Transfer of luminescence-center energy to surface plasmons

Yu. M. Gerbshteĭn, I. A. Merkulov, and D. N. Mirlin

A. F. Ioffe Physico-technical Institute, USSR Academy of Sciences
(Submitted June 2, 1975)
Pis'ma Zh. Eksp. Teor. Fiz. **22**, No. 2, 80–82 (July 20, 1975)

The existence of resonant energy transfer from molecules excited near the surface of a metal to surface plasmons is experimentally established.

PACS numbers: 78.60.D, 73.20.

It was observed that luminescence of excited centers is accompanied by a decrease of the lifetime[1] and emission intensity[2] near the surface of a metal. This phenomenon is attributed to nonradiative processes that take place near the metal surface. The transfer of energy from the excited luminescence center to a surface plasmon of the metal was recently considered[3,4] as the possible mechanism of the nonradiative transitions. In other words, it is assumed that the excited atom on the surface of the metal is "de-excited" not only in the form of photons but also in the form of surface plasmons. We present below the results of a direct experiment that confirms the validity of this assumption.

It is known that surface polaritons (plasmons, phonons) are nonradiative and interact with a plane electromagnetic wave incident on a smooth surface. In recent optical experiments this difficulty is circumvented by using the method of disturbed total internal reflection (DTIR).[5,6] The accompanying radiative broadening makes it possible, in principle, to observe not only the absorption of p-polarized light by surface polaritons, but also the inverse process—emission of light.[7,8]

In this study, the surface plasmons were revealed by the photons radiated by them into a quartz prism following excitation of luminescence of a thin (<100 Å) luminor ("yellow-green lumogen") coated on a flat silver surface (Fig. 1). The luminescence was excited by the 365- and 254-nm mercury lines at an angle $\psi = 33°$ smaller than the angle of total internal reflection of the prism. The gaps between the metal and the prism (~0.5 μ) were chosen such that strong bands of absorption by the surface plasmons were observed in the DTIR spectra. In the experiment we measured the radiation angular distribution, which was registered by a photomultiplier through a monochromator. The angle ϕ corresponding to the maximum of the emission band determined the wave vector k_x of the surface plasmons in accord with the relation $k_x = (\omega/c)\sqrt{\epsilon}\,\sin\phi$, where ϵ is the dielectric constant of the prism.

The angular distribution of the s- and p-polarized luminescence for the wavelength $\lambda = 580$ nm is shown in Fig. 2. The figure shows also the DTIR spectrum,

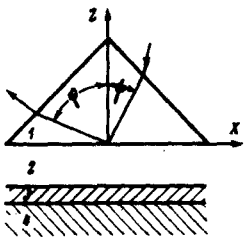

FIG. 1. Geometry of observation of light emission by surface plasmons: 1—quartz prism, 2—air gap, 3—luminor film, 4—metal, ψ—angle of incidence of luminescence-exciting light, ϕ—angle at which the radiation is observed.

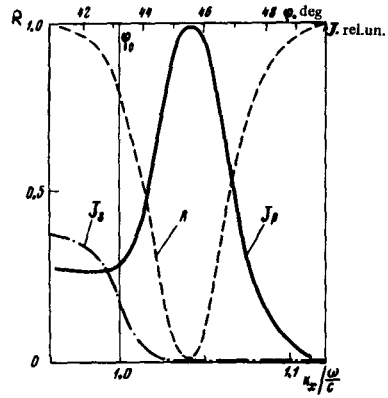

FIG. 2. Absorption and emission of light by surface plasmons: R—absorption of p-polarized light (DTIR spectrum), J_p, J_s—emission of p- and s-polarized light, ϕ_0—prism total internal reflection angle.

Copyright © 1976 American Institute of Physics

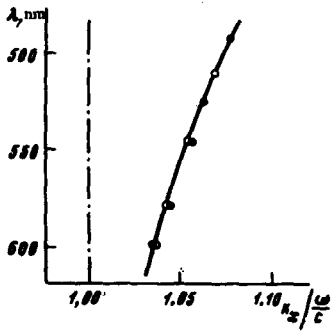

FIG. 3. Dispersion dependence of the surface plasmons, measured by determining the absorption (DTIR method) and emission of p-polarized light. Points—obtained from the DTIR spectra, circles—from the emission spectra, I—dispersion dependence of light in vacuum ($\omega = ck$).

i.e., the angular dependence of the specular reflection of the p-polarized light of the same wavelength (curve R), and notes the value of the angle of the total internal reflection ϕ_0. The strong band on the curve R in the region $\phi > \phi_0$ of the total internal reflection is due to absorption of light by the surface polarons. The angular dependence of the s-polarized luminscence (curve J_s) is characterized by the presence of radiation in the angle region $\phi < \phi_0$, and obviously corresponds to luminescence, which can be observed also without the prism. For the p-polarized luminescence, there is observed in addition a strong emission band in the region $\phi > \phi_0$ (curve J_p). Comparison of the curves J_p and R shows that the position of the maximum of the emission band practically coincides with the position of the minimum of the band of light absorption by the surface plasmons.

Similar measurements were made at other wavelengths in the luminescence spectrum of the luminor. With increasing frequency, the p-polarized luminescence band shifts towards larger angles ϕ and becomes broader. These results agree with measurements of the position and width of the band of light absorption by the surface plasmon. Figure 3 compares the positions of the maxima in the emission and DITR spectra for various values of k_x. It is seen from the figure that the dispersion law determined from the luminescence spectra practically coincides with the dispersion law of the surface plasmons as measured from the DTIR spectra.

The presented experimental data thus demonstrate the presence of a mechanism of resonant transfer of energy from excited luminor molecules to a system of surface plasmons of a metallic substrate. A similar effect probably takes place for any adsorbing molecules provided the frequency of the dipole transition in the molecule coincides with the region of existence of surface polaritons of the adsorbent.

The authors are grateful to B.P. Zakharchenya for a discussion of the results.

[1]K.H. Drexhage, J. Lumin. 1, 693 (1970).
[2]C.W. White and N.H. Tolk, Phys. Rev. Lett. **26**, 486 (1971).
[3]J.I. Gersten and N. Tzoar, Phys. Rev. **B9**, 4038 (1974).
[4]H. Morawitz and M.K. Philpott, Phys. Rev. **B10**, 4863 (1974).
[5]A. Otto, Zs. Phys. **216**, 398 (1968).
[6]V.V. Bryksin, Yu.M. Gerbshtein, and D.H. Mirlin, Fiz. Tverd. Tela **13**, 2125 (1971) [Sov. Phys.-Solid State **13**, 1779 (1972)].
[7]V.V. Bryksin, Yu.M. Gerbshtein, and D.N. Mirlin, Fiz. Tverd. Tela **14**, 3368 (1972) [Sov. Phys.-Solid State **14**, 2849 (1973)].
[8]J. Schoenwald, E. Burstein, and J.M. Elson, Sol. St. Comm. **12**, 185 (1973).