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Surface plasmon-polariton resonances in metal-coated holographic azopolymer gratings

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Surface plasmon polariton (SPP) is an electromagnetic excitation that propagates along the interface between a metal and a dielectric medium and is generated by resonant interaction between the surface charge oscillation and the electromagnetic field of light. This excitation decays exponentially with increasing distance from the surface and for this reason cannot be observed in far-field experiments unless the SPP is transformed into light. Three methods are mainly applied to couple light on a metal-dielectric interface and observe SPP – using a prism, a non-periodic or periodic structure (e.g. diffraction grating) on the surface. In this article a study of surface plasmon resonance is presented using a diffraction grating to couple light on the dielectric–metal interface. Surface relief gratings holographically recorded in azopolymer film are used as a substrate and are subsequently coated with thin film of aluminum (Al). The presence of SPR is experimentally verified by the observed resonance peaks in transmission of TM polarized light.

Keywords: Surface plasmon polaritons, Holographic gratings, Azopolymers

INTRODUCTION

The proximity of the SPP to the interface leads to an extraordinary sensitivity of SPP to surface conditions [1], which is extensively used for sensing applications. That is why SPP are of interest to a wide spectrum of scientists from physicists, chemists and materials scientists to biologists. Surface plasmon polariton-based devices exploiting this sensitivity become increasingly popular as a label-free method for measurement. Previously we have studied resonant optical transmission and surface plasmon polariton resonances with 1D periodic metal-coated relief structures [2-4]. The main goal of these investigations was to demonstrate how the position of the resonance peak in transmission can serve as a very sensitive probe of the optical properties of symmetric structures consisting of an upper layer and a continuous metal film on top of a relief grating acting as a substrate. As a model system for substrate, we used polycarbonate relief diffraction gratings. On the relief structure, an Al film was deposited in a vacuum installation, by dc magnetron sputtering. For an upper layer we used different contact liquids (all grade *pro analysis*, transparent in the wavelength region of the resonance peak) and a cover glass. With the increase of the refractive index of the contact fluids, the resonance peak was red shifted. Thus, a calibration curve was plotted and it allows to determine an unknown refractive index of a given compound. Development of new kind of devices was proposed and the potential of the SPP techniques in holographic sensing was demonstrated [4-8].

The aim of this paper is to show that surface relief structures, or surface photopatterning, in azopolymers can be applied for design and fabrication of sensing devices based on surface plasmon polariton resonance phenomenon.

Holographically recorded relief gratings are suitable for investigations of resonances because of their high sensitivity, high diffraction efficiency, and low cost. The main advantage of holographic recording of gratings is the possibility to obtain relief gratings with different characteristics. In such way, the conditions to observe a resonance can be controlled and optimized. For this study relief diffractive structures have been prepared by holographic recording in azopolymer synthesized in Institute of Optical Materials and Technologies (IOMT). The material used for holographic recording is capable to form relief in specific

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conditions, depending on the polarization of the recording laser beams.

EXPERIMENTAL

Azopolymer

The azopolymer used in our experiments is a side-chain azobenzene-containing polymer and its chemical structure is shown in Fig. 1.

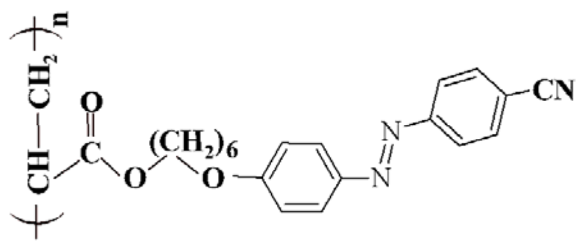

Fig. 1. Structure of the azopolymer used in the present study.

It was synthesized by process consisting of three stages: preparation of the azo dyes; preparation of the chromophore monomers and radical-type polymerization of the chromophore monomers. Two types of azo dye were synthesized: (A) 4-(4-hydroxy-phenylazo) benzonitrile and (B) 4-[4-(6-hydroxyhexyloxy) phenylazo] benzonitrile. Dye A was synthesized by dissociation of 4-aminobenzonitrile and coupling with phenol using standard technology. Dye B was synthesized from dye A by etherification with 6-bromo-1-hexanol. By etherification with acryloyl chloride azo dye B was transformed in monomer [9]. Polymer, used in our experiment and shown on Fig. 1 is a homopolymer obtained from monomer of the dye 4-[4-(6-hydroxy-hexyloxy) phenylazo] benzonitrile. The differential scanning calorimetry (DSC) data indicate glass transition temperature $T_g = 35$ °C. The polymer is liquid-crystalline and its average molecular weight is $M_w = 2.05\times10^3$ g/mol, as measured by gel-permeation chromatography (GPC).

Holographic recording

In Fig. 2 the holographic set up for recording of relief azobenzene gratings is shown. Argon laser with wavelength 488 nm was used. In order to obtain two laser beams with orthogonal linear polarizations, a Wolaston prism was placed splitting the beam into two linear polarizations – horizontal and vertical.

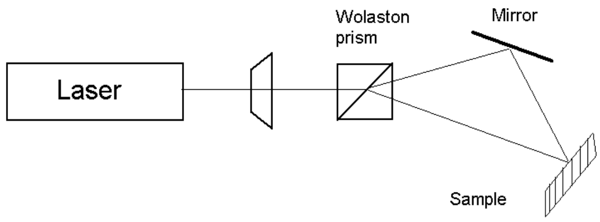

Fig. 2. Set-up for holographic recording.

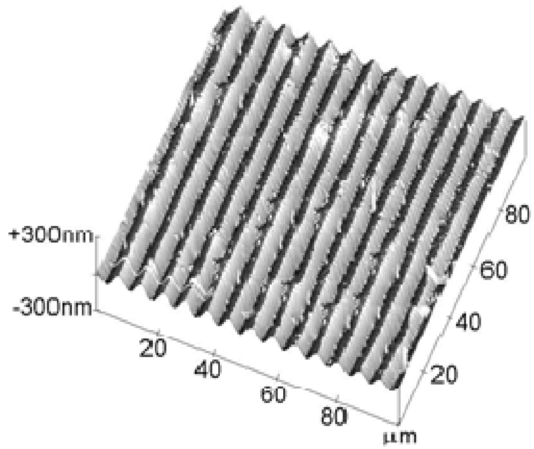

Fig. 3. AFM image of relief holographic azobenzene grating with 50 nm surface relief amplitude and spatial frequency of 150 l/mm.

AFM imaging of the holographic azopolymer gratings

Atomic force microscope (AFM) surface scan of the relief holographic grating recorded in the azopolymer film was made. It is shown in Fig. 3. As it can be seen from this plot, the spatial frequency of the grating is 150 l/mm, and the surface relief amplitude is 50 nm.

Metal thin films coating

For metal-coating of the azopolymer gratings only aluminum was used, because of their specific features. Azopolymers are reversible materials for holographic recording and the relief structures formed in them can be erased thermally at temperatures above 100 °C. Therefore, the metal-coating with silver and gold by a thermal evaporation method is not suitable for these materials. Thin aluminum film was deposited by dc magnetron sputtering technique in argon atmosphere with pressure 0.25 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 gratings.

RESULTS AND DISCUSSION

Azo dyes are compounds that are characterized by the presence of one or more azo groups -N = N-, linking the aromatic radicals. The azoaromatic group exists in two configurations – *trans* and *cis*. Irradiation of a polymer system containing azochromophores with a wavelength within the absorption band, leads to a *trans-cis* isomerization of the dye molecules. Reverse *cis-trans* isomerisation can be induced thermally or optically, and after it the molecule can be randomly oriented. The *trans* molecules oriented in direction parallel to the polarization of the light beam are subjected again to the *trans-cis* isomerization. The process continues until the azomolecules are oriented in such way, that light has minimal influence on them i.e. in direction perpendicular to light polarization. As a result of the reorientation of the azochromophores, anisotropy is induced in the medium as well as surface relief.

The formation of surface relief in amorphous side-chain azobenzene copolymer was reported for the first time by Rochon *et al.* [10] and Tripathy and coworkers [11]. In both cases, the surface relief was obtained by scalar holographic recording (when only the intensity of the light field is modulated) and sinusoidal form of relief was observed with AFM. Several types of polymers have been studied [12], and it was shown that cross-linking of the polymer is not required for the formation of a surface relief. Later it was found that the higher intensity of the recording beams leads to more effective formation of the relief [13]. Surface relief was observed also in the case of polarization holographic recording (when the intensity of the light field is constant, but the polarization is spatially modulated) in azopolymer recording medium[14]. The dependence of the spatial frequency of the relief grating on the geometry of the polarization recording is described in Ref. 15. When the recording beams are with *s* and *p* polarizations, relief grating with doubled frequency compared to the frequency of the anisotropic lattice is observed. This method is also used in our experiments in order to achieve higher amplitude of the surface relief and in the same time higher spatial frequency. Many materials have been studied for use in recording holographic gratings [16-19]. In some of them like acrylamide -based photopolymers it is shown formation of photoinduced surface relief and the use of this feature for sensors application [20,21].

Fig. 4 depicts the transmission ratio TM/TE for the azopolymer gratings coated with Al. 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 Varian CARY 5E precision spectrophotometer. A high-quality Glan-Taylor prism providing extremely pure linear polarization with a ratio 100 000:1 in the optical range of 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.

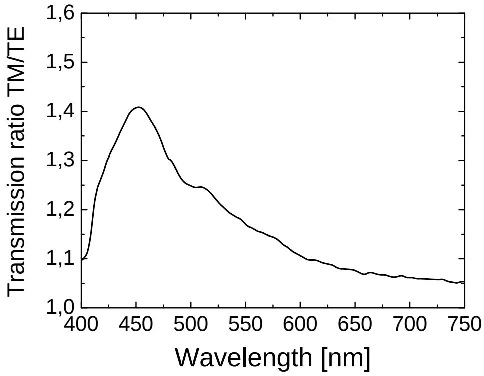

Fig. 4. Transmission ratio TM/TE for the azopolymer gratings coated with Al.

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, as shown in Fig. 4. The observed values of the TM/TE ratio are in good agreement with the surface plasmon polariton theory. According to this theory, when such resonance is observed there is a significant difference in the optical transmission for the two linear polarizations TM and TE.

CONCLUSION

Our experiments indicate that we can use holographically recorded relief gratings for surface plasmon polariton sensor applications. These applications however require high surface relief and high spatial frequency. Finding the right conditions and materials for recording with high relief and spatial frequency is our goal for future development of the subject.

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ПОВЪРХНОСТНИ ПЛАЗМОН-ПОЛАРИТОННИ РЕЗОНАНСИ В МЕТАЛИЗИРАНИ ХОЛОГРАФСКИ АЗОПОЛИМЕРНИ РЕШЕТКИ

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(Резюме)

Повърхностните плазмон-поларитони (ППП) са електромагнитни вълни, които се разпространяват на границата между метална и диелектрична среда и се генерират от резонансното взаимодействие между осцилациите на повърхностните заряди и електромагнитното светлинно поле. За наблюдаването на ППП се използват основно три метода: чрез призма, непериодични или периодични структури на повърхността.

В тази статия ние представяме изследване на ППП, използвайки метализирана релефна дифракционна решетка. Използваната релефна решетка е записана по холографски метод, след което е метализирана с тънък слой алуминий (Al). Наличието на ППП резонанс е експериментално установено в режим на пропускане на ТМ поляризираната светлина.