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Surface plasmon-polariton resonances in metal-coated polycarbonate gratings

D. I. Nazarova*, L. L. Nedelchev, R. N. Todorov and P. S. Sharlandjiev

Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences

Acad.G.Bonchev Str., bl.109, 1113 Sofia, Bulgaria

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In this article a study of surface plasmon resonance (SPR) is presented using a diffraction grating to couple light on the dielectric–metal interface. A polycarbonate surface relief gratings obtained from commercially available DVD-R stampers are used as substrates and are subsequently coated with silver and gold thin films (with physical thickness d = 15-25 nm) . The presence of SPR is experimentally verified by the observed resonance peaks in spectral transmittance of TM polarized light. Furthermore, the spectral positions of these peaks are determined for the given film thickness – 510 nm for the Ag layer and 760 nm for the Au layer. The results are compared with previous study of SPR peaks in aluminum thin films.

Keywords: Surface plasmon polariton, Gratings, Resonances

INTRODUCTION

Surface plasmon polariton (SPP) is an electromagnetic excitation that propagates along the planar interface between a metal and a dielectric medium and whose amplitude decays exponentially with increasing distance into each medium from the interface [1]. In such way SPP is a surface electromagnetic wave, whose electromagnetic field is confined to the near vicinity of the dielectric–metal interface. This confinement leads to an extraordinary sensitivity of SPP to surface conditions which is extensively used for studying adsorbates on a surface, surface roughness, and related phenomena. That is why SPP are of interest to a wide spectrum of scientists ranging from physicists, chemists and materials scientists to biologists. SPP-based devices exploiting this sensitivity become increasingly popular as a label-free method for measurement and are widely used in chemo- and bio-sensors based on surface plasmon resonance (SPR). The large field enhancement associated with SPR is also the basis for many surface analytical techniques such as surface-enhanced Raman scattering [2], surface-enhanced fluorescence [3, 4] and infrared absorption spectroscopy [5]. SPR sensing has been exploited in the development of immunosensors [6], accelerating drug discovery [7, 8], and detecting protein-DNA interactions [9, 10].

Three methods are mainly used to couple light on a metal-dielectric interface and observe SPP – using a prism, a non-periodic or periodic structure on the surface. Diffraction gratings are a typical example of the last method.

In our previous work we studied polycarbonate gratings metal-coated with Al [11] and extraordinary transmission was observed i.e. a peak in transmission of linearly polarized light parallel to the grating vector (denoted as TM). It was shown that such structures are suitable for sensor applications. When applying various homogeneous and inhomogeneous upper layers (over the metal coating), nature of the resonant curve of transmission does not change, but a shift of the peaks towards higher wavelengths is observed with an increase of the refractive index. This makes it possible to determine the unknown refractive index of transparent liquids in a given operating range. For upper layers consisting of suspensions of dispersed nanoparticles a shift of the resonance peak towards larger wavelengths is found with an increase of the concentration of the nanoparticles. This allows determining the concentration of the nanoparticles in the suspension by the spectral position of the resonance peak. Hillier and coworkers have also demonstrated that a diffraction grating consisting of a commercial DVD coated with a thin metal film supports surface plasmon

* To whom all correspondence should be sent:
E-mail: dimana@iomt.bas.bg

enhanced light transmission [12-15]. They demonstrate the ability to determine film's thickness tracking the position of the plasmon peak and for ex situ sensing by analyzing thin films of various thicknesses and detecting a model immunoreaction between bovine serum albumin and anti-bovine serum albumin. This transmission SPP device based on metal-covered grating is a simple and sensitive platform, which can be used for biomolecular interactions analysis or in the study of a variety of surface adsorption processes.

Herein we present a study of one-dimensional metalized diffraction gratings, in which at specific wavelength resonant optical transmission is observed. For this purpose, commercially available polycarbonate DVD stampers used are coated with a thin layer of various metals (Al, Au, Ag). The influence of these metals on the behavior of the resonance peak in transmittance is studied.

EXPERIMENTAL

Polycarbonate substrate preparation.

In the present work we use polycarbonate DVD stamped gratings. They are factory made relief gratings with a storage capacity of 4.7 GB. These structures are high quality plastic diffraction gratings and are useful as a model for testing, because they are cheap, readily available and highly standardized within a certain series. The DVD-Rs consist of two 0.6 mm thick circular polycarbonate pieces that sandwich a metal and a dye layer between them. One of the polycarbonate pieces possesses a continuous spiral groove that assists in laser tracking during reading/writing of data. This is, in fact, the grating used in our experiments. The other piece is a cover with protective function preventing physical damage to the metal and dye layers. For preparation of the gratings, the two polycarbonate pieces of the DVD-R were manually separated. The grooved polycarbonate piece useful for us is easily distinguishable from the smooth one as it diffracts light. The dye is easily removed from the surface by washing in ethanol followed by drying. Details about the grating characteristics are given in section 3.2.

Metal Thin Films Coating

For metal coating of polycarbonate substrate various metals were used (aluminum, gold and silver). Thin aluminum film was deposited by dc magnetron sputtering technique in argon atmosphere with pressure $2.5.10^{-1}$ Pa in thin film deposition system Leybold Heraeus Z700 P2. The low energy of the Al ions ensures that there is no interaction between them and the polycarbonate gratings. Thin gold and silver films were deposited by thermal evaporation in high vacuum 5.10^{-3} Pa in deposition system Leybold Haraeus A 702 Q. The thickness of the layers was controlled by quartz monitoring technique. The deposition rate was 0.02 nm/s [16]. As a result the substrate was coated with 15-25 nm thin metal layers from the above mentioned metals.

ATOMIC FORCE MICROSCOPE (AFM) IMAGING.

AFM images of the used sample surfaces were acquired before and after metal-coating with AFM DS 40-45 (Danish Micro Engineering).

RESULTS AND DISCUSSION

To understand the nature and origins of the SPP phenomena in the transmittance spectra, we investigated the role of surface plasmons. Optical excitation of SPP at a metal-dielectric interface requires matching of the momentum of the incident light and the SPP. The SPP have a complex wave vector k_{SPP}, the real part of which is described by the dispersion relationship shown below [17,18]. Let us first consider a *p*-polarized (transverse magnetic or TM) wave. In a wave with such polarization the magnetic vector is perpendicular to the plane of incidence – the plane defined by the direction of propagation and the normal to the surface. Solving Maxwell's equations under the appropriate boundary conditions yields the SPP dispersion relation that is the frequency-dependent SPP wave-vector, k_{SPP}:

$$k_{SPP} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \tag{1}$$

where ε_m and ε_d are the dielectric constants of the metal and dielectric layers and ω is the angular frequency.

When we consider *s*-polarized (transverse electric or TE) wave, its electric vector is perpendicular to the plane of incidence. Solving Maxwell's equations for *s*-polarized light, shows clearly that surface plasmon polariton cannot exist in this light polarization [17]. Since the momentum of incident light in air is lower than the one given by Eq. (1), a coupling device is needed. There are three main techniques to provide the missing momentum. The first makes use of prism coupling to enhance the momentum of the incident light

[19,20]. The second involves scattering from a topological defect on the surface, such as a subwavelength protrusion or hole, which provides a convenient way to generate SPPs locally [21].

The third makes use of a periodic corrugation in the metal's surface [22]. For a periodically modulated interface such as a grating between a metal and a dielectric with a period *a*, the surface component of the wave vector of incident light can be increased or decreased. If the light with a wave vector k is incident on the grating at an angle θ_0, the components on the surface will have a wave vector $(\omega/c)\sin\theta_0 \pm \upsilon g$, were υ is an integer $(0, \pm1, \pm2,...)$ indicating the diffracted order and $g = 2\pi/a$. If $\varepsilon_d = 1$, then the dispersion equation for surface plasmon polariton is given by

$$k_x = \frac{\omega}{c}\sin\theta_0 \pm \upsilon g = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m}{\varepsilon_m + 1}} = k_{SPP} \quad (2),$$

or

$$k_x = \frac{\omega}{c}\sin\theta_0 \pm \Delta k_x = k_{SPP} \quad (3)$$

where Δk_x comes out from any perturbation on the surface [1]. In the above equations the projections of the wave vectors on the *x* direction were used (on the surface of the boundary between a metal and dielectric). If $\Delta k_x = 0$ the dispersion relation has no solution. The wave vector of the surface plasmon polariton is a component of the wave vector of the incident light in the plane of propagation. The charges on the surface of the metal have to maintain the electric field perpendicular to the surface i.e. must change the sign of the dielectric permittivity of the border. The frequency-dependent real parts of the metal and the dielectric material permittivity must have opposite signs in order for SPP to exist at such an interface. This condition is satisfied for metals because ε_m is both negative and complex (the latter corresponding to absorption in the metal). Since in the visible range dielectrics have positive permittivity, the permittivity of the metal must be negative. This condition is fulfilled for metals in the visible and near infrared regions of the spectrum (such as aluminum, gold, silver and copper), which have a large negative real part (small positive imaginary part is related to the loss due to absorption and scattering in the metal). Permittivity of metals can be found in [23].

The metal-coated substrates used in this study were obtained by depositing semi-transparent metal films with 15÷25 nm thickness onto gratings derived from commercial DVDs. In Fig. 1(a) AFM image of the clean polycarbonate grating before deposition of thin metal film is presented. Fig. 1(b) shows the AFM image of the same grating after coating with gold. As seen, there are no significant differences in the basic characteristics of the diffractive grating before and after coating.

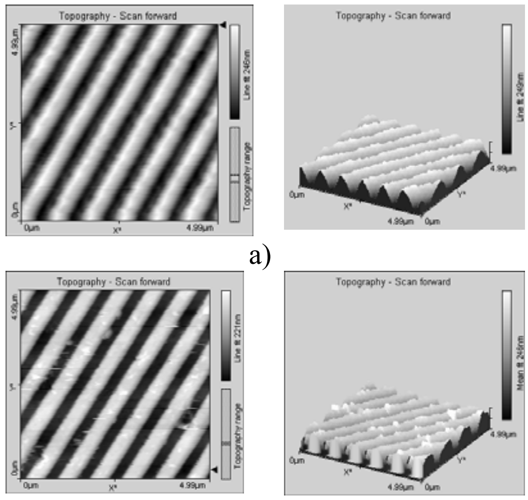

Fig. 1. AFM image of the grating before coating (a), and of the grating coated with 20 nm gold layer (b).

The grating period is determined to be 750 nm. The groove profile is neither sinusoidal, nor rectangular. That means that there are higher harmonics in the Fourier transform of the grating modulation. The groove depth is estimated to be 170 nm. Refractive index of the polycarbonate substrate is 1.57.

The diffraction from clean gratings (not coated with metal film) was measured in transmission with He-Ne laser (633 nm) at normal incidence. The diffraction efficiencies of the ±1 orders are 16 and 21 % respectively, and lay in one plane with the zero order. Thus, the intrinsic conical form of the grooves can be ignored.

In Fig. 2 the transmittance spectra of the polycarbonate substrate before metal-coating for TM and TE polarized light are given. TM corresponds to light polarization perpendicular to the grating vector and TE to light polarization parallel to the grating vector. The spectra are measured with CARY 5E high-precision spectrophotometer. A high quality Glan-Taylor prism which provides extremely pure linear polarization with a ratio 100 000:1 in the range 250-3000 nm is used as a polarizer. The experimental data show no difference in transmission spectra for the two polarization states before metal-coating.

In contrast, the transmittance of the metal-coated gratings for TM and TE polarizations is different. This is clearly seen when we determine the ratio between them – TM/TE. This ratio is measured for gratings coated with three different metals (Al, Au and Ag) and the results are shown in Fig. 3. As we can expect from the theory, there is a significant

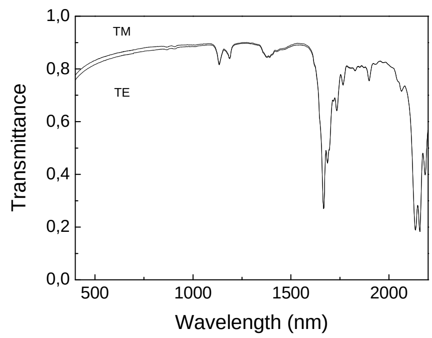

Fig. 2. Transmission of non-coated polycarbonate substrate.

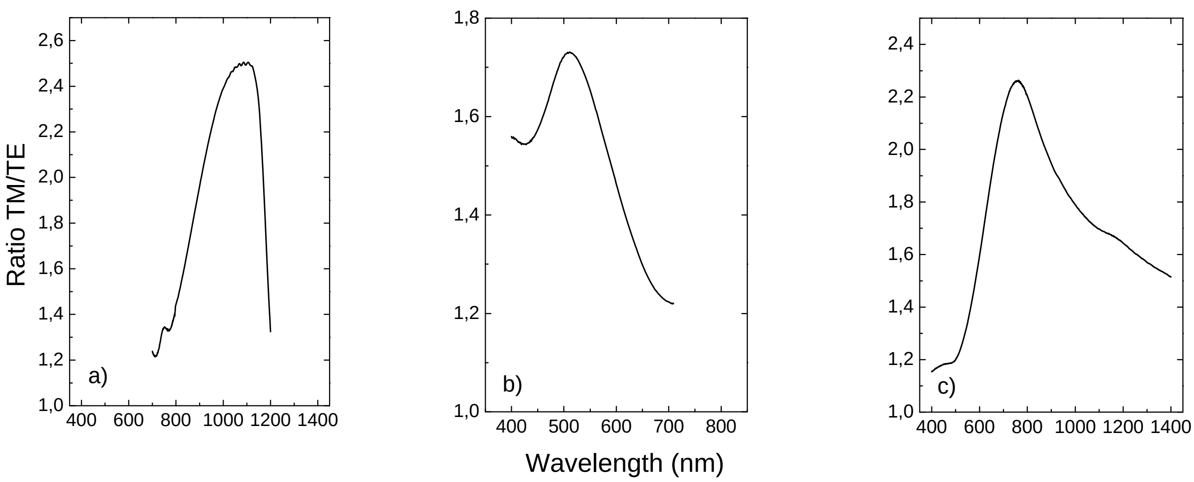

Fig.3. Transmission ratio TM/TE for the gratings coated with Al (a), Ag (b) and Au (c).

difference in the transmission for the two linear polarizations TM and TE.

The well-developed resonance peak in the case of Al is situated at 1090 nm, for the grating coated with Ag layer it is located at 510 nm and for the Au at 760 nm.

CONCLUSION

According to the theoretical considerations, for all three metals resonant structures are observed. The increased light transmission for these films at TM polarization represents a considerable enhancement over the similar spectrum for TE polarization. Resonances in aluminum and gold are very well pronounced, the silver film also shows a 75% enhancement over the TE spectra.

The locations of these spectral peaks in transmittance, as well as their magnitude are found to vary with the thickness of the metal films for the same grating parameters. The study of the behavior of the resonance peaks in the transmission of gratings coated with silver and gold but with different upper layers is a subject of future research.

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ПОВЪРХНОСТНИ ПЛАЗМОН-ПОЛАРИТОННИ РЕЗОНАНСИ ОТ МЕТАЛИЗИРАНИ ПОЛИКАРБОНАТНИ ДИФРАКЦИОННИ РЕШЕТКИ

Д. И. Назърова, Л. Л. Неделчев, Р. Н. Тодоров, П. С. Шарланджиев

Институт по Оптически Материали и Технологии, Българска Академия на Науките, ул. Акад. Г. Бончев, бл. 109, 1113 София, България

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(Резюме)

В тази статия представяме изследване на повърхностни плазмон-поларитонни (ППП) резонанси на базата на дифракционни решетки. Използвали сме поликарбонатни релефни решетки от DVD-R стемпери, метализирани с тънки слоеве от Au и Ag. Присъствието на резонанси е експериментално доказано за TM поляризираната светлина. Резултатите са сравнени с докладваните по-рано за тънки слоеве от Al.