Aperiodic arrays of metal nanostructures with controllable adhesion for applications in metamaterials

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Abstract

In this work we introduce a method for fabrication of metal nanostructures with controllable adhesion on large-area substrates. Aperiodic arrays of gold and silver nanostructures with feature size down to 15 nm were produced with this method. The measured optical spectra show that the nanostructures with and without an adhesion sublayer exhibit different optical responses. The described method can be used to fabricate stable metamaterial layers made of essentially any vaporizable metal on large-area silicon or glass substrates. Other applications can be found, e.g., in Raman spectroscopy and solar cells.

1. Introduction

In spite of fast progress in the theory of optical metamaterials, many of the proposed concepts is difficult if not impossible to realize in practice. The reasons of this are the limited resolution of optical and electron beam lithography and a low speed of the conventional beam writing techniques for large scale fabrication of the required nanostructures. An alternative approach can be based on self-organization of some materials to obtain periodic or random distributions of nano-objects for further processing [1]. Self-organization can take place on a substrate surface or in the whole volume of the material, which can provide a fast and inexpensive technique to fabricate large-scale metamaterials. The main drawback of this method is that the created nano-objects often have different sizes and separation distances in the sample, which leads to spectral broadening of the optical response of the material. Another drawback, of more technological character, is that self-organization usually requires poor adhesion of the material to the substrate, which makes their further processing difficult.

In this work we propose a nanofabrication method for creating aperiodic arrays of metal nanostructures with good adhesion to the substrate. The method is well compatible with the modern thin film technology and, therefore, it can be used even in the mass production. In the first step of the proposed method, metal nanostructures with poor adhesion to the substrate are self-organized with any accessible method. Then the nanostructures are used as a mask for etching the substrate, after which the metal is removed. In the final step the substrate is covered with an adhesion layer and a metal of interest. As an example, we fabricate plasmonic nanostructures of different configurations on an optically transparent or opaque substrate and measure their transmission and reflection spectra. The transmission spectra of the structures on a transparent substrate with and without adhesion sublayer are shown to be different.

2. Method of fabrication

Among the existing methods for fabrication of metal nanostructures on a flat substrate by making use of self-organization only laser ablation, ion-beam mixing, and vacuum evaporation are compatible

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with the conventional microfabrication technology. Most often these methods are applied to produce a random array of gold or silver nanoislands on a flat dielectric surface [2]. The obtained array possesses a poor adhesion to the substrate and its further processing is rather limited. Furthermore, the separation between the nanoislands is usually very small, which leads to a strong substrate-mediated electromagnetic interaction between the islands and, as a result, a featureless optical spectrum. In the proposed method a good adhesion of metal to the substrate is achieved with the help of an adhesion sublayer and the electromagnetic interaction is reduced by lifting the nanostructures above the substrate.

In the proposed method, the original, self-organized, metal nanostructures are used as a mask for anisotropic dry etching of the substrate (see Fig. 1a and b). For this etching a good adhesion is not required. Due to erosion of the mask during the etching, the separation between the islands can be increased [3]. In the next step we remove the residues of the original metal by selective wet etching and obtain a nanotemplate made of the substrate material (Fig. 1 c). The template elements (nanopillars) follow the shapes of the original nanoislands and, in general, can be made to have any lateral geometry. The template is then covered with a thin adhesion layer of an easily oxidized metal (e.g., Ti or Cr). It is important to cover only the horizontal surfaces of the template and leave the sidewalls uncovered (Fig. 1d). This requirement is fulfilled when using a standard metal coating by evaporation at normal incidence. The final step is coating of the template with a functional layer of Au or Ag, for example. This time the metal is evaporated onto the template at an angle (see Fig. 1e). The deposition angle is chosen to be large enough to minimise metal coating between the pillars. The final step is done immediately after the deposition of the adhesion layer to prevent possible oxidation of the latter.

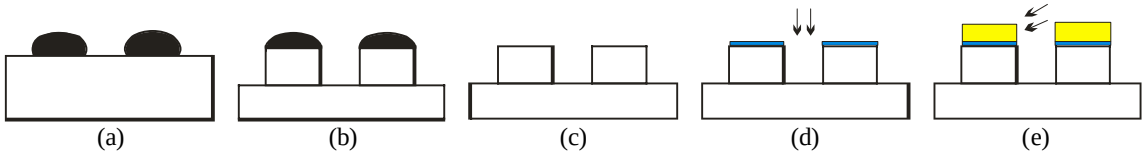

Fig. 1: Fabrication steps: (a) formation of a self-organized mask, (b) reactive ion etching of the substrate, (c) removal of the mask, (d) deposition of the adhesion layer, and (e) deposition of the functional layer.

3. Practical nanostructures

The method was tested by fabricating identical arrays of gold and silver nanostructures in two variations ï with and without the adhesion sublayer. The samples were fabricated on 0.7 mm thick wafers of borosilicate glass. The process was optimized by using 0.5 mm thick silicon substrates with a 60 nm thick layer of SiO_2, which made it possible to observe the fabricated nanostructures with SEM. The self-organized mask was prepared by deposition of 4.5 nm thick Ag layer on each of the substrates by electron-beam evaporation and annealing it at 400 C during 30 minutes. The resulting nanoislands have an average diameter of 20 nm and an average period of 30 nm on the substrate. After performing reactive ion etching (RIE) of the substrate based on CF_4 and CHF_3 gases and removing the Ag mask in a diluted nitric acid, a silver or gold layer with a thickness of 6 nm was deposited at an angle of 70°.

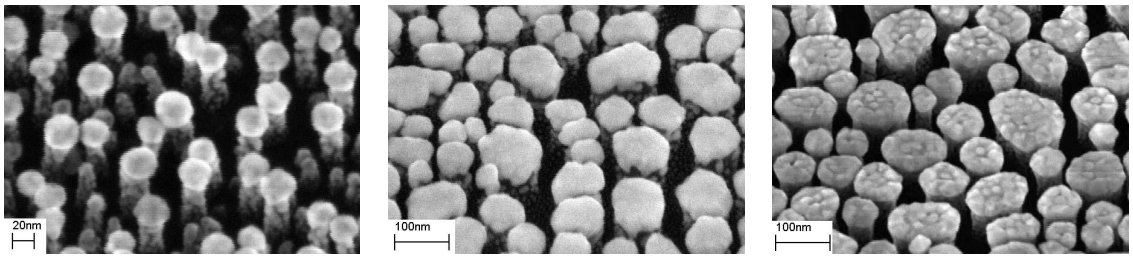

Fig. 2: SEM images of the fabricated gold nanostructures: (a) nanospheroids with about 20 nm diameters, (b) an array of gold islands without an adhesion sublayer, and (c) the gold islands on an identical template, but with a sublayer of Ti.

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During the deposition, the samples were rotated to provide a more uniform deposition. Fig. 2a illustrates gold nanospheroids produced in this way. The structures shown in Figs. 1b and 1c were fabricated at different fabrication conditions in order to illustrate the possibility to adjust the average size and separation distance of the islands. These structures have been fabricated on identical templates, but for the sample shown in Fig. 2c a titanium sublayer with a thickness of 1 nm was deposited prior to gold. Without the adhesion sublayer, the islands resemble spheroids, while the islands on a layer of titanium are rather disk-shaped.

The optical transmission (absorption) spectra of the nanostructures fabricated on transparent substrates were measured in the range from 300 to 850 nm. The influence of the thickness of a Ti sublayer on the spectrum of an array of gold nanostructures (similar to that of Fig. 2a) is shown in Fig. 3a. The sublayer is seen to flatten and red-shift the spectrum. For silver nanostructures, on the other hand, the spectrum is already significantly red-shifted and flattened by only a 1 nm thick sublayer of Ti (see Fig. 3b). These spectral modifications can be explained by a relatively small size of the metal nanospheroids and, in addition, by (a) a high optical density of titanium and (b) more oblate shapes of the nanospheroids formed on an adhesion sublayer. We have also found that the spectra depend on the illumination direction, especially in the presence of Ti. The peak wavelength of absorbance is seen to be red-shifted when the sample is illuminated from the substrate side (see the dashed curves in Fig. 3b).

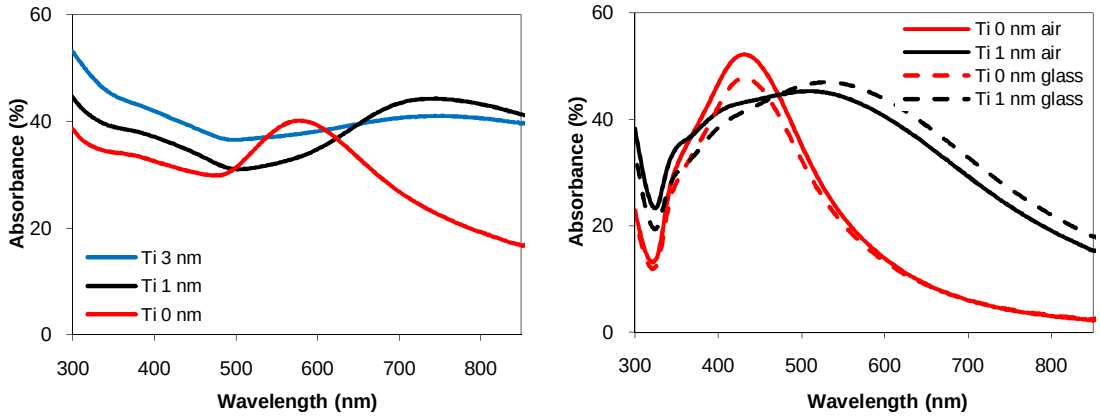

Fig. 3: Dependence of absorbance of (a) gold and (b) silver nanostructures on the thickness of a sublayer of Ti. The dashed curves in (b) show the spectra obtained for the samples illuminated from the substrate side.

4. Conclusion

The described fabrication method allows obtaining aperiodic arrays of mechanically stable metal nanoislands with sizes down to 15 nm on a large-area glass or silicon substrate. The average size and separation distance of the nanoislands are adjustable. The method can be used for fabricating more complicated metal nanostructures than those described in this work, e.g., nanocrescents [4], nanocylinders, nanospheroid pairs, and labyrinth-like nanostructures, which can be used to create flat nanolayers of plasmonic metamaterials.

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