Restructuring and modification of metallic nanorod arrays using femtosecond laser direct writing

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Local restructuring of metallic nanorod arrays and the fabrication of metallodielectric microstructures using direct femtosecond laser writing technologies have been studied. Femtosecond laser ablation has demonstrated the possibility to create sharp boundaries (down to a single nanorod) on the nanorod array. Polymer structures on the nanorods can be used to control the resonance wavelengths and thus the effective refractive index of surface plasmons supported by the array. The structured nanorods and their polymer composites are important for applications in light guiding and the development of nonlinear optical nanodevices. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2398904]

Development of highly integrated optical devices and sensors requires structural elements comparable to and smaller than the wavelength of light in order to nanolocally control the electromagnetic field. One widely investigated approach employed to achieve this is the use of appropriately designed metallic and metallodielectric nanostructures to manipulate light in the form of various surface plasmon excitations such as surface plasmon polaritons, localized surface plasmons, etc.[1,2] The guiding of light along metallic nanosphere chains as well as nanowires placed along the dielectric substrate have been recently studied.[3,4] The guiding of plasmonic excitation in the nanorod arrays, similar to the guiding along the spherical nanoparticle chains, associated with the strong electromagnetic coupling between nanorods is also expected. Such a resonant coupling which results in the modification of the plasmonic resonances related to the nanorods has recently been observed.[5] Plasmonic nanostructures can provide both passive and active all-optical elements with the latter capable of operating at low control light intensities due to electromagnetic field enhancement related to surface plasmons.[2]

However, the task of combining both requirements, guiding of light and all-optical control, is not straightforward since each may require different size scales of metallic nanostructures for optimal operation: structures of tens of nanometers to exploit the field enhancement due to localized surface plasmons at the control light wavelength and structures of hundreds of nanometers for guiding of the signal light.

The conventional solution to this problem is to start from an extended plasmonic guide and fabricate in (or onto it) a smaller-scale nanostructure to achieve the field enhancement, such as a set of nanoholes or nanoparticles. Here, we study an alternative approach: starting from a system of nanoscale metallic entities (nanorods), we investigate the possibility of fabricating larger-scale plasmonic metallic and metallodielectric elements for plasmonic light guiding. The proposed approach provides an inexpensive source of large areas (up to 1 cm^2) of metallic nanorods (diameter down to 20 nm) needed for tailoring linear and nonlinear behavior of surface plasmon excitations. Such nanostructures can be easily integrated in complex plasmonic circuits for sensing and telecommunication applications.

So far, femtosecond-laser-based direct writing technologies have been applied to the fabrication of surface plasmon polariton structures in thin metal films and thin layers of positive and negative photoresists on plane substrates.[6,7] In this letter we report on the investigation of the fabrication of dielectric microstructures on metallic nanorod arrays as well as on the local restructuring of the arrays via laser ablation and/or laser melting of the individual nanorods. The application of a femtosecond laser allows a precise adjustment of the optical power delivered to the target material.[8] This provides the possibility for high resolution restructuring of the nanorod arrays.

Large area structures of metallic nanorods have been fabricated using electrochemical deposition of Au into anodized aluminium oxide (AAO) templates. These templates are comprised of self-organized arrays of quasiperiodic hexagonally packed nanopores.[5] The AAO matrix was then chemically removed to achieve arrays of free standing nanorods attached to the substrate. It is possible to fabricate nanorods with diameters of about 20–40 nm and lengths of about 50–400 nm using this technique.

First, we discuss the fabrication and optical properties of nanorod/polymer composites. The photosensitive material which has been used for metallodielectric structure writing is the commercially available maN-1405 negative photoresist. It has a refractive index in the range of 1.61–1.67 in the visible region and shows high transparency in the red and near-infrared spectral ranges. For the structure writing experiments, the resist is first homogeneously spin-coated onto a sample. A layer thickness of 500 nm has been obtained for a spin-coating speed of 3000 rpm. Femtosecond laser pulses are focused with a 100× microscope objective with a numerical aperture of 0.8 (Fig. 1). The material is polymerized due to the nonlinear absorption of the infrared radiation. In the polymer structuring experiment, a Coherent Mira 900B oscillator emitting at a wavelength of $\lambda = 780$ nm with a pulse duration of $\tau = 100$ fs has been used. The samples are

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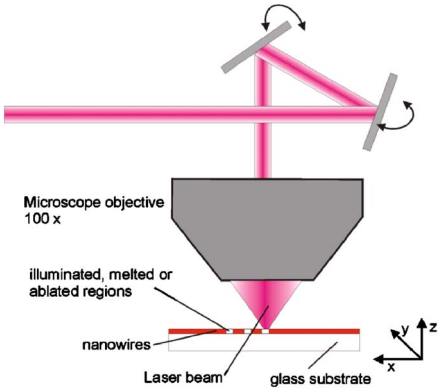

FIG. 1. (Color online) Schematics of the femtosecond laser writing setup used for the restructuring of nanorod arrays. Computer-controlled rotating mirrors are used for the steering of the laser beam during writing.

positioned with respect to the focusing objective by a three-dimensional translation stage. By scanning the laser beam over the sample surface, structures of different geometries may be written. After illumination, the remaining resist can be removed with the developer, maD-533S. It should be noted that the processing parameters for the polymerization of the maN-1405 resist on the metal nanorod samples are in the same range as for the structuring of this resist on dielectric, e.g., glass substrates.

The structures were fabricated using different light powers between 10 and 16 mW [Fig. 2(a)]. These polymer structures exhibit strong optical contrast. All of the various structures created can be clearly identified and it is apparent from this figure that when moving from the top of the image towards the bottom, we observe structures created with lower laser intensities. Low laser power provides the most promising conditions for structuring with the greatest spatial confinement of the polymerization process [Fig. 2(d)]. In this case (10 mW laser power), features with a lateral dimension of the order of several hundred nanometers have been created. Additionally, it is apparent from the presented scanning electron micrographs that the nanorods have survived both the polymerization process and monomer removal.

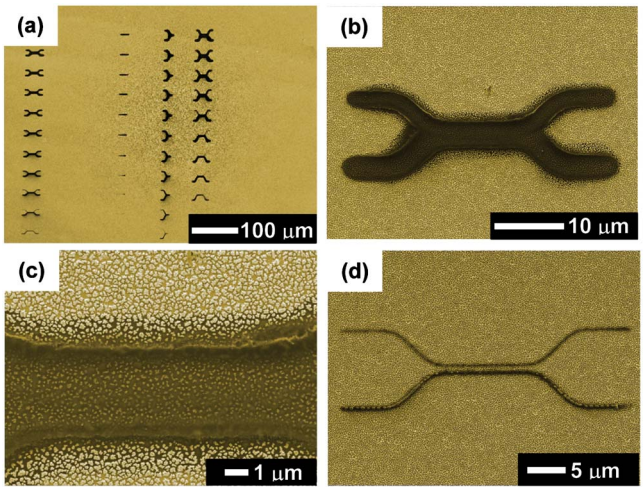

FIG. 2. (Color online) Scanning electron microscopy (SEM) images of the polymer structures created onto the nanorod arrays. (a) Various structures written with different laser light intensities. The intensity decreases from 16 to 10 mW whem moving from top to bottom. (b)–(d) zoom into the images. The structure in (b) and (c) has been written with 16 mW and in (d) with 10 mW laser power.

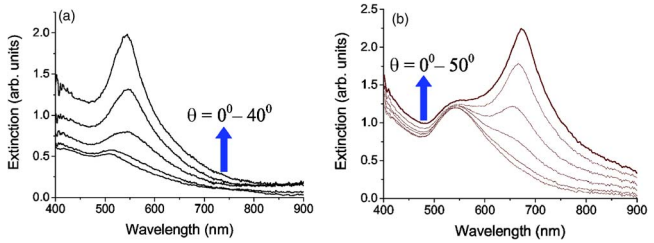

FIG. 3. (Color online) Extinction spectra of the Au nanorods (length of 350 nm, diameter of 25 nm, and spacing of 40 nm) in the region without (a) and with (b) polymer present measured at different angles of incidence (changed in 10° steps) of *p*-polarized light.

At higher laser powers, the lateral dimensions of the polymer structures increase [Figs. 2(b) and 2(c)]. There also appear to be slight variations in the degree of polymerization across the stripes which are most likely present as a result of deviations in the transmitted laser power through the microscope objective when scanning the beam under large angles to the optical axis for writing the large area structures. Despite this, the nanorods have been almost entirely unaffected by the procedure.

The extinction spectra of the nanorod arrays outside and inside the polymer structures were measured at different angles of incidence. The spectra reveal the usual absorption related to the plasmonic modes which arise from both the transverse and longitudinal resonances related to the nanorods.[5] In the case of bare nanorods (the refractive index of the surroundings is $n=1$), both resonances are located close to each other at around 520 nm and can only be distinguished by the strong angular dependence of the longitudinal mode (Fig. 3). In the areas with deposited polymer, the longitudinal resonance occurs at about 700 nm, in accordance with the nanorod length and the refractive index of the nanorod surroundings.[5] The effective refractive index for guiding the light coupled to the longitudinal resonance of the polymer-nanorod composites can be estimated at about $n_{\mathrm{eff}} \approx 1.2$ on the basis of the plasmonic excitation resonant wave vectors in the areas with and without polymer, that is much higher than in conventional waveguides and similar to surface plasmon waveguides. Therefore, strong light confinement is to be expected in such guides. It is interesting to note that with maN-1405 polymer the angular dispersion of the

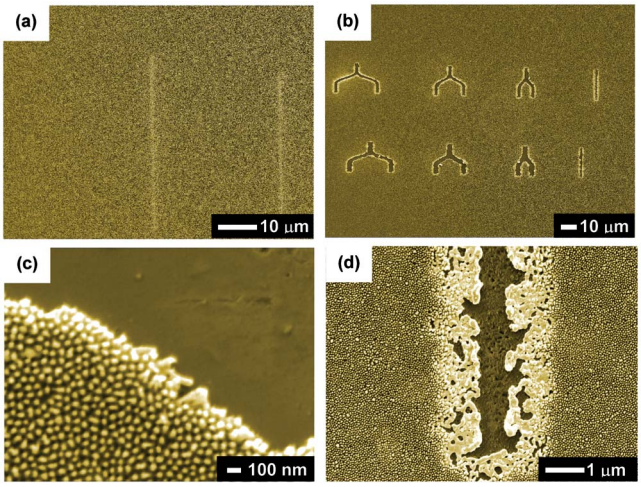

FIG. 4. (Color online) SEM images of the structures created by (a) melting and (b)–(d) ablation of the nanorods. The pulse energy is 0.25 nJ in (a) and 80 nJ in (b) and (c) and 120 nJ in (d).

TABLE I. Laser pulse parameters used for the different restructuring methods: (*p*) polymerization, (*m*) melting, and (*a*) ablation.

Structure	Laser	Repetition rate (MHz)	Average power (mW)	Pulse energy (mJ)	Linewidth (μm)
p	MIRA	80	10	0.125	0.5
p	MIRA	80	16	0.200	3
m	MIRA	80	20	0.250	1
m	MIRA	80	30	0.375	2
a	RegA	0.25	10	40	0.5
a	RegA	0.25	12	48	1
a	RegA	0.25	30	120	3

longitudinal resonance is opposite to the angular dispersion of the same nanorod array in the AAO matrix: with the increase of the angle of incidence the peak shifts towards longer wavelength range. This may be related to the dispersion of the refractive index of the polymer and/or the thickness of the polymer film.

As the next step, we have studied direct restructuring of the nanorod arrays using both ablation and melting of the nanorods. An experimental setup similar to that described above was used. First, we have studied the effect of melting the nanorods in order to fabricate continuous metallic structures in the nanorod arrays. Melted nanorod structures have been written with the beam from the laser oscillator allowing more exact energy deposition into the sample for controlled melting. Due to the high repetition rate of the laser oscillator of 80 MHz, the pulse energy in this case is only 0.375 nJ (average laser power of 30 mW). With these parameters, linewidths of 2 μm have been obtained. Thinner lines with widths of 1 μm and less have been fabricated by reduction of the average laser power to 20 mW. The nanorods in the irradiated areas appear partially melted and demonstrate irregular grouping. The boundary between the melted and freestranding nanorods in the fabricated structures is not distinct probably due to the inhomogeneous in the melting process [Fig. 4(a)].

In order to ablate the nanorods from the substrate, high laser pulse energies are required. For this purpose, a high repetition rate femtosecond amplifier system (RegA 9000 from Coherent) has been used. It delivers pulses at a wavelength of $\lambda=780$ nm with a pulse duration of $\tau=200$ fs and repetition rate of 250 kHz. For ablation of the nanorods, pulse energies up to 120 nJ have been applied, corresponding to an average laser power of 30 mW. The ablation threshold for the nanorods is estimated to be around 40 nJ (10 mW average power). Pulse energies and laser powers needed for the ablation of the nanorods appear to be a little lower than for the ablation of smooth gold films. The ablation thresholds of nanorods and of smooth films differ only by 2–3 mW. This reduction is not very pronounced and can be explained by the increased absorption of the gold nanorods compared to that of a smooth film.

Structures including simple lines, splitters, and double splitters have been written [Figs. 4(b)–4(d)]. Examination of the specific elements of the structure shows that ablation of the nanorods can be achieved successfully with high precision. At optimal laser parameters, the ablation can create a sharp boundary with single nanorod sharpness. However, for higher energy of laser pulses a boundary exists on either side of the structured area due to the melting of the nanorods adjacent to the ablated area, where the pulse energy is lower (due to the Gaussian shape of the beam profile) and insufficient to achieve ablation. Thus, irregularities can exist at the boundary of the ablated area similar to those observed during the study of molten nanorods. The melted boundary accounts for a large proportion of the total width of the fabricated structure and for some laser pulse parameters extends from a hundred nanometers to several microns from the ablated area.

In conclusion, we have demonstrated the possibility to locally restructure metallic nanorod arrays using femtosecond laser writing and to create complex metallodielectric microstructures needed for the development of photonic device applications. The fabrication parameters for the different restructuring methods are summarized in Table I. Polymer structures on the nanorod arrays can be used to control the resonance wavelength and hence the effective refractive index of surface plasmons; this approach may be used for the development of light guiding applications in straight and curved structures. In addition, nonlinear polymers can be used for microstructure fabrication thus providing an opportunity to develop nonlinear optical nanodevices. For optimal fabrication parameters, ablation with precision determined by neighboring nanorods can be achieved. However, the accuracy is strongly dependent on the laser power and the properties of the nanorod array that may cause melting at the boundary to occur.

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