

Tarnishing of silver subwavelength slit gratings and its effect on extraordinary optical transmission[☆]

M.V. Gorkunov^{*}, V.V. Artemov, S.G. Yudin, S.P. Palto

A.V. Shubnikov Institute of Crystallography, Russian Academy of Sciences, 119333 Moscow, Russia

Received 6 September 2013; received in revised form 2 October 2013; accepted 3 October 2013

Available online 14 October 2013

Abstract

We study the impact of tarnishing of silver subwavelength gratings on their optical performance. We report that in the course of months under regular laboratory conditions, the gratings undergo tarnishing very differently from plain silver films: instead of thin layer of evenly distributed silver sulfide, a random pattern of rare larger crystals is formed across the grating area. As typical of plasmonic metamaterials, the gratings appear to be very sensitive to the arising structural disorder and show a very specific modification of the optical transmittance spectra – total degradation of the Wood diffraction anomaly and attenuation of the near-infrared transmission peak. The identified ‘optical fingerprints’ of the microscopic grating contamination pave a way for prospective plasmonic sensor applications.

© 2013 Elsevier B.V. All rights reserved.

Keywords: Plasmonic metamaterials; Extraordinary optical transmission; Subwavelength gratings; Silver tarnish; Effects of disorder

1. Introduction

Optics of materials based on submicro- and nano-size structured metal films, as well as clusters and arrays of metal particles and wires, has developed into a vast intensively growing research area of plasmonic metamaterials with numerous prospective applications [1,2]. By varying the shape and arrangement of metal particles one can tailor the effective optical properties of such arrays and gratings, which, as many believe, will allow creating optical materials required for superlenses [3] and optical cloaks [4]. In a shorter prospective, presence of various intrinsic resonances made it possible to apply such composites for spectral filtering [5,6] while the enhancement of local fields allowed creating plasmonic

nano-lasers [7–9]. The high sensitivity of the structures to the microscopic environment and nano-size contaminations can be utilized in novel gas sensors [10] and bio-sensors [11–13].

Functional optical properties of plasmonic metamaterials are determined primarily by the size and shape of metal constituents and do not depend critically on the chemical composition as long as the light absorption stays low. For the telecommunication near infrared (IR) range the latter condition is not very restrictive with respect to metals and one can comfortably choose between gold, silver, aluminum, copper, tungsten and others [14,15]. However, the choice is substantially narrowed for those who are interested in the visible range and here silver appears to provide the highest optical quality factor accompanied by a relatively good chemical stability.

The design and modeling of plasmonic metamaterials strongly relies on the concept of local optical metal

[☆] The article belongs to the special section Metamaterials.

^{*} Corresponding author. Tel.: +7 4991356240.

E-mail address: gorkunov@crys.ras.ru (M.V. Gorkunov).

permittivity, in which the nano-sized metal particles are considered as specifically shaped fragments of dielectric medium with certain complex permittivity known from the experiments on thin films [15]. The concept although being on its edge when applied to nano-size particles still captures relatively well the essence of the observed optical phenomena. At the same time, accurate quantitative reproduction of experimental results often remains problematic for theorists [16], and it has been argued that various effects, such as metal non-locality [17], surface roughness [18], and contamination [19–21] can be responsible for the discrepancies. In particular, the role of contamination of silver structures with sulfur adsorbed from air has been the subject of a certain controversy in Refs. [21–23].

The contamination of silver with atmospheric sulfur, i.e., silver tarnishing, has been relatively well studied on flat silver films decades ago [24]. The natural tarnish that occurs during silver exposure to laboratory air in the course of months has been found to exhibit some quantitative difference from that obtained artificially by chemical etching of silver with hydrogen sulfide gas. In both cases, the tarnishing resulted in increasing the light absorption substantially at wavelengths below 600 nm. At the same time, the effect was negligible in the near IR at wavelengths of 1 μm and above.

The knowledge of microscopic details of tarnishing of silver nanostructures is still scarce. It has been established that the tarnishing gives rise to morphological changes of silver nanoparticles [25] and can relatively rapidly attenuate the plasmonic resonance of small nanoparticles of several nanometers in diameter [26]. However, the optically observable consequences of tarnishing of more complex light transmitting subwavelength silver structures have not been revealed and the question whether the impact of tarnishing can be reduced to the presence of a thin light absorbing cladding remains open.

To clarify the details of natural tarnishing of light transmitting silver nanostructures and its effect on their optical performance, we have chosen one-dimensional (1D) lamellar silver gratings with subwavelength periodicity and slits of the width of several tens of nanometers. Such gratings are known to exhibit the extraordinary optical transmission (EOT) first discovered in the arrays of holes in metal films [27] and later found also in the arrays of slits [28–31]. In sufficiently thick 1D gratings, the nonzero transmission occurs only for TM-polarized light and has a very peculiar spectral dependence with very high (almost up to 100% in theory) transmittance peaks accompanied by pronounced deeps of the order of only a few percent at

other wavelengths. The phenomenon has attracted significant attention in the past decade and it took several years before the full understanding of the underlying interplay of complex physical mechanisms has been achieved [32,33].

In this paper we investigate the microscopic details of tarnishing of fabricated silver subwavelength slit gratings and report that the microscopic tarnish patterns seen on the gratings are very different from those on the surrounding flat silver areas. The corresponding modification of the gratings EOT spectra are very specific and can be explained as a result of the structural disorder produced by tarnishing.

The paper is organized as follows: the experimental methods used for fabrication and characterization of the gratings are described in Section 2; the observed microscopic details of grating tarnishing as well as their optical spectra before and in the course of tarnishing are given in Section 3; analysis and theoretical interpretation of the results is presented in Section 4, while Section 5 presents concluding remarks.

2. Experimental methods

2.1. Grating fabrication

The gratings have been fabricated in a silver film that has been deposited onto a glass substrate by vacuum sputtering. The slit milling by the focused ion beam (FIB) has been performed on the dual beam electron microscope Quanta 3D FEG with typical parameters: the gallium ion energy 30 keV, the total ion beam current 30 pA, and the FIB spot size less than 10 nm. The microscope technical parameters have limited the total grating area to 30 $\mu\text{m} \times 30 \mu\text{m}$, which allowed preparation of samples consisting of about a hundred of slits. Note that it is known that already a few tens of slits are enough for a correct EOT manifestation [34].

2.2. Electron microscopy and microanalysis

After the fabrication, the milling quality has been monitored by the SEM microphotographs on FEI Quanta 3D FEG. The more detailed SEM images of the tarnished gratings have been taken on the JEOL JSM-7401F electron microscope that supports the Gentle Beam regime allowing obtaining high resolution SEM microphotographs using low accelerating voltages (1 kV and even less) and thus resolving fine details of the silver grating surface. The chemical characterization via elemental microanalysis of the tarnished grating surfaces has been performed by means of

Download English Version:

<https://daneshyari.com/en/article/1543105>

Download Persian Version:

<https://daneshyari.com/article/1543105>

[Daneshyari.com](https://daneshyari.com)