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Indium tin oxide refractometer in the visible and near infrared via lossy mode and surface plasmon resonances with Kretschmann configuration

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An indium tin oxide (ITO) refractometer based on the generation of lossy mode resonances (LMRs) and surface plasmon resonances (SPRs) is presented. Both LMRs and SPRs are excited, in a single setup, under grazing angle incidence with Kretschmann configuration in an ITO thin-film deposited on a glass slide. The sensing capabilities of the device are demonstrated using several solutions of glycerin and water with refractive indices ranging from 1.33 to 1.47. LMRs are excited in the visible range, from 617 nm to 682 nm under TE polarization and from 533 nm to 637 nm under TM polarization, with a maximum sensitivity of 700 nm/RIU and 1200 nm/RIU, respectively. For the SPRs, a sensing range between 1375 nm and 2494 nm with a maximum sensitivity of 8300 nm/RIU is measured under TM polarization. Experimental results are supported with numerical simulations based on a modification of the plane-wave method for a one-dimensional multilayer waveguide. © *2016 AIP Publishing LLC*.
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The field of sensors has been one of the greatest beneficiaries of the discovery of surface plasmon resonances (SPRs) and lossy mode resonances (LMRs). Many works, usually devoted to chemistry and biological sensing, have shown the applicability of these resonances to measure changes in the refractive index of a medium in contact with a thin film, i.e., a refractometer.[1–7] SPRs in thin-films are generated by the coupling of light to a surface plasmon polariton.[8] Traditionally, SPR refractometers are based on the excitation of the surface plasmon in a Kretschmann configuration, which consists of a glass prism deposited with a thin metallic film. Although this system is bulky compared with, for instance, optical fiber refractometers based on waveguide coupling, it presents superior sensitivity[9] (i.e., higher variation in the resonance wavelength per refractive index unit—RIU). On the other hand, the development of LMR refractometers is more recent and up to this work has been limited to fiber sensors.

Due to their different physical nature, several features distinguish LMR from SPR refractometers. For SPRs, the thin-film must satisfy the condition that the real part of its permittivity must be negative and larger in magnitude than both its own imaginary part and the permittivity of the material surrounding the thin-film. Metals such as gold or silver fulfill these conditions in the visible range and thus they have been traditionally used for SPR excitation. On the other hand, for LMRs the real part of the thin-film permittivity must be positive and larger in magnitude than both its own imaginary part and the real part of the permittivity of the material surrounding the thin-film.[10] In this respect, metals are not adequate to generate LMRs. However, other materials such as indium tin oxide (ITO) satisfy both the conditions for LMR and SPR generation at short and long wavelengths, respectively, allowing to have both resonances in a single structure.[11,12] Other differences are that LMR can be excited under both TE and TM polarization (SPR only takes place under TM polarization) and that several resonances can be originated in the spectrum.[5–7]

Refractometers based on SPR excitation in ITO thin-films with Kretschmann configuration have been already implemented.[12,13] SPRs are typically obtained for angles ranging between 40° and 70° and thus, with an equilateral prism, the resonance can be easily excited.[10] However, LMRs need incidence angles approaching 90°,[11] i.e., grazing angle incidence, which is not trivial, so refractometers based on LMRs have been exclusively limited to fiber sensors.[5–7] In Ref. 14, we demonstrated, both theoretically and experimentally, LMR and SPR excitation in ITO thin-films with Kretschmann configuration in a single setup. For the experimental characterization, we used a right angle prism with all its sides polished, specifically designed for this purpose, using a setup similar to that shown in Fig. 1 (more details can be found in Ref. 14). In this letter, we explore the sensing capabilities of this device for a wide variety of refractive indices and demonstrate for the first time a practical refractometer based on simultaneous LMR and SPR excitation in Kretschmann configuration.

The experimental measurements were done with a Bruker Vertex 80V Fourier Transform Infrared spectrometer equipped with a tungsten source (operation bandwidth, 330–10 000 nm), a calcium fluoride beamsplitter (250–10 000 nm) and two detectors, a Si diode (400–1111 nm) and an InGaAs diode (800–1724 nm). The setup is depicted in Fig. 1(a). A grazing angle unit was used to select the incidence and transmission angles. This device consists of two concave mirrors whose angular positions can be controlled independently with a precision of 1°. This way, the angular response in reflection can be accurately obtained. The polarization of the light entering the grazing angle unit can be selected by means of a linear polarizer. To characterize the refractometer, the setup depicted in

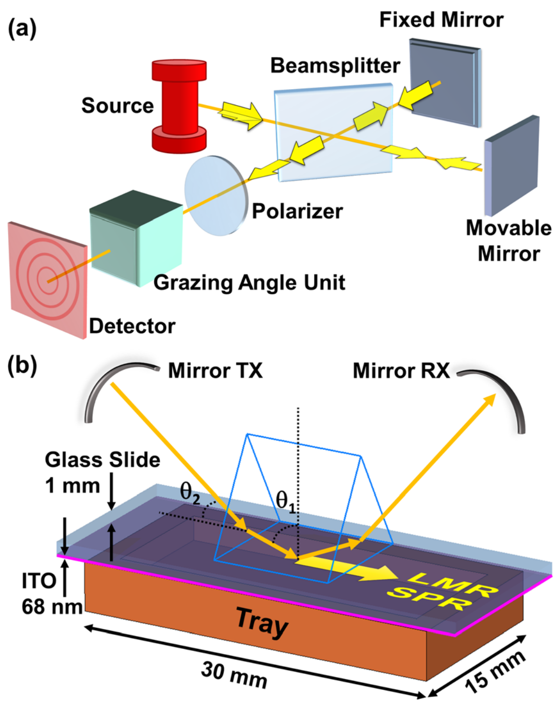

FIG. 1. (a) Schematic of the FTIR operation showing the components. The grazing angle unit has been represented as a green box. (b) Sketch of the experimental setup showing the prism laying on a glass slide coated on the bottom side with a thin ITO layer. The ITO layer is in contact with the solution contained in the tray. Incidence angles on the prism (θ_2) and on the ITO layer (θ_1) are explicitly shown.

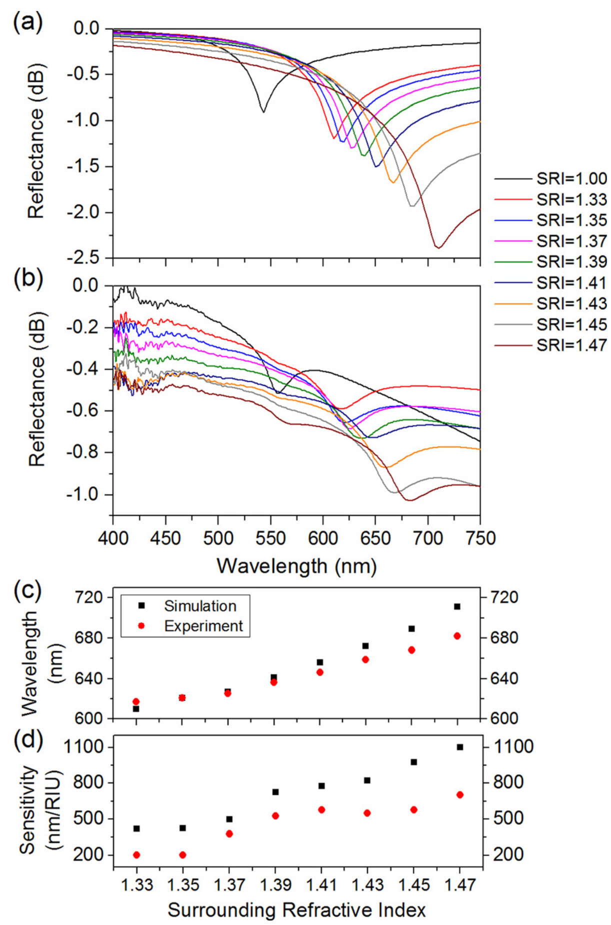

FIG. 2. (a) Theoretical and (b) experimental reflectance under TE polarization in the visible range when the SRI is varied. (c) Resonance wavelengths. (d) Sensitivity.

Fig. 1(b) was placed inside the grazing angle unit. In this case, a plastic tray (specifically manufactured with a 3D printer) was added to contain the solutions under test.

In order to excite LMRs in ITO thin films, a grazing incidence angle approaching 90° is necessary. Therefore, we selected for the experiment an incidence angle on the ITO film $\theta_1 = 89.33°$ which corresponds to an incidence angle on the air-prism interface $\theta_2 = 1°$ (see Fig. 1). Moreover, although the maximum resonance of SPRs takes place for incidence angles ranging from 40° to 70°,[12] they can also appear at angles near 90°.[14] Both TE and TM polarization were explored since LMRs take place at both polarizations, although SPRs are excited only under TM incidence.

The sensing capability of the device was evaluated by obtaining the resonance wavelengths of the LMRs and SPRs when the ITO layer is immersed in a liquid with a known refractive index. The experiment was performed for a surrounding refractive index (SRI) ranging from 1.33 to 1.47 (step of 0.02). These values of SRI were achieved by carefully mixing water (n = 1.33) and glycerin (n = 1.47) with the adequate percentage of each substance. The tray was filled with the solution up to a proper level to ensure full contact with the ITO thin-film. The refractive index of each particular solution was measured independently with a portable digital refractometer from Mettler Toledo. For calibration purposes, the case when the tray is empty, which corresponds with an SRI = 1, was also evaluated.

Simulation and experimental results for TE polarization from 400 nm to 750 nm are presented in Figs. 2(a) and 2(b), respectively. Simulation results were obtained with the well-known plane wave method for a one dimensional multilayered waveguide.[4,14,15] In both cases, absorption dips due to excitation of LMRs are clearly observed. As shown, the dip is shifted to longer wavelengths as the refractive index of the solution is increased. Therefore, the device works as a refractometer in the visible range enabling the detection of the refractive index of a sample in contact with the ITO layer. In Fig. 2(c), the resonance wavelengths obtained numerically and experimentally are compared showing a good agreement between them. From the figure, we can estimate a relatively broad sensing range that extends from 617 nm to 682 nm. The sensitivity varies from 200 nm/RIU when the SRI = 1.33, up to 700 nm/RIU when the SRI = 1.47 (from 420 up to 1100 in the simulation) (Fig. 2(d)).

In Fig. 3, the results for TM polarization for wavelengths ranging from 400 nm to 750 nm are shown. Again, the experimental curves have a good agreement with the simulated ones. As expected for TM polarization, LMRs take place at shorter wavelengths leading to a sensing range that extends from 533 nm to 637 nm. The sensitivity varies from 350 nm/RIU up to 1200 nm/RIU, overcoming the results obtained for TE polarization.

Finally, TM polarization results in the near infrared are presented in Fig. 4. The resonances observed in this figure correspond with the SPRs. It must be highlighted that, although deeper resonances could be expected for SPRs, they are excited out of their optimal incidence angle. In

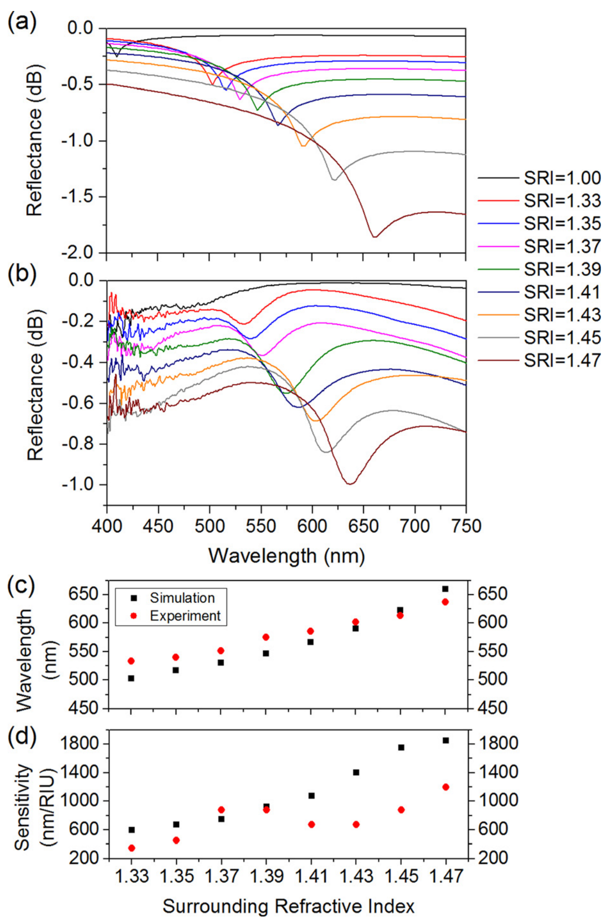

FIG. 3. (a) Theoretical and (b) experimental reflection under TM polarization in the visible range when the SRI is varied. (c) Resonance wavelengths. (d) Sensitivity.

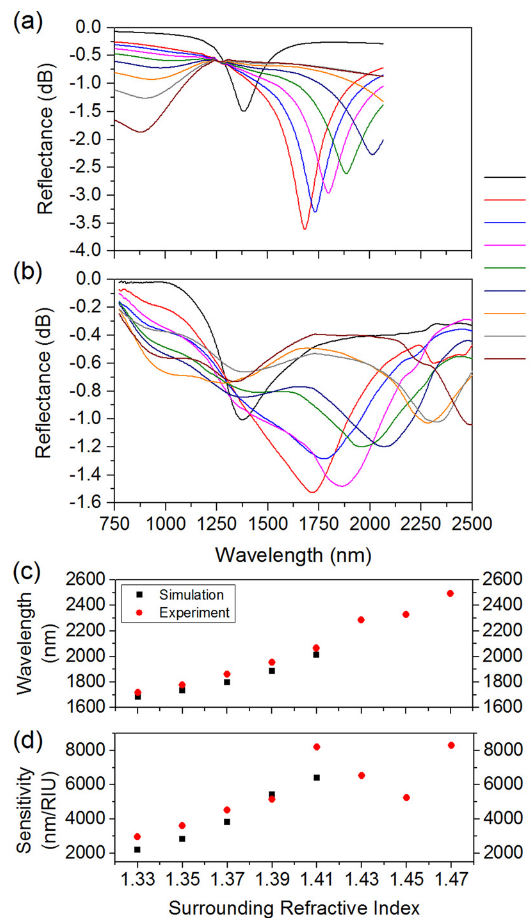

FIG. 4. (a) Theoretical and (b) experimental reflectance under TM polarization in the near infrared range when the SRI is varied. (c) Resonance wavelengths. (d) Sensitivity.

Fig. 4(c), a sensing range between 1375 nm and 2494 nm is observed for the SPRs. A maximum sensitivity of 8300 nm/RIU is obtained, in agreement with already reported results of SPR refractometers in Kretschmann configuration.[9] Simulation results for wavelengths beyond 2066 nm are not depicted since ITO was not characterized above this wavelength, and results for TE polarization in the near infrared are not shown because no resonances take place in this spectral range.[14]

In summary, we have presented the first experimental demonstration of a refractometer based on the generation of resonances in the visible range under TE and TM polarization via LMRs and in the near infrared under TM polarization via SPRs with a Kretschmann configuration. A grazing angle unit has been used to excite LMRs and SPRs on an ITO coated glass slide with an incidence angle equal to 89.33°. A solution of glycerin and water has been used to obtain SRI between 1.33 and 1.47. A maximum sensitivity of 700 and 1200 nm per RIU has been obtained with the LMR under TE and TM polarization, respectively, whereas 8300 nm per RIU has been attained with the SPR. This indicates that with an ITO coated device, the performance with the SPR is better than with the LMR. However, LMRs generated with other materials such as SnO_2 permit to reach sensitivities above 5000 nm per RIU[16] that could be a possible line of research for improving the performance of the device, which presents potential applications in chemistry or biology to sense enzymes or antibodies capable of varying their refractive index in the presence of the specific analytes.

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