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Experimental and Theoretical Investigation of Silver-Coated ZnO Nanorod Arrays As Antennas for the Visible and Near-IR Spectral Range

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Abstract—A new design of optical antennas consisting of zinc oxide (ZnO) nanorods covered by a thin metal film is proposed. Arrays of highly oriented ZnO nanorods perpendicular to a substrate and covered by a thin silver film have been obtained using methods of carbothermal synthesis and magnetron sputtering. The problems of electromagnetic wave diffraction on a single metal/dielectric nanovibrator (situated at the interface of dielectrics) and on a two-dimensional periodic array of these nanovibrators have been solved. The results of calculations of the electrodynamic characteristics of optical antennas with various lengths have been compared to experimental data.

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Optical antennas (OAs) with submicron (nanometer) dimensions are widely used to increase the efficiency of energy transfer from an exciting electromagnetic field to the local field and vice versa. This property of OAs can be used to enhance photophysical processes in light-sensitive structures [1–5], improve determination of DNA structure and detection of individual molecules [6, 7], etc. In applications to microscopy, OAs can replace traditional focusing lenses and objectives and concentrate radiation into regions with dimensions below the diffraction limit [8]. The properties of OAs are not analogous to those of antennas for the radio-frequency range, which have relatively large linear dimensions because a different physical nature of processes involved in their operation. This difference implies the impossibility to use scaling principles for an adequate physical description. The difference in the principles of physical description on the passage to antennas with submicron (nanometer) dimensions is related to the fact that the properties of solid-state plasma predominate over the properties of metal conductivity because of the presence of a free-electron gas that is sensitive to the excitation at a wavelength in the optical (infrared) spectral range. Additional distinctions are related to a different way of antenna excitation. The OAs can be in the form of carbon nanotubes [9], metal and metal–dielectric vibrators and spheres [10–14].

This Letter presents the results of an experimental and theoretical investigation of an OA of new design based on an array of zinc oxide (ZnO) nanorods oriented perpendicularly to a substrate and covered by a thin metal (silver) film.

The arrays of ZnO nanorods were prepared using the method of carbothermal synthesis on fused silica substrates with dimensions of 5 ×10 mm, which were preliminary covered by an ~200-nm-thick ZnO sublayer formed by a pulsed laser deposition technique. The self-organized growth of ZnO nanorods without catalysts was carried out in an evaluated silica tube with an inner diameter of 30 mm placed inside a horizontal resistive furnace. The buffer gas (argon) pressure was 50 Torr. The substrate temperature during growth was ~930°C, the precursor temperature was ~950°C, the heating time was 35 min, and the period of exposure at the working temperature was 10 min. In this way, two samples with arrays of ZnO nanorods vertically oriented relative to the substrates were prepared. The morphological parameters of as-synthesized ZnO nanorod arrays are presented in Table 1.

Table 1. Morphological parameters of synthesized ZnO nanorod arrays

Sample no.	Average dimensions of nanorods		Surface distribution density ρ, 10^8 cm^{-2}
	length L, μm	diameter d, nm	
1	0.7	170	4.7
2	1.8	130	5.6

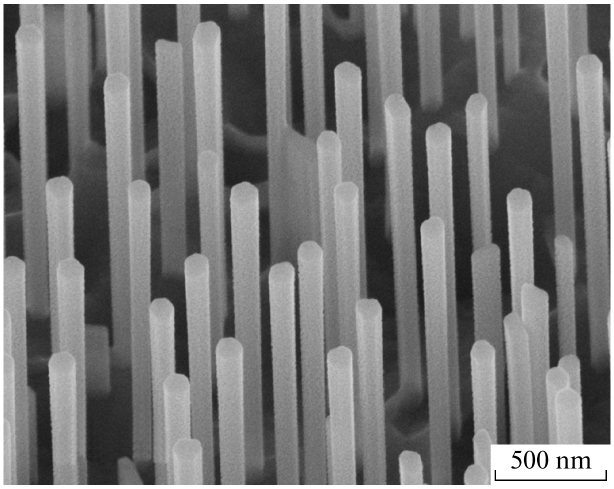

Fig. 1. The typical SEM micrograph of an array of 1.8-μm-long ZnO nanorods covered by a 20-nm-thick layer of silver. The image was obtained at an angle of 30° relative to the normal.

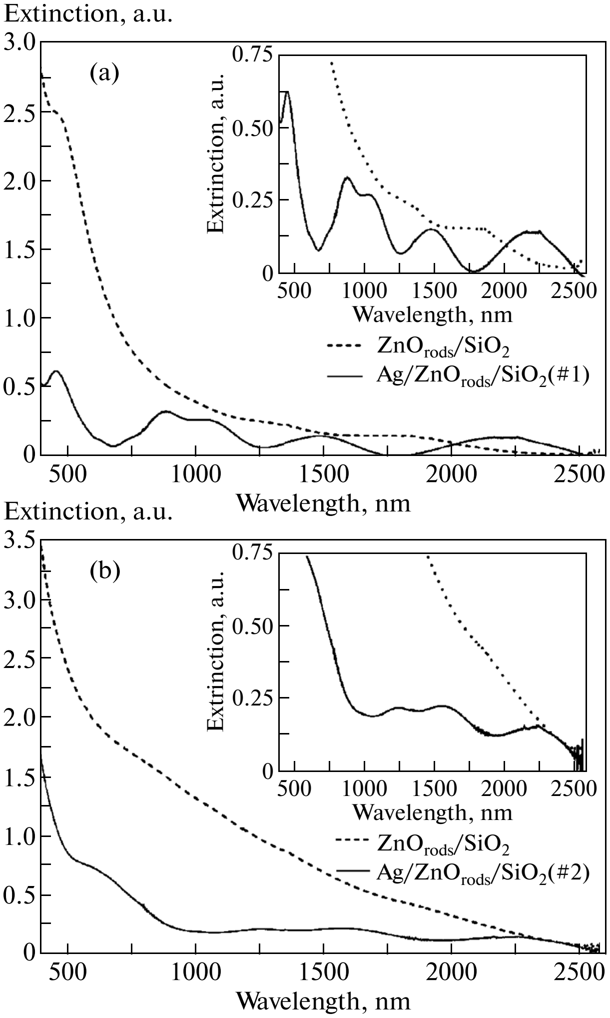

Fig. 2. Experimental extinction spectra of an array of ZnO nanorods with an average length of (a) 0.7 μm (sample 1) and (b) 1.8 μm (sample 2) measured before (dashed curve) and after (solid curve) deposition of an Ag layer. The insets show the same experimental curves on a greater scale.

Then, the arrays were covered by a 20-nm-thick layer of silver that was obtained by magnetron sputter deposition in the bottom-up geometry at a discharge current of 100 mA and a discharge voltage of 300 V. Substrates with nanorod arrays were oriented at 15° relative to the horizon on a rotating holder, which ensured uniform silver coverage over the entire length of rods. Figure 1 shows the typical micrograph of one sample as observed by scanning electron microscopy (SEM). The spectra of optical density (extinction) $D = -\ln(I/I_0)$ were measured on a Varian UV-Vis-IR spectrophotometer in an interval of light wavelengths from 0.2 to 3 μm and recorded in the regime of subtraction of the optical density of substrate.

We have theoretically studied the diffraction of an arbitrarily polarized electromagnetic wave on metal-coated ZnO nano-objects of two types on SiO_2 substrates with a ZnO sublayer, including a single nanocrystal and a regular double-periodic array of nanocrystals. For the sake of simplicity, it was assumed that nanocrystals had a cylindrical shape and that the dispersion of the refractive index in ZnO crystals ($n = 1.95$) could be ignored. The system with a single nanocrystal was modeled using a method described in [15, 16], which was modified by introducing the Green's function for a multilayer medium.

The regular double-periodic array of nanovibrators (NVs) was theoretically studied by solving a three-dimensional integro-differential equation for dielectric structures as described in [17, 18]. In this equation, variables represent Cartesian coordinates of the electric-field-strength distribution $E_r(x, y, z)$ inside a dielectric surface nonuniformity. These equations are relatively simple and advantageous in that their solution is not complicated by nonuniformity and nonlinearity of the dielectric and directly yields the electric-field distribution in the dielectric.

The extinction spectrum of the array of rods with average length 0.7 μm measured after the deposition of a silver coating displays five additional absorption maxima (absent in the spectrum of uncoated array) in a wavelength range of 400–2600 nm (Fig. 2a). We believe that these spectral features can be related to plasmon resonances of the NV array, which result in an approximately threefold decrease in the optical density level. The extinction spectrum of the array of rods with average length 1.8 μm measured after the deposition of a silver coating acquires up to four additional absorption maxima due to plasmon resonances of the NV array in the indicated wavelength interval, where the optical density level exhibits an approximately fourfold decrease (Fig. 2b). The maxima in the spectrum of an array of longer rods are more smeared and less intense than those observed for shorter rods.

Figure 3 presents the results of calculations of the optical density of NV arrays with different distances s between nanorods. These calculations naturally took into account both the wave reflected from the metal and losses in the metal. The complex refractive index of Ag was taken from reference data [19]. The shape of the curves depends on the period of the NV array, but the resonance wavelengths (except for shorter waves) vary rather weakly and agree well with those observed in the experiment (Table 2). Both the theoretical characteristics and experimental spectra of the array of 0.7-μm-long NVs exhibit a greater number of resonances as compared to that for a single NV. Some resonance wavelengths for the NV array are close to those for a single NV [15, 16]. These resonances can be interpreted as being due to the NV proper (i.e., the resonances of waves propagating along the NV), while others represent resonances of the waves propagating in the array in the direction perpendicular to NVs. The wavelengths of longitudinal resonances in single NVs and NV arrays differ because of the interaction between NVs in the latter case. In addition, the electrodynamic model for single NVs is less strict than that for an array. In a short-wavelength region, there are many high-Q resonances. The number of resonances in a longer rod is greater than in a shorter one, which is valid for all vibrators, including those for the RF spectral range. This peculiarity is not experimentally observed, which may be explained by the overlap of closely spaced resonances due to a statistical distribution of synthesized rods with respect to lengths, diameters, and cross-sectional shapes.

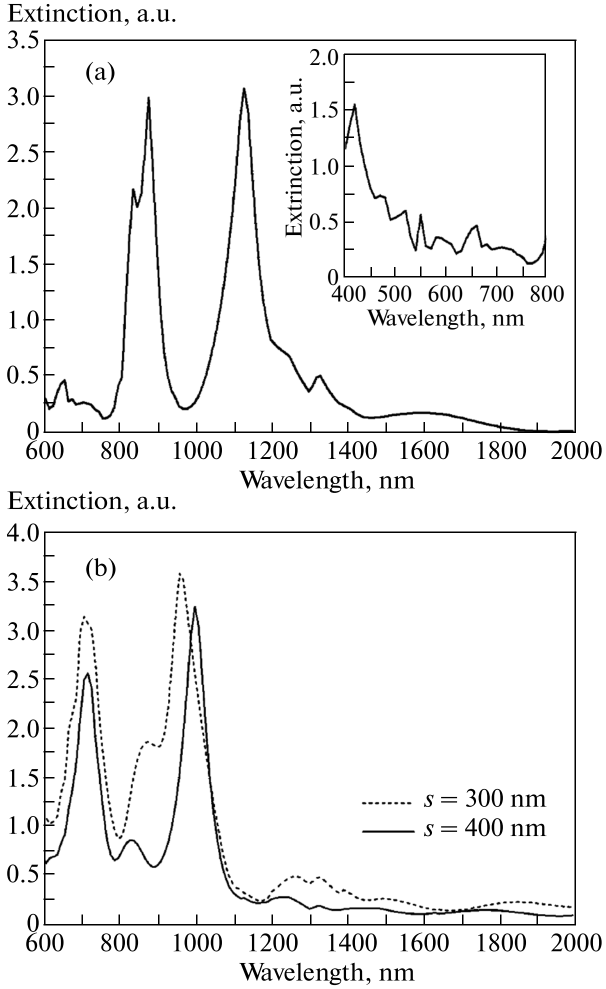

Fig. 3. Theoretical frequency dependences of the optical density of the arrays of NVs with lengths (a) 0.7 and (b) 1.8 μm.

Thus, we have proposed OAs of a new type consisting of arrays of ZnO nanorods covered by a thin metal film is proposed. Additional maxima in the curves of extinction coefficient of these arrays have been observed and interpreted. It is established that these

Table 2. Comparison of the spectral positions of maxima in theoretical and experimental extinction spectra of single NVs and NV arrays

NV length	Spectral position of maximum, nm		
	Experiment	NV array	Single NV
$L = 0.7$ μm	500	550	–
	–	650	620
	890	900	880
	1060	1120	1100
	–	1340	1370
	1500	1600	–
$L = 1.8$ μm	640	–	620
	–	700	720
	–	820	800
	–	1000	1000
	–	–	1100
	1250	1250	1250
	1600	1720	1750

maxima are determined by the plasmon resonances of optical antennas.

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