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Angular resolved transmission spectra of corrugated metallic films and gratings: Localized and surface plasmons

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ABSTRACT

We report on the optical properties of silver films and nanowires grown on laser-patterned polyethyleneterephthalate (PET) foils. Polymer substrates with Laser Induced Periodic Surface Structures (LIPSS) were used as templates for vacuum evaporation of silver. Metal deposition under normal and grazing angle of incidence resulted in corrugated silver layers and nanowire gratings, respectively. The samples were studied with polarization resolved transmission spectroscopy. Angle dependent spectra were recorded by tilting the sample stepwise from 0 to 50°, with the plane of incidence parallel or perpendicular to the nanowires. The energy of the localized plasmon excited on the nanowire grating by light polarized perpendicular to the nanowire axis depends mostly on the dimension of the nanowires (width). On the other hand, transmission spectra of the thin corrugated metal layer show a strong angular dependence, owing to the propagating nature of the corresponding surface and interface plasmons.

1. Introduction

The optical properties of metal/dielectric interfaces have been intensively investigated over the last decades. Research involves applications such as Surface Enhanced Raman Scattering (SERS) [1], gas detection technology [2], biosensing [3] or molecular imaging of living systems [4]. The characteristic response of these materials to electromagnetic fields stems from the excitation of surface plasma waves.

Surface Plasmon Resonance (SPR) is an optical phenomenon caused by the collective oscillation of conduction electrons at the metal surface under the driving force of the incident electromagnetic field. Resonant effects occur when the natural frequency of the electron oscillation coincides with the frequency of the incoming light wave. The coupling of the electromagnetic field to the electron plasma oscillations gives rise to propagating, evanescently confined surface waves, also known as Surface Plasmon Polaritons (SPPs).

SPPs at flat metal/dielectric interfaces obey the dispersion relation:

$$k(E) = \pm \frac{E}{\hbar c} \mathrm{Re}\left(\sqrt{\frac{\varepsilon_1(E)\varepsilon_2(E)}{\varepsilon_1(E)+\varepsilon_2(E)}} \right), \quad (1)$$

where k is the in-plane wave vector of the SPP, E denotes the resonance energy and $\varepsilon_1(E)$ and $\varepsilon_2(E)$ are the dielectric functions of the dielectric and the metal, respectively. The imaginary part of the right hand side in Eq. (1) describes the damping of the SPP along its propagation direction. SPPs cannot be directly excited by light illumination, because the wave vector $k(E)$ in Eq. (1) is always greater than the surface-projected wave vector $k_{el}(E,\theta) = E/(\hbar c) n_1 \sin\theta$ of the electromagnetic wave on the dielectric side of the interface for any given photon energy E, angle of incidence θ, and refractive index $n_1 = \sqrt{\varepsilon_1}$ of the dielectric [5]. Therefore, special techniques for phase-matching have to be employed for SPPs excitation, such as the prism coupling based on attenuated total internal reflection in the Kretschmann [6] or the Otto [7] configuration. It is often more convenient to study plasmon resonances on rough surfaces, where surface irregularities act as scattering centers. Scattering gives rise to additional momentum and wave vector transfer Δk, thus enabling phase-matching (momentum conservation) $k(E) = k_{el}(E,\theta) + \Delta k$. A special case of rough topography are surfaces with periodic corrugation or gratings [8]. In this case well controlled phase-matching is enabled via the addition of integer multiples of the reciprocal lattice vector of the grating, namely $\Delta k = m \cdot g$, with $m \in \mathbb{Z}$ and $g = 2\pi/a$ for a one

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dimensional grating with periodicity a. The phase-matching condition thus reads [9]:

$$k(E) = k_{el}(E,\theta) + mg = \frac{E}{\hbar c} n_1 \sin\theta + m\frac{2\pi}{a} \quad (2)$$

Excitations of resonances occur naturally in nanoparticles with lateral dimensions smaller than the wavelength of the incident light. Oscillations trapped in a small particle volume have non-propagating character (Localized Surface Plasmon Resonance, LSPR). The optical properties of metallic nanoparticles are governed by their size, shape and dielectric environment [10,11] and are often complicated by the presence of a supporting substrate, surface adsorbates [12] or electromagnetic coupling between closely spaced individual wires or particles [13,14].

Nano-patterning of polymer surfaces [15,16] with subsequent preparation of metallic nanowires [17] was studied by our group earlier. In the present work we compare the optical properties of silver nanowire gratings with those of periodically corrugated, continuous silver films. Corrugated films and nanowire gratings were prepared by laser modification of polyethylene terephthalate (PET) substrates followed by vacuum evaporation of silver under normal or grazing angle of incidence, respectively. The samples were studied with polarization resolved transmission spectroscopy.

2. Experimental

2.1. Materials, apparatus and procedures

Periodically patterned surfaces were produced by irradiating biaxially oriented PET foils (Goodfellow Ltd., thickness 50 μm) with a KrF excimer laser (COMPexPro 50 F, Coherent Inc., wavelength 248 nm, pulse duration 20–40 ns, repetition rate 10 Hz). The laser light was linearly polarized with a UV-grade fused silica prism (model PBSO-248-100). The modification was performed under normal incidence with 6000 laser pulses and a fluence of 7 mJ/cm^2, which resulted in a ripple-like pattern with a periodicity of 230 nm [15,17].

Irradiated PET samples were used as substrates for deposition of silver (SAFINA, a.s., purity 99.99%) by vacuum evaporation (LEYBOLD-Heraeus, Univex 450) at room temperature and a base pressure of 3.10^{-4} Pa. Two different angles of incidence were used for evaporation to obtain continuous corrugated silver films or gratings (Fig. 1). The corrugated film was fabricated by depositing 60 nm of silver under normal angle of incidence (Fig. 1A). The nanowire grating was obtained by deposition at 70° grazing angle of incidence using two separate evaporation steps (20 nm each) from opposite sides of the polymer ridges (Fig. 1B). Using this protocol, the final nanowires exhibited a gutter-like geometry [18].

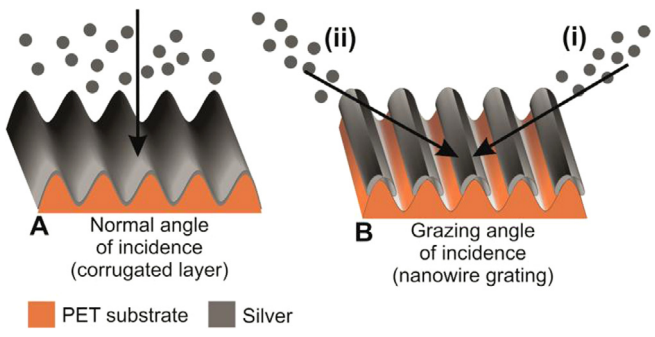

Fig. 1. Schematic illustrating: (A) preparation of a corrugated silver layer by evaporation under normal angle of incidence; (B) preparation of a nanowire grating by two subsequent ((i) and (ii)) evaporations under grazing angle of incidence.

Direct assessment of the silver thicknesses was accomplished by scratch tests on glass substrates, which were coated simultaneously with the PET templates, using Atomic Force Microscopy (AFM) in contact mode.

2.2. Analytical methods

The optical properties of the samples were studied by Variable Angle Spectroscopic Ellipsometry (VASE, J. A. Woollam Co., XLS-100), where the cross-polarized transmission mode was used to determine the polarization depended transmission. Spectra were recorded with the sample tilted stepwise from $\theta = 0°$ (normal incidence) to $\theta = 50°$ in steps of 10°. Considering the uniaxial geometry of the samples, two orthogonal azimuthal orientations were employed in which the plane of incidence was aligned either perpendicular or parallel to the wires or grooves (Fig. 2). We will refer to these two experimental geometries as "s-tilting" and "p-tilting", respectively, since in the first case (s-tilting) the s-polarization component of the incoming light beam is parallel to the wires or grooves (Fig. 2A), whereas for p-tilting the p-polarization component is parallel to the wires or grooves (Fig. 2B).

3. Results and discussion

Fig. 3 shows the spectra of the silver nanowire array for s and p polarization and the two tilting geometries. For normal incidence ($\theta = 0°$) and light polarized perpendicular to the nanowire axis (black lines in Fig. 3A and B) the transmission spectrum is dominated by a minimum at 1.82 eV, which can be associated with the dipolar plasmon peak [17]. For s-tilting the position of the plasmon peak slightly shifts from 1.82 eV (0°) to 1.77 eV (50°) (Fig. 3A). Increasing the angle of incidence changes the in-plane wave vector component k_{el} of the incident light beam, which for s-tilting is oriented perpendicular to the nanowires. The redshift thus reflects the dispersion $E(k_{el})$ of the plasmon mode arising from the dipole-dipole coupling between the individual nanowires of the array [14]. The coupling effect is even more obvious from the shift of the local transmission maximum from 2.52 to 2.36 eV. With increasing sample tilt a further local transmission minimum evolves at about 2.65–2.75 eV, which can be associated with the quadrupolar plasmon mode. This excitation is attributed to the irregular cross-section of the gutter-like nanowires, as the incident beam starts to interact more strongly with the edges of the metallic structures for higher angles of incidence. Fig. 3B (p-tilting) also shows the excitation of the surface plasmon along the nanowire minor axis at 1.82 eV. However, there are no significant spectral changes in the optical spectra with increasing tilt angle, except an overall decrease of the transmission. This can be understood by the fact that the nanowires are continuous and rather uniform along their long axis and, hence, no energy dependence on the wave vector component (dispersion) along this direction is to be expected. The decreasing overall transmission can be related to the increasing reflectance due to increasing effective metal thickness with increasingly grazing angle of incidence. Since the length of the nanowires is much higher than the wavelength of the incident light no plasmon can be excited by light polarized along the nanowire major axis, as evidenced in Fig. 3C for s-polarization and s-tilting. Interestingly, however, for p-polarization and p-tilting, increasing the sample tilt leads to a sharp transmission minimum at 3.7 eV (Fig. 3D). Here, the increasing tilt is responsible for an increasing electric field component along the surface normal, i.e., along the thickness of the nanowires. Hence, the incoming light may now excite plasmonic oscillations in the nanowires along the second minor axis.