Guided-mode-resonance-enhanced measurement of thin-film absorption

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Abstract: We present a numerical and experimental study of a guided-mode-resonance (GMR) device for detecting surface-bound light-absorbing thin films. The GMR device functions as an optical resonator at the wavelength strongly absorbed by the thin film. The GMR mode produces an evanescent field that results in enhanced optical absorption by the thin film. For a 100-nm-thick lossy thin film, the GMR device enhances its absorption coefficients over 26 × compared to a conventional glass substrate. Simulations show the clear quenching effect of the GMR when the extinction coefficient is greater than 0.01. At the resonant wavelength, the reflectance of the GMR surface correlates well with the degree of optical absorption. GMR devices are fabricated on a glass substrate using a surface-relief grating and a titanium-dioxide coating. To analyze a visible absorbing dye, the reflection coefficient of dye-coated GMR devices was measured. The GMR-based method was also applied to detecting acid gases, such as hydrochloric vapor, by monitoring the change in absorption in a thin film composed of a pH indicator, bromocresol green. This technique potentially allows absorption analysis in the visible and infrared ranges using inexpensive equipment.

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1. Introduction

Absorption spectroscopy is a powerful technique used in a wide variety of analytical applications in chemistry, biology, and physics [1, 2]. The Beer-Lambert law describing the measured absorption signal involves an exponential dependence on the optical path length through the sample. A sufficiently long path length (~1 cm) allows a robust and accurate absorption measurement. In thin films, it can range from tens to hundreds of nanometers, resulting in an absorption signal that is below the detection limit of standard laboratory techniques. The ability to measure such weak absorption is especially important for detecting surface-absorbed analytes. Sophisticated techniques, such as ellipsometry, interferometry, and photoacoustics, have been applied to measure absorption in thin films [3–5]. Alternatively, cavity-enhanced techniques effectively increase the optical path length by placing the sample within an optical cavity, where excitation light undergoes multiple passes through the sample [6–8]. Nanophotonic devices that support optical cavity modes have also been utilized to amplify the interaction of the excitation light and analyte [9–12].

In this paper we demonstrate and characterize a guided-mode resonance (GMR) substrate for measuring optical absorption by thin films. GMR structures have been extensively studied for application to optical filters, displays, and biosensors [13, 14]. Previous results have demonstrated that GMR structures can significantly increase the emission intensity of fluorescence molecules through an enhanced absorption effect. Electric fields associated with GMR modes, evanescently confined to a surface, are strongly enhanced in comparison with the electric field of the excitation source [15]. We here demonstrate and characterize a GMR substrate for measuring optical absorption by thin films, in particular the thin films of chemical and biological molecules that exhibit weak optical absorptions. The measurement using a GMR substrate only requires an inexpensive instrument, compared to the conventional ellipsometry, which relies on dedicated equipment and fitting algorithm [16].

The outline of this paper is as follows. Section 2 clarifies the principle of GMR-enhanced absorption by a numerical analysis. Experimental results, including the fabrication of a GMR substrate, the analysis of a light-absorbing dye, and the detection of acid gas, are presented in Section 3. Section 4 concludes and discusses future prospects.

2. Principle of GMR-enhanced absorption

The cross section of a GMR substrate is shown in Fig. 1(a). The surface-relief grating is formed using UV curable epoxy on a surface of glass coverslip. A titanium-oxide layer of specified thickness (t_{TiO2}) is deposited onto the grating structure. Acting as a light confinement layer, the high-refractive-index titanium-oxide layer supports resonance modes that are evanescently confined near the GMR surface. The periodic modulation of the grating, which satisfies the second-order Bragg condition, allows the phase matching of excitation light with a GMR mode. Compared with the excitation light, the near-field intensity associated with the GMR modes is strongly enhanced and can therefore boost absorption by

materials located on the GMR surface. By adjusting geometric parameters, a GMR device can be engineered to achieve a desired spectral response that efficiently matches the absorption characteristics of specific dye molecules [17].
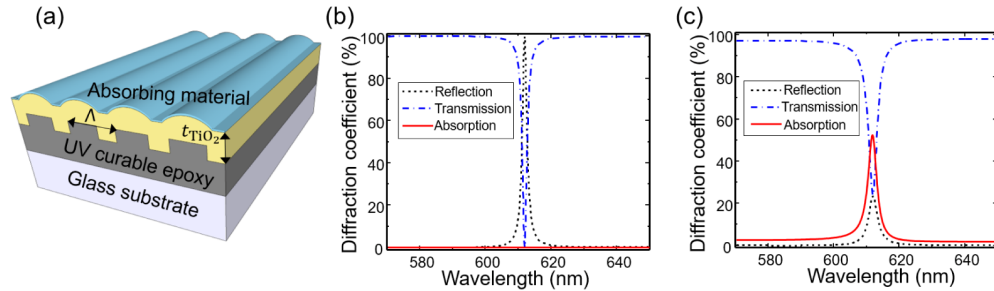

Fig. 1. (a) GMR sensor substrate. The absorbing material is deposited onto the GMR surface. (b) Simulated transmittance and reflectance of the TM resonance mode in the GMR structure. (c) Simulated absorption spectrum and transmission and reflection spectra in the GMR structure.

We designed a GMR substrate to enhance the absorption of red absorbing dyes with an absorption band near the wavelength λ_{abs} = 612 nm, as the results of transitions between electronics states. A commercial electromagnetic simulation software (DiffractMOD, RSoft Design Group) was used to analyze the enhanced absorption. A one-dimensional GMR structure supports two orthogonal modes: transverse-electric (TE) polarized and transverse-magnetic (TM) polarized. We chose to work with TM-polarized modes because they have a greater Q-factor than TE modes, resulting in stronger absorption. Simulations suggested a GMR periodicity Λ = 416 nm, a grating depth d = 80 nm, and t_{TiO2} = 80 nm. The optical response of the TM resonant mode for this GMR structure coated with a 100-nm-thick lossless thin film is shown in Fig. 1(b), where the transmittance (T) minimum and reflectance (R) maximum identify the resonant mode. Without material loss, the GMR resonance causes 0% transmittance (100% reflectance) at the resonant wavelength λ_r = 612 nm.

2.1 GMR-enhanced optical absorption

We numerically calculated optical absorption at the GMR surface by introducing an extinction coefficient (κ = 0.01), as the imaginary part of the refractive index in the simulation model, for the thin film. Figure 1(c) shows the absorption spectrum together with the transmission and reflection spectra. At the resonant wavelength (λ_r = 612 nm), the absorption coefficient is A = 53%. On a planar glass substrate, the absorption coefficient for a lossy thin film with identical geometrical parameters is only 2%. Thus, the GMR substrate enhances absorption by a factor of 26.5. The simulation model ignored the material dispersion. Figure 2(a) plots the absorption coefficient as a function of the extinction coefficient, covering the range $10^{-5} < \kappa < 1$, for the GMR and planar glass substrates. The absorption coefficient was calculated at λ_r = 612 nm and the thin-film thickness was 100 nm. For $\kappa < 0.05$, the GMR substrate displays a significantly higher absorption coefficient than the glass substrate.

2.2 Resonance quenching effect

A high extinction coefficient (κ > 0.01) quenches the GMR mode and consequently reduces the enhancement capability. As shown in Fig. 2(a), the absorption coefficient peaks at κ = 0.01. At greater κ, absorption starts to decrease because of the quenching of the GMR resonance. The high extinction coefficient deteriorates the enhancement capability of the GMR. When κ exceeds 0.1, the GMR enhancement effect becomes entirely dominated by the thin film itself. The GMR absorption coefficients thus approach the glass-substrate values. Further evidence of the quenching effect is given by the near-field spatial distribution shown in Fig. 2(b). The influence of the loss-induced quenching of the GMR mode is clearly

manifested in the near-field intensity. As a result, the GMR-enahnced absoption is unsuitable for hihgly lossy thin films, such as metals and semiconductors.
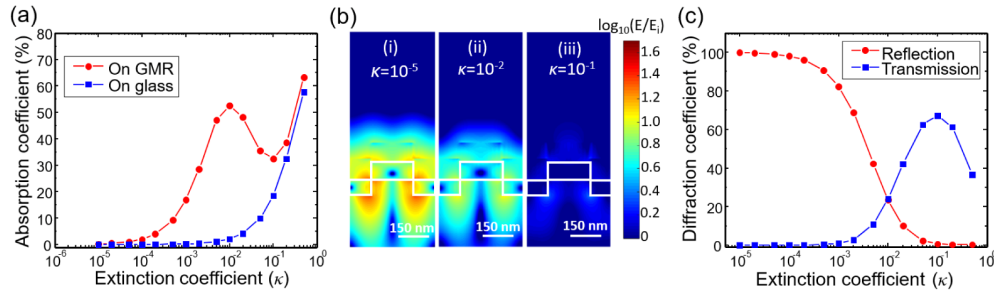

Fig. 2. (a) Simulated absorption coefficients as functions of the extinction coefficient for a thin-film-coated GMR structure and a glass substrate. The coefficients are calculated at the GMR resonant wavelength. (b) Near-field distribution cross section within one period of the GMR structure, under the resonant condition, for three different extinction coefficients: (i) 10^{-5}, (ii) 10^{-2}, and (iii) 10^{-1}. The white lines indicate the TiO_2 boundary. (c) Calculated reflectance and transmittance as functions of the extinction coefficient, when the GRM substrate operates at the resonant wavelength.

Excitation light incident on a lossy thin film can be transmitted, absorbed, or reflected. Conservation imposes the relation $T + R + A = 1$. It is therefore necessary to measure both transmittance and reflectance to calculate absorption. GMR offers an alternative approach for determining absorption. As shown in Fig. 2(c), both the reflectance and transmittance of a GMR substrate vary with κ. In this study, we exploited the GMR reflection spectra to facilitate the absorption measurement.

3. Experimental results

3.1 Design and fabrication of the GMR substrate

A sub-wavelength grating was fabricated on a glass coverslip using a low-cost nano-replica molding technique, previously described in detail [18]. Briefly, the one-dimensional grating structure was replicated from a patterned silicon master stamp (SNS-C24, LightSmyth Technologies, Inc.) with a grating period $\Lambda = 416$ nm, a duty cycle of 50%, and a depth $d = 110$ nm. The grating pattern was formed using UV-curable epoxy (NOA 85, Norland Product Inc.). A ~100-nm-thick TiO_2 dielectric film (refractive index $n = 2.0$) was then deposited by electron-beam evaporation. A photograph of the fabricated GMR device is shown in Fig. 3(a), where the grating area is 8×8 mm^2. The scanning-electron-microscope image in Fig. 3(b) confirms the regularity of the replicated grating pattern.
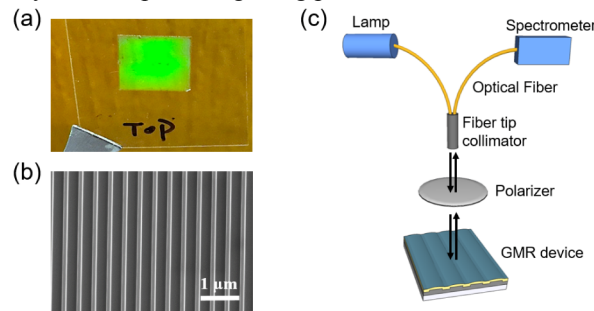

Fig. 3. (a) Photograph of the GMR device fabricated on a glass coverslip. (b) SEM image of the top view of the TiO_2-coated grating pattern. (c) Schematic diagram of the reflection measurement setup.

3.2 Measurement setup

The optical response of the GMR device was characterized using the setup illustrated in Fig. 3(c). Excitation was done with broadband light from a tungsten halogen lamp coupled to a bifurcated optic fiber. During measurements, a ~3-mm-diameter spot on the device was illuminated at normal incidence from above. A linear polarizer was placed between the collimator and the sample so that only the TM-polarized GMR mode was measured. The reflected light was collected using the bifurcated cable, which was connected to a spectrometer (USB 2000, Ocean Optics). The GMR device was mounted onto a kinetic mirror mount to adjust its orientation in relation to the incoming light.

3.3 Detection of the light-absorbing dye

In order to characterize the enhanced absorption, an absorbing dye was measured on the GMR device. Before the experiment, the GMR devices and glass reference samples were cleaned and the absorbing dye (Epolight 5262, Epolin Inc.) was dissolved in methanol to obtain concentrations ranging from 0.001 to 0.1 mg/mL. These dye solutions were then drop-cast onto the substrates and air dried. The Epolight 5262 is a narrowband (~60 nm) light absorber with peak absorption wavelength ~620 nm. Characterized using an ellipsometer, the extinction coefficients of dye films range from 0.011 to 0.108.

Figure 4(a) plots the reflection spectra measured on GMR substrates with dye concentrations of 0.001, 0.005, 0.01, 0.05, and 0.1 mg/mL. The peak of the reflection spectra represents the GMR mode. As the dye concentration increases from 0.001 to 0.1 mg/mL, the reflection coefficient decreases significantly from 78.4% to 45.5% at the resonant wavelength (λ_r = 618 nm). The full width at half maximum (FWHM) of the GMR mode increases at higher dye concentrations because of the quenching of the resonance. The reflectance at 618 nm is plotted as a function of the dye concentration in Fig. 4(b). To examine the effect of the GMR mode further, the reflectance measured with the glass substrate coated with the same dye solution is shown for reference. The enhancement of the reflectance by GMR over the plain glass slide is clearly depicted in the plot. This allows the detection of small changes in dye absorption, particularly for low dye concentrations. For instance, when the dye concentration is 0.005 mg/mL, the reflectance changes 5% on the GMR substrate. In contrast, for the same dye concentration, the change of transmittance is less than 1% on the glass substrate.
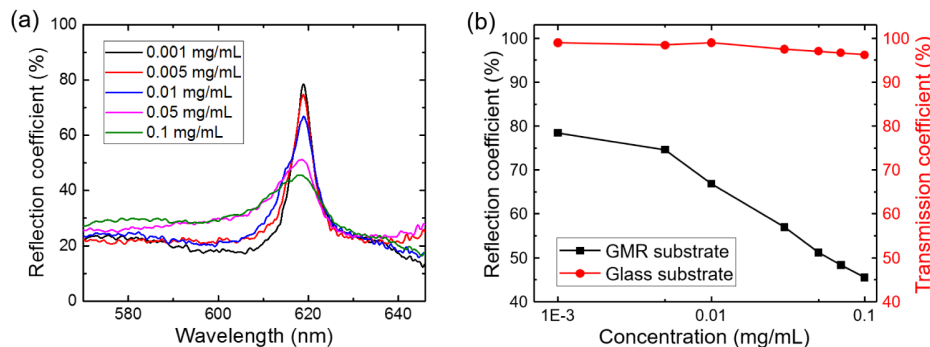

Fig. 4. Enhanced optical absorption by dye molecules on a GMR substrate. (a) Reflection spectra for a GMR substrate with different dilutions of absorbing dye. (b) Reflectance measured at 618 nm for the different dye dilutions on a GMR substrate (red spots) and on a glass substrate (black squares).

3.4 Detection of acid gas

As an example of a possible application, we exploited GMR-enhanced absorption to detect acidic gas. We activated the GMR device by coating it with a layer of bromocresol green (BCG, Sigma-Aldrich), a common colorimetric pH indicator. In its basic form, the BCG dye

absorbs strongly at 610 nm but less so with decreasing pH [19]. This experiment exploits the GMR-enhanced absorption to monitor changes in BCG absorption caused by exposure to an acid gas. The BCG dye was dissolved in 1 µg/mL methanol, and NaOH was added to the solution to adjust the pH. Drops of BCG solution (15 µL) were deposited onto the surface of the GMR device and dried in air. Above a pH of 5.4, the BCG sample absorbed strongly at 610 nm, which resulted in a strong quenching of the GMR mode.
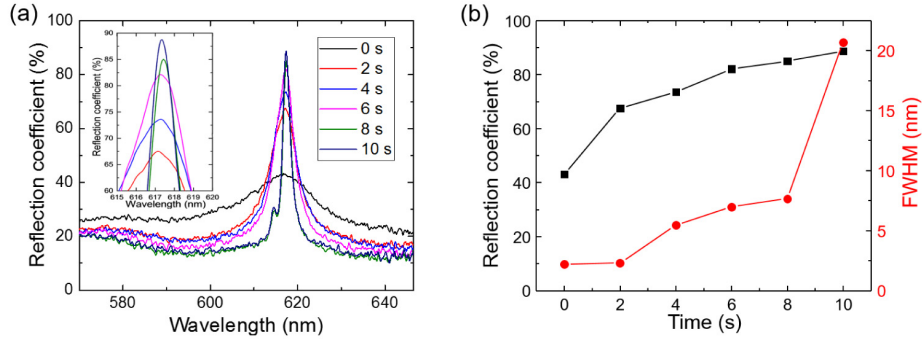

Fig. 5. (a) Reflection spectra of a BCG-coated GMR device after different exposure times to HCl vapor. Inset: magnified reflection spectra near the resonant wavelength. (b) Transmission coefficients of BCG (black squares) and FWHM (red spots) as functions of exposure time.

The BCG-coated GMR device was measured before being exposed to an acid gas. The reflection spectra are plotted in Fig. 5(a) and show a low reflectance around 40%. The sample was exposed to hydrochloric (HCl) acid vapor for 2, 4, 6, 8, and 10 s consecutively until the reflectance remained stable. After each exposure, the reflection spectrum was measured. The HCl vapor decreased the pH of the BCG and consequently reduced its absorbance in the red at the GMR resonant wavelength. As a result, the reflectance at λ_r = 618 nm increased significantly to 87%. Figure 5(b) summarizes the measured reflectance as a function of the exposure time. The exposure to HCl vapor increases the FWHMs of the resonant peak (Fig. 5(b)), which indicates that the acid gas diminishes the quenching effect on the GMR mode.

4. Conclusion

In summary, we reported a numerical and experimental study of a GMR device used for enhancing measurements of absorptive thin films. The increased near-field intensity associated with the GMR mode increases the optical absorption by the material deposited on the GMR device surface. For materials with a large extinction coefficient, the resonant effect is quenched owing to strong material loss. Thus, the GMR device is engineered to facility the optical absorption of molecules with weak absorption coefficients or at low concentrations. The GMR substrate reflectance can be used to quantify this absorption. We characterized the GMR device performance by coating an absorbing dye onto its surface and measuring the resulting reflectance. At the resonant wavelength, the ability of the GMR device to distinguish small changes in optical absorption was significantly enhanced. Our approach was applied to detect HCl vapor by monitoring the change in absorbance of the pH indicator BCG. Induced by the HCl vapor, the transition of the BCG from its basic form to an acidic form was recorded on a GMR device. Unlike an ellipsometer, the GMR enhanced absorption, in its current format cannot provide the quantitative characteristics of thin films. Future work will exploit this technique to characterize the thickness, refractive index, and extinction coefficient of a thin film as an alternative to ellipsometry. The method can also be used to facilitate measurements of the vibrational absorption of molecules, by engineering the device structure to exhibit GMR modes at mid-IR wavelengths.

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