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Excitons and optical nonlinearities in hybrid organic-inorganic nanostructures

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Properties of electronic excitations in nanostructures based on organic materials and inorganic semiconductors, having respectively Frenkel excitons and Wannier – Mott excitons with close energies, are discussed. It is known that Frenkel excitons can have large oscillator strengths. At the same time, Wannier – Mott excitons are characterized by large resonance optical nonlinearities because of comparatively low saturation concentrations. In nanostructures containing organic and inorganic semiconductor quantum wells, the resonance interaction between exciton states in quantum wells results in the hybridization of Frenkel and Wannier – Mott excitons [1]. New exciton states may have, as Frenkel excitons, large oscillator strengths of the transition and, at the same time, as Wannier – Mott excitons, they may exhibit large resonance optical nonlinearities. As a result, these nonlinearities increase several hundreds times compared to nonlinearities inherent in the semiconductor quantum well [2]. A similar effect was also considered in a microcavity, where exciton resonances are close to the photon resonance in a microcavity [3]. For the case of small resonance splittings compared to the width of the exciton resonance in an organic layer, the irreversible energy transfer from an exciton in a semiconductor quantum well to the organic material is considered. This transfer is analogous to the Förster transfer. For sizes of a semiconductor quantum well and a barrier of the order of 100 A, energy transfer occurs over a time which is much shorter than the exciton lifetime in the semiconductor quantum well [4]. This effect can be of special interest for applications: electric pumping of excitons in a semiconductor quantum well can be used to produce bright luminescence of organic molecules (see review [5]).

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The outlook for nanolocal femtosecond spectroscopy and nanolithography

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Achievements in nanophysics and technology in the field of nano- and optoelectronics are associated with the advancement to progressively smaller spatial and time scales. This requires the development of fundamentally new methods for fabricating nanostructures and nondestructive control. One of the important problems of nanophysics is the development of optical methods that combine high spatial, time, and spectral resolution and allow one to study ultrafast processes in single nanostructures, clusters, and molecules.

In this connection, we will discuss several problems related to the action of laser pulses on a system consisting of the tip of a scanning probe microscope (SPM) and a substrate, and the use of the possibilities appearing in connection with these problems in nanooptics and nanotechnology.

Consider first an auxiliary problem about natural local plasma vibrations in a system consisting of the SPM metal tip and a substrate and their excitation by laser radiation (see Refs [1, 2] and references therein). If the distance d between the tip and a substrate is considerably smaller than the radius of curvature R of the tip, then the localization radius L of a plasmon is of the order of $\sqrt{dR}$ and increases with increasing d. The eigenfrequencies of the system also depend on R and d, and, of course, on the material of the tip and substrate, the minimum frequency related to in-phase vibrations of electrons in the tip and substrate decreasing as d decreases (detailed calculations are reported in Ref. [1]).

An external electromagnetic field focused in the region under the tip sharply increases near it due to the 'lightning rod effect' and also if the above modes are resonantly excited. In this case, the external field frequency, the distance between the tip and substrate, etc. are controlling parameters of the problem. The localization region of a strong near field is determined by the polarization of the tip-substrate system and decreases at $d < R \ll \lambda$ to a size considerably less than the wavelength. Thus, for $R \sim 20$ nm and $\lambda = 620$ nm, the localization radius of a strong field under a tungsten tip is approximately 20, 7, and 4 nm for d equal to 5, 0.5, and 0.3 nm, respectively. The field strength under the tip can be, depending on its shape, a nonmonotonic function of d and, in addition, it strongly depends on the value ε of the one-particle decay at a given frequency. In this connection, it would be profitable to use silver as a substrate and (or) coating for the SPM tip. As for the Landau damping of local plasmons (LPs), its ratio to the frequency is of the order of r_{TF}/L (where r_{TF} is the Thomas – Fermi screening radius) [2], so that it can be considerable only for LPs that can appear on irregularities of the SPM tip.

Thus, the 'lightning rod effect' and (or) resonance excitation by an external laser field of plasma vibrations induce a strong near field in the SPM tip-substrate system. This field can be used for both optical studies and with a subwavelength resolution (nanooptics) and nanotechnology.

As for nanotechnology, a strong field in the subwavelength region can be used to modify a surface at the nanometer scale (see below for a discussion of the relevant experiment), to induce nanolocal chemical reactions, to perform nanolocal ultrahigh-density magneto-optical (or

ferroelectric) data recording. A strong near field can also be used for control and local modification of biological objects. In addition, interesting possibilities are opened up for linear and nonlinear nanooptical studies of single nanostructures and molecules base on this method: surface enhanced Raman scattering controlled with a nanotip, nanolocal second-harmonic generation, etc.

The most attractive is the possibility to use the above-mentioned near-field spectroscopy in conjunction with methods of femtosecond spectroscopy to achieve even higher time resolution. For this purpose, for example, a normal pump-probe method can be used [3], by focusing pump and probe femtosecond pulses near an SPM tip over a sample.

In this case, the combination of high spectral and time resolutions contradicts the uncertainty relation between energy and time. Indeed, the duration of spectral measurements can be arbitrarily long, while the time resolution is determined by the delay of the probe pulse relative to the pump pulse and depends on the difference between the paths of these pulses (i.e., the time resolution is determined in this case by the accuracy of measurements of distances). Thus, this method allows one to obtain high spatial, time, and spectral resolutions in one experiment. This can also be achieved by combining femtosecond spectroscopy with near-field microscopy using a tip made of a glass fiber (possibly partially coated with a metal film).

In this connection, note the possibility of using the near field of a fiber laser (in particular, a femtosecond laser) as a microscope tip.

Another interesting possibility for nanolocal femtosecond spectroscopy is the determination of the cross-correlation function of laser pulses from a change in the tunneling current caused by the action of these pulses or the use of photoelectron emission from an SPM tip for this purpose.

Note that the sensitivity of a fiber-laser microscope can be sharply increased if the measurements are performed near the generation threshold and the lasing spectrum is studied. In this case, in contrast to the method of intracavity laser spectroscopy, dips in the lasing spectrum are related to characteristic losses of the laser near field outside the cavity.

Finally, consider one realized possibility — the nanolocal modification of a surface by the near field of femtosecond laser pulses near a scanning tunneling microscope (STM) tip ('a light pen') [4] (see also Ref. [5] and references therein), which can be used in principle for ultrahigh-density data recording. The use of ultrashort laser pulses in nanolithography is advantageous for the following reason. Femtosecond laser radiation produces nonstationary states in a sample, which can cause nonthermal instability and photoinduced phase transitions on the sample surface. One of the examples is the specific femtosecond melting of solids. Another example is the production of a quasi-dimensional grating on a surface with the help of femtosecond laser pulses.

Radiation from a Ti:sapphire laser with wavelengths of 813 and 406 nm, a pulse duration of 40 fs, and a repetition rate of 82 MHz was used. The radiation power was varied with light filters to 80 – 100 mW at a wavelength of 813 nm. The maximum power of the second harmonic (406 nm) was 5 – 7 mW. The diameter of a spot on the sample surface was 1 mm. The dependence of the effect on the radiation exposure was studied over a broad range from 2 s to 15 min. The angle of incidence ϑ of the laser beam was restricted by the design of the experimental setup and was $\vartheta \geqslant 76°$. Pyrolytic graphite, gold films, etc. were used as samples.

The experimental procedure was as follows. First, the same area of a sample was examined several times with the help of an STM, the image reproducibility was checked, and the transverse drift was estimated. Then, one of the figures — a point, a line, or a cross, was drawn by positioning the STM tip at given points, with simultaneous illumination of the contact region by laser pulses. Upon positioning to a point, the tip was displaced by 4 nm from the surface and then returned. The lines and crosses consisted of such points. After irradiation, the processed region was repeatedly examined with an STM to find photoinduced modifications of the surface. The experiments revealed the following effects:

(1) The appearance of an X-like structure after being drawn by a local laser radiation field by positioning point by point. The lines of the persistent X-like structure were typically 100 nm thick and 1.5 nm in depth.

(2) The formation of a groove 20 nm in width and 5 nm in depth in the region of the action of a tip and radiation upon positioning of the tip point by point.

The formation of a persistent structure after the nanolocal action of femtosecond laser radiation shows that this method of nanolithography is promising. Optimum regimes and the specific mechanism of the nanolocal action of femtosecond laser radiation require further investigation. It is possible that this mechanism represents the condensation of photoinduced vacancies. It is likely that the formation of a one-dimensional grating with a period of 100 nm on a pyrolytic graphite surface, which we observed under the action of normally incident femtosecond laser pulses, is described by a similar mechanism.

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Spectroscopy of ions with the 5d electrons in the ground state

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The spectra of ions with the 5d electrons in the ground state have recently been extensively studied in the Laboratory of Atomic Spectroscopy of the Institute of Spectroscopy, RAS. The renewed interest in these ions was stimulated, on the one hand, by the recent observation of spectral lines of 5d elements in chemically peculiar stars detected with the help of the high-resolution spectrometer of the Hubble Space