Sensors and Actuators A 216 (2014) 128–135

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

journal homepage: www.elsevier.com/locate/sna

Surface plasmon based sensor with order-of-magnitude higher sensitivity to electric field induced changes in dielectric environment at metal/nematic liquid-crystal interface

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ARTICLE INFO

Article history:
Received 12 February 2014
Received in revised form 3 May 2014
Accepted 17 May 2014
Available online 27 May 2014

Keywords:
Electro-optic sensor
Liquid-crystal
Surface plasmon

ABSTRACT

A highly sensitive surface plasmon based sensor is developed for monitoring changes in the dielectric environment at metal/dielectric interfaces. It consists of high-index prism/30–40 nm gold/nematic liquid crystal (E44)/indium-tin-oxide/glass structure, which enables measurements of surface plasmon resonance (SPR) curves by using the Kretschmann configuration. The baseline sensitivity of the device to changes in the refractive index is evaluated by using Au/air, Au/water, and Au/nematic liquid crystal (E44); the measured baseline sensitivity is in excellent agreement with theoretically predicted optimal sensitivity. The sensitivity of the device to electric field induced changes in the refractive index of the material at the interface, however, is 28-times higher than previously known value for a similar sensor. Effects related to the periodic alignment of the liquid crystal on gold surface and surface plasmon mediated diffraction are investigated.

1. Introduction

Since the realization of the surface plasmon excitations (SPEs) in the 1950s [1–3], there has been substantial interest in SPEs, and it has led to numerous applications of SPEs-related techniques. For example, (a) the high sensitivity of the surface plasmon resonance (SPR) to differences in the optical properties of materials across dielectric/metal interface has led to the development of numerous biosensors and (b) the strong electromagnetic fields associated with SPR have contributed to the development of the surface-enhanced Raman scattering [4,5]. Here, we present results from surface plasmon polariton measurements made on a simple structure consisting of high-index prism/30 nm gold/LC (E44)/indium-tin-oxide/glass. We have carried out three sets of measurements: (1) surface plasmon resonance curves for Au/air, Au/water, and Au/nematic liquid crystal (E44) to determine the sensitivity of the device to changes in the refractive index of the material at the Au/dielectric interface ($S_n = \delta\vartheta_{SPR}/\delta n$), (2) surface plasmon resonance curves for Au/E44 interface as functions of *ac* field to evaluate the sensitivity of the device to electric field induced changes in the refractive index of the material, ($S_E = \delta\vartheta_{SPR}/\delta E$), and (3) surface plasmon mediated diffraction from periodic alignment of the liquid crystal on gold surface. Although, quantitative results are discussed later in the manuscript, it is useful to mention at this point that qualitatively the sensitivity S_n of our device is in excellent agreement with theoretically predicted optimal sensitivity for a similar sensor. Additionally, it is remarkable that the sensitivity S_E of our device to electric field induced changes in the refractive index is 28-times higher than the sensitivity of the only other known similar sensor [6]. In the following, we present brief discussions of pertinent experimental details followed by results and their discussion.

The surface plasmon excitations (SPEs) are quanta of surface-charge-density oscillations coupled to electromagnetic waves. Depending upon whether the noble metal in contact with a dielectric is in the form of a thin film (Kretschmann [7,8] or Otto [9] geometries, discussed below) or isolated NPs, two types of excitations are of interest: (1) surface plasmon polaritons (SPPs) and (2) localized surface plasmons (LSPs). SPPs represent electromagnetic surface waves related to surface charge density oscillations, which are coupled to electromagnetic fields having their intensity maximum at the interface, but decaying exponentially with increasing distance perpendicular to the interface (evanescent waves with decay length, $\xi \leq 100$ nm). Often SPPs are generated along a dielectric/metal interface by "manipulating" the wave vector of a *p*-polarized incident laser beam (electric field of the laser beam being parallel to the plane of incidence) such that its tangential component is larger than the wave vector of light in free

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http://dx.doi.org/10.1016/j.sna.2014.05.020
0924-4247/

space. It requires that the dielectric/metal interface be chosen so as to fulfill the requirement for the existence of an interface mode, according to which one of the dielectric functions must be negative with absolute value exceeding that of the other medium. The SPPs are characterized by a wave vector given by [8]

$$k_{spp} = \frac{\omega}{c}\left[\frac{\varepsilon_d \varepsilon_m(\omega)}{\varepsilon_d + \varepsilon_m(\omega)}\right]^{1/2} \quad (1)$$

where ε_d is the isotropic, real and positive dielectric constant of the dielectric medium and $\varepsilon_m = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is the frequency dependent complex dielectric constant of the metal. At the optical frequencies of interest, the dielectric constants of the noble metals, for example gold and silver, are comprised of a large negative real number and a small imaginary number. For example, at a wavelength of 630 nm, the experimental values of the dielectric constants vary from $-10.8 + i1.47$ to $-12.8 + i1.36$ for gold and $-17.6 + i0.67$ to $-19.2 + i0.89$ for silver [8,10]. Because of the energy-momentum mismatch, the incident radiation does not couple directly with the plasmon mode unless appropriately polarized light is coupled to plasmon modes in the Kretschmann or Otto configurations, which often utilize high-index prism coated with thin film of the noble metal (30 nm thick). In certain cases, the metal/dielectric interfaces may be formed when metal NPs are embedded in a dielectric medium. It is then possible to observe localized surface plasmons. Interesting effects, related to both SPPs and LSPs, have been observed in liquid crystal (LC), as well as in polymer-dispersed liquid crystals (PDLCs) containing Au nanoparticle [11–14]. Since SPPs are sensitive to the dielectric properties of materials across an interface, SPR can be modulated by tuning dielectric environment at the interface. In cases, in which LC is one of the materials at the interface, SPR modulation can be accomplished by externally applied electric fields. The field-induced LC alignment changes the dielectric properties of the liquid crystal, which in turn influences SPPs excited at the metal/LC interface. Such an attempt has been made, in which the wavelength and radiation direction of fluorescence have been modulated by voltage applied across LC cell containing dye [15]. In this work, a laser beam first excites the dye molecules within LC cell and the excited dye molecules, in turn, excite SPPs at 45-nm thick gold film over a high-index prism used in the Kretschmann configuration. With increasing values of *dc* electric fields across a 30-μm gap cell, Li et al. [15] have observed that the fluorescence peak wavelength can be modulated continuously from 645 nm at zero field to 686 nm at 21 V (7×10^5 V/m). The present work stems from our interest in liquid crystalline based materials and methods by which their electro-optic properties can be modified [11,14,16–25]. In comparison to the work by Li et al. [15], we have adopted significantly different approach to modulate SPPs by *ac* (1 kHz) electric field applied across high-index prism/Au-film/LC interface in the Kretschmann configuration. The use of *ac* voltages, as opposed to *dc* voltages used by Li et al. is significant and important for liquid crystalline materials. As it is well-known, in the case of liquid crystalline materials *dc* fields can damage device due to undesired accumulation of charged impurities at electrodes and, therefore, *ac* fields of appropriate frequencies are preferred [25].

In the present work, we have studied changes in the surface plasmon polariton resonance (SPPR) as functions of: (1) the dielectric constant of the material to establish baseline data on how the resonance changes with the nature of the material at the interface, (2) electric fields (1 kHz) applied across the Au/E44 interface to examine how the resonance curves change as a result of field-induced changes in the refractive index of the material at the interface and (3) evaluated whether the gold surface-LC interactions leading to periodic alignment of the liquid crystal molecules on the gold surface, coupled with the surface plasmon polaritons, can give rise to diffraction effects. To our knowledge, such detailed results have not been presented. Additionally, our observation of an extremely high sensitivity of the device to *ac* electric fields, which is 28-times higher than known values, may lead to the development of sensors for processes occurring at metal/fluid interfaces. Our electric field dependent data reinforce the view that changes observed in the SPPR curves arise from modulations in the LC refractive index at the interface. We discuss these results in terms of the well-known Pockels and Kerr effects [26,27], which provide further insight on the effects of the applied *ac* electric fields on the electro-optical properties of liquid-crystalline materials. Our observation of the periodic alignment of LC molecules on gold surface and surface plasmon mediated interference effects is intriguing and the results are expected to facilitate development of sensitive sensors for processes occurring at metal/dielectric interfaces.

2. Experimental details

2.1. Device fabrication

As sketched later in Fig. 5, a device was fabricated by sandwiching ≈40 μm thick film of liquid crystal (E44) between 30 nm thick gold coating over the base of a high-index prism (Edmund Optics, N-SF11, refractive index = 1.7847 @ 632 nm) and an Indium-Tin-Oxide (ITO) coated glass slide. This particular liquid crystal exhibits nematic phase over a wide temperature range, from −10 °C to 100 °C with refractive indices of $n_o = 1.52395$ for ordinary waves and $n_e = 1.77526$ for extraordinary waves @ $\lambda = 632.8$ nm. The gold coating and ITO were insulated from each other by using SiO_2 beads of diameter ≈40 μm and they were used as electrodes to apply (1 kHz) electric fields across the device. This particular frequency is chosen based on our previous results, which have shown the optimum response of E44 to occur near 1 kHz. [25] Since the LC molecule alignment and thereby the electro-optical properties of the sensor are controlled by the nature of the surface (e.g., surface material, smoothness, impurities, and lattice defect), it is important to know the microstructure of the gold film. We have, therefore, examined surface topography, crystalline structure and impurities in the film by using atomic force microscopy (AFM) and X-ray diffraction (XRD). A typical AFM scan is shown in Fig. 1. The quartz crystal film thickness monitor and AFM scans show that the gold film is 30 nm thick and the smoothness of its surface topography is characterized by a root-mean-square deviation of about 5 nm. The XRD spectra, shown in Fig. 2, were measured by Bruker

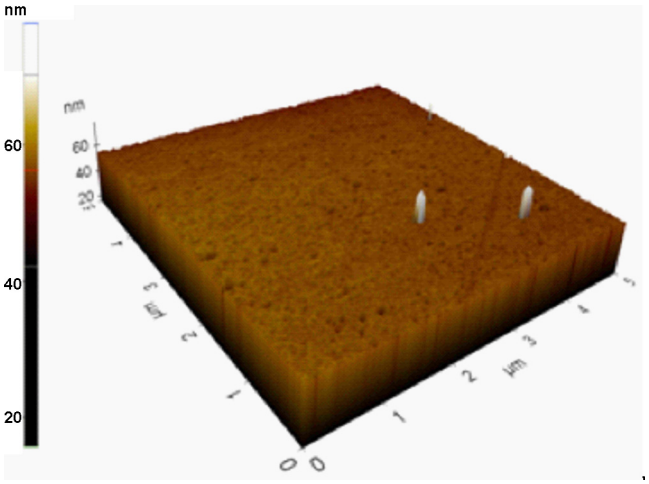

Fig. 1. Surface topography of a 5 × 5 μm region of Au film using AFM tip in a non-contact mode at a scanning rate of 0.5 Hz.