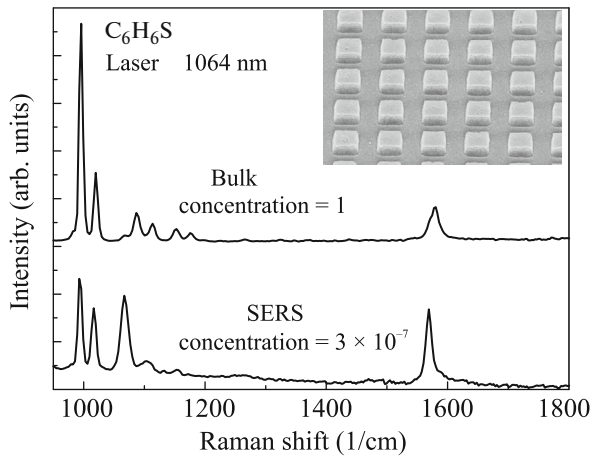
Fig. 1. Raman spectra of thiophenol (C_6H_6S) measured for laser photoexcitation at a wavelength of 1064 nm in the case of bulk liquid thiophenol (concentration of 100%) and in the case where a drop of thiophenol solution with a concentration of 3×10^{-7} was dried on the SERS substrate. The inset shows the electron microscopy image of one of the studied SERS structures with the geometrical parameters $a = 500$ nm, $p = 1000$ nm, $h = 200$ nm, and $t = 80$ nm.

Fig. 2. Raman SERS spectra of thiophenol (C_6H_6S) measured upon laser photoexcitation at a wavelength of 1064 nm for concentrations of 10^{-4}, 10^{-6}, and 10^{-8}. The inset shows the intensity of the SERS signal versus the concentration of thiophenol. Closed circles are the measured linear concentration dependence of the Raman signal in the case of bulk thiophenol.

was dried on the SERS substrate. It is seen that the inelastic scattering spectra are in good agreement with each other, demonstrating close Raman modes, and the level of the signal from the SERS substrate is comparable with the bulk signal, although the concentrations of the analyte are different by seven orders of magnitude. The SERS spectrum shown in Fig. 1 was obtained from the SERS substrate, which was incompletely optimized in the structure parameters h and t. To find the maximum of the SERS enhancement, we varied (a) the height of dielectric columns h and (b) the thickness of the silver film t.

The inset of Fig. 1 shows the electron microscopy image of one of the SERS structures with dielectric columns, which was coated with a thick silver layer. The geometrical parameter of this structure were $a = 500$ nm, $p = 1000$ nm, $h = 200$ nm, and $t = 80$ nm.

Our previous studies [10−12] demonstrated that the enhancement of the Raman signal in such periodic SERS structures is maximal when the period of the structure is equal to the laser excitation wavelength. In the case of laser excitation at a wavelength of 1064 nm and the parameters $a = 500$ nm, $p = 1000$ nm, $h = 200$ nm, and $t = 80$ nm, we reached record enhancement factors of the Raman signal up to 2×10^8 [12]. Figure 2 shows how inelastic light scattering spectra measured on the SERS substrate with the above geometrical parameters change when the concentration of thiophenol in the solution was varied from 10^{-4} to 10^{-8}. It is seen in this figure that the three main scattering lines are clearly seen in the Raman spectrum even at lowest concentrations and the signal/noise
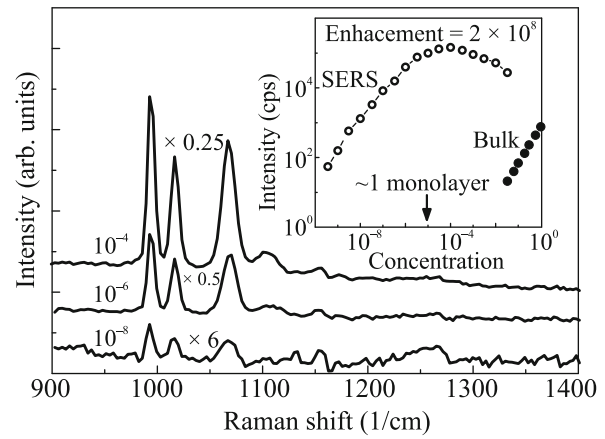
ratio remains acceptable down to a concentration of 10^{-8}. An increase in the collection time allows recording the SERS signal down to a concentration of 3×10^{-10}.

According to the inset of Fig. 2, the use of the SERS substrate allows measuring the Raman signal from thiophenol with a concentration down to 10^{-9} and below. This certainly indicates a giant enhancement factor of the Raman signal on the studied SERS substrates: this enhancement factor is noticeably higher than 10^8 upon pumping at a wavelength of 1064 nm. We note that the further optimization of the metallic coating consisting of a combination of metallic layers with different thicknesses made it possible to increase the SERS enhancement factor by an additional order of magnitude and to attain the enhancement factor up to 2×10^9. The corresponding results will be reported elsewhere.

A colossal SERS enhancement factor exceeding 2×10^8 observed under laser excitation at a wavelength of 1064 nm is a quite surprising result and requires explanation. As mentioned in the beginning of this paper, the SERS enhancement factor is determined by the square of the Q factor of the metallic film $Q = \epsilon_1^2/\epsilon_2$. Both permittivities ϵ_1 and ϵ_2 strongly depend on the frequency [5]. In particular, $\epsilon_1 = -4.68$ and $\epsilon_2 = 2.42$ for gold at a wavelength of 532 nm; consequently, the Q factor of a gold film at 532 nm is about 9.0. At the same time, $\epsilon_1 = -48.4$ and $\epsilon_2 = 3.60$ for gold at a wavelength of 1064 nm; correspondingly, the Q factor of a gold film at 1064 nm is 650, which is larger than that at a wavelength of 532 nm by a factor of 72. Since the SERS enhancement factor is propor-

tional to the square of the Q factor, it can be expected that the SERS enhancement factor for gold at a wavelength of 1064 nm will be almost four orders of magnitude greater than that at a wavelength of 532 nm. A similar analysis of the dependences of the parameters of permittivity components for silver shows that it can be expected that the SERS enhancement factor for silver at a wavelength of 1064 nm will be more than two orders of magnitude greater than that at a wavelength of 532 nm.

The aforementioned dependences of the intensity of the Raman SERS signal on the concentration of thiophenol, which provide a record high SERS enhancement factor of 2×10^8, were obtained at a fixed height of dielectric columns $h = 200$ nm. In [12], we established that this height of columns is nearly optimal, but we did not study the dependence of the SERS enhancement factor on the height of columns h. It is noteworthy that detailed measurements of the dependence of the SERS enhancement factor on the height of columns in metastructures necessary to determine optimal parameters of the structure are still absent. Instead, the parameters (periods, height of columns, and thickness of the metallic coating) of fabricated metastructures were usually chosen using theoretical calculations. However, according to our experiment, the real geometric parameters the structures at which the enhancement of the SERS effect is maximal are inconsistent with calculations. In particular, in [13, 14], where a similar structure was used to study the SERS effect in the case of laser radiation with wavelengths of 488 and 514 nm, respectively, the optimal heights of columns were chosen from theoretical calculations and were 70 nm (about $\lambda/7$) [13] and 50 nm (about $\lambda/10$) [14]. As will be shown below, these "theoretical" heights of columns did not correspond to the optimal h value. To determine the optimal parameter h and to study the mechanism of additional SERS enhancement associated with the formation of standing plasmon-polariton waves in columns, we analyzed a set of 16 SERS substrates that differ only in the height of columns varying from 10 to 1000 nm. All 16 substrates were coated with the same silver layer with a thickness of $t = 80$ nm. Figure 3 shows the dependence of the Raman intensity measured under the same conditions (same analyte concentration and same laser power) on all 16 SERS substrates. This dependence demonstrates that at least three geometrical resonances caused by the formation of standing plasmon-polariton waves in these structures are achieved. The first (main) geometrical resonance occurs at $h = 250$ nm, the second resonance appears at $h = 500$ nm, and the third geometrical resonance occurs at $h = 800$ nm. These three resonances correspond to the ratios of the height to the wavelength of laser radiation of 1/4, 1/2, and 3/4, respectively. It is remarkable that such a set of resonances is a rather extraordinary. The standard condition on the forma-
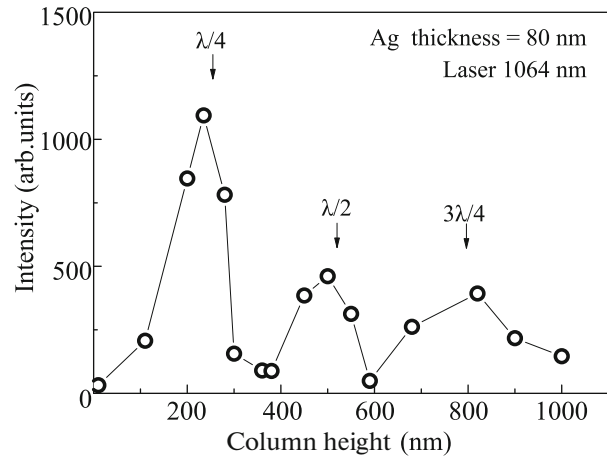

Fig. 3. Intensity of the Raman scattering versus the height of dielectric columns according to the measurements for a series of 16 SERS structures with the fixed parameters $a = 500$ nm, $p = 1000$ nm, and $t = 80$ nm and the parameter h varying from 10 to 1000 nm. All measurements were performed at the same concentration of analyte and the same laser power.

tion of standing waves implies the following relation between the size L and the wavelength λ:

$$L = \lambda(N + 1/2), \quad \text{where} \quad N = 0, 1, 2, \ldots.$$

At the same time, as shown in [15], this standard relation is satisfied only in the case of symmetric boundary conditions. It was also shown in [15] that the resonance condition under asymmetric conditions when one end of a strip is short-circuited by a metal and the second end is free and not short-circuited has the different form

$$L = \lambda(N + 1/2)/2, \quad \text{where} \quad N = 0, 1, 2, \ldots.$$

This condition appears because that the condition of zero field amplitude is absent on the free end of the strip and, therefore, resonance corresponds to the old condition but with the doubled length of the strip. Since our case with dielectric columns coated with a metal on one side corresponds to asymmetric boundary conditions, it should be expected that geometrical resonances will be observed at ratios of the height to the wavelength of laser radiation of 1/4, 3/4, ... Just such resonances are observed as the main resonances in the experiment (see Fig. 3). The manifestation of an additional resonance at $h/\lambda = 1/2$ obviously corresponds to a standing wave, which is formed at edges of columns, and resonance in this case is established between two metallic surfaces in the upper and lower parts of columns. This case corresponds to the symmetric boundary conditions and, consequently, the ratio $h/\lambda = 1/2$ is a natural result.

Although the geometry of resonators used in our work is simple and traditional, results on the dependence on the height of columns seem interesting and

surprising. In particular, in similar silver structures fabricated for laser radiation with a wavelength of 532 nm (with a period of about 500 nm), the dependence of the SERS enhancement factor on the height contains only one maximum at a height of 130 nm (about $\lambda/4$) and does not contain an additional enhancement at 260 nm ($\lambda/2$). This fact means that the efficiency of various enhancement mechanisms of the electromagnetic field depends on the wavelength of laser radiation. As mentioned above, there are two contributions to the enhancement of the SERS effect, one of which is associated with localized surface plasmon-polariton modes and the second contribution is determined by propagating plasmon-polariton modes. The first and second mechanisms can be attributed to resonances at $h = \lambda/4$ and $\lambda/2$, respectively. According to the results obtained in this work, the role of propagating plasmon-polariton modes increases with the wavelength of laser radiation. A similar conclusion can be made by comparing two dependences of the SERS enhancement factor on the height of columns, which were measured for identical metastructures prepared for a laser radiation wavelength of 1064 nm, but are coated with different metals. This dependence in the case of silver coating exhibits enhancement maxima both at $h = \lambda/4$ and at $h = \lambda/2$, whereas only one maximum at $h = \lambda/4$ is observed in the case of gold coating. This result appears because the Q factor of plasma waves at a wavelength of 1064 nm in gold is much smaller than that in silver; for this reason, the contribution of propagating plasmon-polariton modes in gold-coated structures is suppressed compared to localized modes.

In addition, we studied the effect of the thickness of the metallic coating t on the SERS enhancement factor in the case of the SERS substrate, where the parameters of the dielectric structure a, p, and h are optimized and correspond to the maximum enhancement. To this end, we fabricate two SERS substrates with the parameters $a = 500$ nm and $p = 1000$ nm and the heights $h = 250$ and 500 nm. The former and latter structures allow the study of the modes with $h/\lambda = 1/4$ and $1/2$, respectively. It is noteworthy that the variation of the thickness of silver coating from 10 to 1000 nm made it possible to completely remove the silver layer, to return to the initial dielectric structure, and then to deposit a fresh silver layer with a different thickness.

Figure 4 shows the dependences of the Raman scattering intensity on the thickness of the silver coating measured under the same conditions (at the same analyte concentration and the same laser power) on these two SERS substrates. It is seen that the SERS enhancement factor increases strongly with the thickness of silver and reaches the maximum value $t = 80$ nm. This increase is certainly due to an increase in the Q factor of plasma waves in the metallic layer
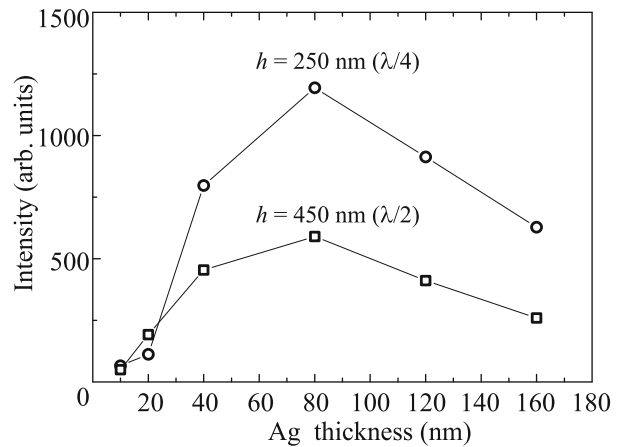

Fig. 4. Intensity of the Raman scattering versus the thickness of a silver coating measured in two SERS structures with the parameters $a = 500$ nm, $p = 1000$ nm, and $h =$ (structure 1) 250 and (structure 2) 500 nm and the parameter t varying from 10 to 160 nm. All measurements were performed at the same concentration of analyte and the same laser power.

because the perfection (homogeneity) of the metallic film is improved.

The drop of the efficiency of the SERS effect at $t > 80$ nm seems surprising because the same result (with the maximum at a thickness of about 80 nm) is observed in our experiments not only for silver coating but also for gold coating. Since the morphologies of the gold and silver film surfaces are different, the drop of the efficiency of the SERS effect at thicknesses of the metallic film above 80 nm is not due to change in the roughness of the surface. We note that the dependences of the SERS enhancement factor with a maximum at $t = 80$ nm are observed for both resonance modes with $h/\lambda = 1/4$ and $1/2$.

We emphasize that our results are important not only (and not so much) for the SERS effect but also for the increase in the sensitivity of detectors for the far infrared spectral range up to terahertz frequencies, where the sensitivity of detectors is insufficiently high. It is important that the enhancement factor of the local field does not decrease but even increases by several times as the frequency decreases from 564 THz (wavelength of 532 nm) to 282 THz (wavelength of 1064 nm). This effect occurs primarily because a decrease in the frequency in this range is accompanied by an increase in the Q factor of plasma waves in the metal and by an increase in the mean free path of propagating plasmon-polariton modes. However, this behavior obviously cannot be sustained and, beginning with certain frequencies, the enhancement effect will decrease. The detailed study of the frequency dependence of the enhancement of the local field on such metastructures in the interval from the near

infrared to far infrared ranges is an important unsolved problem.

To summarize, the properties of periodic dielectric structures coated with a thick metal layer, which allow enhancing an inelastic light scattering signal by more than eight orders of magnitude at a laser pump wavelength of 1064 nm, have been studied. It has been shown that the giant resonance enhancement of the Raman signal in the near infrared spectral range is ensured by additionally enhanced plasma resonance and by geometrical resonance between the sizes of the dielectric structure and the wavelength of laser radiation. The dependence of the enhancement factor of the Raman scattering on the height of columns in periodic dielectric structures, as well as the dependence of the enhancement factor on the thickness of the metallic coating, has been studied. New resonance modes have been revealed, for which the heights of dielectric columns are 1/4, 1/2, and 3/4 of the wavelength of laser radiation. It has been shown that record high enhancement factors of the Raman scattering can be reached in the near infrared range, which is also due to a high Q factor of plasma waves in metals at these frequencies.

REFERENCES

1. M. Fleischmann, P. J. Hendra, and A. J. McQuillan, Chem. Phys. Lett. **26**, 163 (1974).

2. R. B. M. Schasfoort and A. J. Tudos, *Handbook of Surface Plasmon Resonance* (R. Soc. Chem., London, UK, 2008).

3. J. Homola, *Surface Plasmon Resonance Based Sensors* (Springer, Berlin, 2006).

4. W. L. Barnes, A. Dereux, and T. W. Ebbesen, Nature (London, U.K.) **424**, 824 (2003).

5. P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).

6. V. I. Kukushkin, A. B. Van'kov, and I. V. Kukushkin, JETP Lett. **98**, 64 (2013).

7. M. G. Blaber and G. C. Schatz, Chem. Commun. **47**, 3769 (2011).

8. N. G. Greeneltch, M. G. Blaber, G. C. Schatz, and R. P. van Duyne, J. Phys. Chem. C **117**, 2554 (2013).

9. A. D. McFarland, M. A. Young, J. A. Dieringer, and R. P. van Duyne, J. Phys. Chem. B **109**, 11279 (2005).

10. V. I. Kukushkin, Ya. V. Grishina, S. V. Egorov, V. V. Solov'ev, and I. V. Kukushkin, JETP Lett. **103**, 508 (2016).

11. V. I. Kukushkin, Ya. V. Grishina, V. V. Solov'ev, and I. V. Kukushkin, JETP Lett. **105**, 677 (2017).

12. Ya. V. Fedotova, V. I. Kukushkin, V. V. Solov'ev, and I. V. Kukushkin, Opt. Express **27**, 32578 (2019).

13. H. Schneidewind, K. Weber, M. Zeisberger, U. Hubner, A. Dellith, D. Cialla-May, R. Mattheis, and J. Popp, Nanotechnology **25**, 445203 (2014).

14. U. Hubner, K. Weber, D. Cialla, H. Schneidewind, M. Zeisberger, H. Meyer, and J. Popp, Microelectron. Eng. **88**, 1761 (2011).

15. V. M. Murav'ev, A. A. Fortunatov, A. A. Dremin, and I. V. Kukushkin, JETP Lett. **92**, 466 (2010).

Translated by R. Tyapaev