Silica-based monolithic sensing plates for waveguide-mode sensors

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Abstract: We developed a monolithic sensing plate for a waveguide-mode sensor. The plate consists of a SiO_2 glass substrate and a thin silicon layer the surface of which is thermally oxidized to form a SiO_2 glass waveguide. We confirmed that the sensing plate is suitable for high-sensitivity detection of molecular adsorption at the waveguide surface. In addition, a significant enhancement of the sensitivity of the sensor was achieved by perforating the waveguide with holes with diameters of a few tens of nanometers by selective etching of latent tracks created by swift heavy-ion irradiation. Possible strategies for optimizing the plate are discussed.

OCIS codes: (160.6030) Silica; (220.4241) Nanostructure fabrication; (230.7370) Waveguides; (280.4788) Optical sensing and sensors; (310.2790) Guided waves.

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1. Introduction

Highly sensitive sensors are required for the detection of molecules in various fields of application. Evanescent-field-coupled waveguide-mode sensors are effective for this purpose [1–7]. These sensors use a sensing plate whose geometry is based on a sequence of layers with well-selected optical properties. The sensing plate normally consists of a transparent substrate, a thin reflecting layer, and a dielectric waveguide layer [5–7]. The Kretschmann configuration is one popular design for the sensors to excite waveguide modes [8]. In this configuration, the sensing plate is optically matched to the base of a glass prism. Incident light illuminates the reflecting layer through the prism. Weakly guided waveguide modes are excited under appropriate excitation conditions with respect to the wavelength, the polarization state, and the angle of incidence of the light. Waveguide modes can be excited by either P- or S-polarized light [1], but higher sensitivities are achieved by using S-polarized light [9]. Excitation of the waveguide modes changes the reflectivity of the incident light over a narrow angular region. Because a portion of the profile of a waveguide mode is located in the spatial domain outside the waveguide, a change in dielectric properties near the surface of the waveguide alters the dispersion relationship for a waveguide mode. The corresponding change in the excitation condition causes a variation in the reflectivity that can be used as a means of detecting small concentrations of molecules.

In principle, any kind of solid material that reflects light and optically isolates the waveguide from the substrate can be used as the reflecting layer. Silver and gold are typical materials for the reflecting layer, since the use of these metals provides a good sensitivity [3–7]. The reflecting layer and the waveguide layer are usually deposited sequentially on the substrate, so adhesion between the layers and any surface roughness of the layers strongly affect the sensitivity, reliability, and durability of the sensor. Although the use of adhesive layers can solve the problem of insufficient adhesion between the layers to a certain extent, it has been reported that such layers cause a significant deterioration in the sensitivity [9]. A thorough analysis of a wide selection of solid materials suggested that Si may be the optimal material for the reflecting layer: silicon provides not only good sensitivity, but also extremely good chemical stability [9].

In an attempt to expedite efforts to improve the stability of the sensing plate without an accompanying loss of sensitivity, we developed a monolithic sensing plate consisting of a SiO_2 glass substrate, a Si reflecting layer, and a thermally grown SiO_2 glass waveguide layer. In the fabrication process, we used a silicon-on-quartz (SOQ) substrate consisting of a single crystalline layer of Si on a SiO_2 glass substrate [10–12]. The waveguide was formed by thermal oxidization of the Si layer by water vapor. This technique is well known as an effective method for the formation of a thick layer of oxide within a short processing time [13]. In the present case, because the waveguide and the reflecting layer are atomically bonded, the plate is expected to show a high stability.

Besides stability, sensitivity is, of course, one of the most important benchmark characteristics of a sensor. It has been reported that perforating the waveguide with nanosized holes improved the sensitivity of a waveguide-mode sensor [5–7]. To achieve a high sensitivity, we attempted to perforate the monolithic sensing plate by selective etching of the

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latent tracks created by swift heavy-ion irradiation, which is known to be an effective method for forming high-aspect-ratio nanosized holes in SiO_2 glass [6,7,14,15].

Overall, in the present contribution, we developed a high-performance waveguide-mode sensor utilizing a monolithic sensing plate with a perforated waveguide. Its performance will be evaluated theoretically and numerically, and guidelines will be provided that permit to further optimize its sensing capabilities.

2. Experimental details

The substrate used was an SOQ substrate (Shin-Etsu Chemical) comprising a 440-nm thick single crystalline Si (100) layer on a 1.2-mm thick SiO_2 glass substrate. The substrate was cut into plates measuring 25 × 25 mm. The plates were thermally oxidized in an electric furnace in an atmosphere of O_2 containing water vapor at 1000 °C at ambient pressure for 1 h. The oxidized layer forms the waveguide layer, and therefore, the fabricated sensing plate is structurally monolithic.

For measuring reflectance, the Kretschmann configuration was adopted. Figure 1 is a schematic showing the experimental setup. The monolithic sensing plate was optically matched to the base of an isosceles prism (SiO_2 glass) having a vertex angle of 30°. A Teflon cuvette containing 1/15 M phosphate-buffered saline (PBS) was connected to the waveguide-side of the plate. The prism, the sensing plate, and the cuvette were mounted on a goniometer. The plate was irradiated with an S-polarized He–Ne laser beam (632.8 nm) and the reflected light was detected by a photodiode mounted on another goniometer and moved in synchronization with the sample.

The waveguide was perforated by sequential swift-heavy-ion irradiation and etching with hydrofluoric acid (HF) vapor. Ion irradiation was performed by using the 12 UD Pelletron tandem accelerator at the University of Tsukuba, and the waveguide was irradiated with Au ions at room temperature in a vacuum of about 5×10^{-4} Pa. The average energy and the total fluence of the ions were 137 MeV and 5×10^{9} cm^{-2}, respectively. For the vapor etching, the irradiated plate and a 20% aqueous solution of HF were placed in a container so that the plate was not immersed in the solution but was suspended close to its surface. During the etching, the temperatures of the HF solution and the plate were kept at 20 °C and 33 °C, respectively, and the plate was exposed to the HF vapor for 20 min. The resulting nanosized pores were observed by scanning electron microscopy (SEM; Hitachi High-Technologies, S4800).

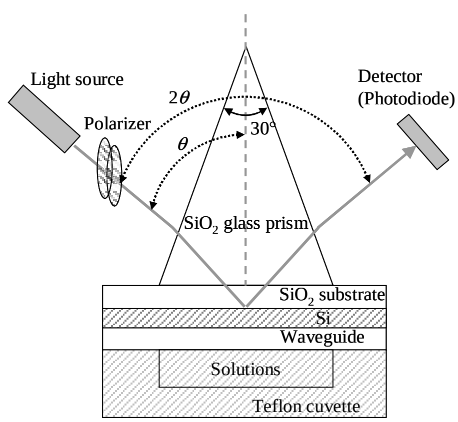

Fig. 1. Schematic of the experimental setup using the Kretschmann configuration.

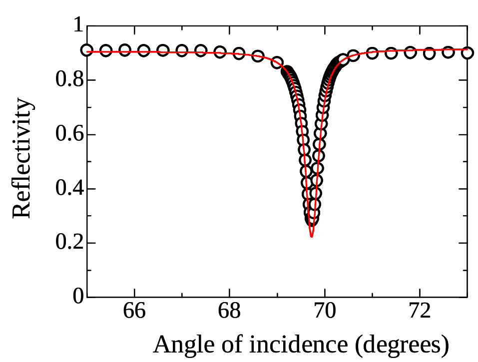

Fig. 2. Observed reflectivity of the sensor with a monolithic sensing plate as a function of the incident angle (black circles). The red curve is drawn by fitting the experimental result to the theoretical result calculated by using the thin-film transfer-matrix technique.

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To demonstrate the sensitivity of the sensor, the specific adsorption of streptavidin on biotinyl groups was examined. First, a layer of (3-aminopropyl)triethoxysilane (3APT) was formed on the surface of the waveguides by immersing the samples in 0.5% v/v solution of 3APT in ethanol for 24 h. Next, the 3APT-modified surfaces were rinsed with ethanol and immersed in 0.5 mM solution of 5-[5-(*N*-succinimidyloxycarbonyl)pentylamido]hexyl-D-biotinamide [biotin-$(AC_5)_2$-OSu] in 1/15 M PBS buffer (pH 7.4) to permit coupling of the amide with the 3APT layer. The plates were rinsed with the buffer and mounted on the observation setup. A cuvette filled with the buffer was connected to the plates and, to observe the specific adsorption, a 1.5 μM solution of streptavidin in the buffer was injected into the cuvette.

3. Results

The black circles in Fig. 2 show the observed reflectivity as a function of the angle of incidence for the monolithic sensing plate without nanosized holes. A sharp dip is observed in the spectrum as a result of coupling between the incident light and a waveguide mode. The red curve is drawn by fitting the experimental result against a theoretical simulation of the reflectivity. The calculation was performed by means of the thin-film transfer-matrix technique. In the calculation, we assumed that the sensing plate consists of two layers made of isotropic homogenous materials on the substrate. The values of complex refractive indices of the substrate and the Si reflecting layer were assumed to be those of SiO_2 glass (n = 1.456) and single crystalline Si ($n + k$i = 3.882 + 0.019i), respectively [16], because the SOQ substrate consists of these materials. The refractive index of the waveguide was assumed to be the same as that of SiO_2 glass, because it has been report that thermal oxidization of single crystalline Si results in high-purity SiO_2 glass [13,17]. The thicknesses of the Si reflecting layer and the waveguide were free parameters and were subject to variation in the fitting routine. The fitting reproduced the experimental results well. The calculated thicknesses of the Si reflecting layer and the SiO_2 glass waveguide were 219 and 482 nm, respectively, showing that a Si layer on the SOQ substrate with a thickness of 221 nm was converted into a 482-nm waveguide.

By using the monolithic sensing plate, we observed the specific adsorption of streptavidin on biotin. Figure 3(a) shows the reflectivity observed before (circles) and after (red triangles) the adsorption. A shift in the resonance position of 0.19° was observed. Figure 3(b) shows the change in reflectivity (ΔR) before and after the adsorption obtained by subtracting the spectrum before the adsorption from that after the adsorption. A maximum positive ΔR of 0.337 was obtained at an incident angle of 69.70°, and a maximum negative ΔR of −0.376 was obtained at an incident angle of 69.97°.

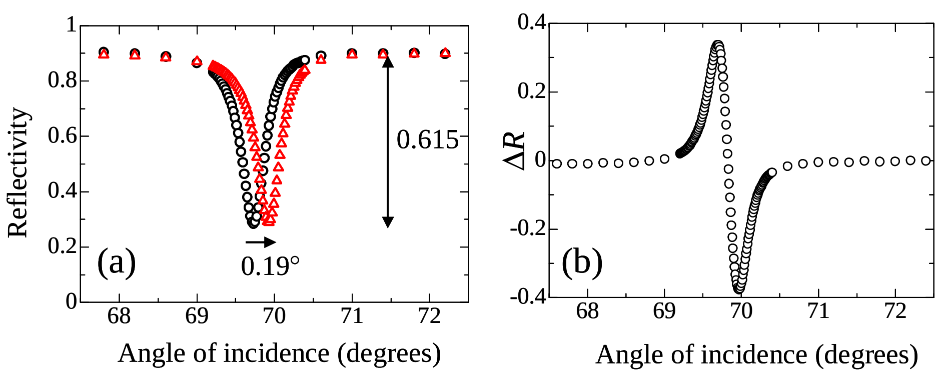

Fig. 3. (a) Reflectivity observed before (circles) and after (red triangles) the adsorption of streptavidin on biotin as a function of the angle of incidence. The monolithic sensing plate was used for the observation. (b) Change in reflectivity (ΔR) as a result of the adsorption obtained by subtracting the spectrum before the adsorption from that after the adsorption.

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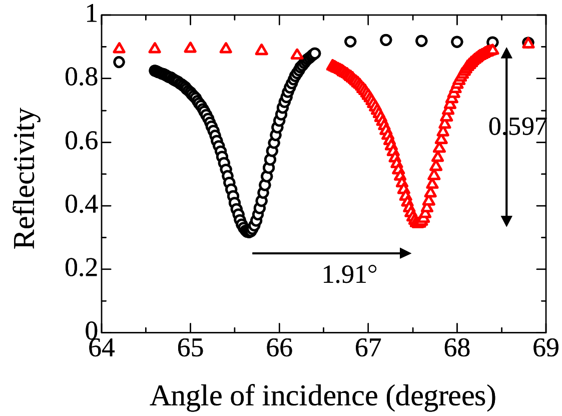

Fig. 4. Reflectivity before (circles) and after (red triangles) the adsorption of streptavidin on biotin as a function of the incident angle, as observed by using the perforated plate.

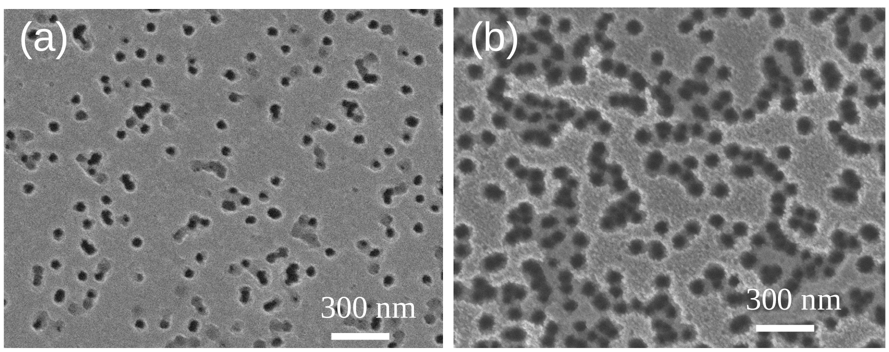

Fig. 5. (a) SEM micrograph of the surface of the perforated waveguide of the monolithic sensing plate, and (b) SEM micrograph of the surface of the perforated SiO_2 glass deposited by radio-frequency magnetron sputtering.

Figure 4 shows the reflectance before (circles) and after (red triangles) the adsorption observed by using the perforated monolithic sensing plate. A shift in the resonance position of 1.91° was observed, which was ten times larger than that seen in Fig. 3(a). Also note that the shift is three times larger than the full-width at the half maximum of the resonance. Figure 5(a) shows the SEM micrograph of the surface of the perforated waveguide. The etching successfully formed nanosized holes with diameters of ~50 nm without any serious damage to the surface of the waveguide.

For comparison, the vapor etching was applied to a 400-nm SiO_2 glass film deposited on a Si substrate by radio-frequency magnetron sputtering. The deposition conditions are discussed elsewhere [6]. Before etching, the film was irradiated with Au ions under the same conditions as discussed above. The etching conditions were also the same as described above, except for the etching time, which was limited to 10 min, because the etching conditions were too harsh for this film and the surface was significantly roughened. The resultant surface image is shown in Fig. 5(b).

4. Discussion

The oxidization forms a layer of high-purity SiO_2 glass that operates as a waveguide, as shown Fig. 2. Figure 6 shows the simulated amplitude of an electric field of an excited waveguide mode in a sensing plate with a SiO_2 substrate, a 220-nm thick Si reflecting layer, and a 480-nm thick SiO_2 glass waveguide. The calculation was performed by means of the transfer-matrix technique. The surface of the waveguide was assumed to be soaked in water. The incident light was an S-polarized beam with a wavelength of 632.8 nm, and the incident angle was chosen at the position where the resonance was strongest. The light irradiated the sensing plate through an isosceles SiO_2 glass prism having a vertex angle of 30°. The model system is nearly identical to the system used in the experiment. Strong optical confinement of the electric field in the waveguide is recognized. Interference fringes due to Fabry–Perot oscillations of the light in the Si reflecting layer are also visible. The most important thing that can be deduced from the field distribution is the strong field enhancement at the waveguide surface. Modification of the dielectric conditions close to the surface will cause a change in the dispersion because the mode is perturbed. This change in the dispersion is at the heart of the operating principle of the waveguide-mode sensor.

As shown by the experiment, the monolithic sensing plate can detect the adsorption of streptavidin on biotin. The sensitivity, i.e. the maximum absolute value of ΔR, shown in Fig. 3 is 0.376, which is better than that of 0.263 obtained by a waveguide-mode sensor using a Au reflecting layer with Cr adhesive layers, as reported elsewhere [9]. In addition to the good sensitivity, the present sensing plate has high chemical, physical, and thermal stability, since the plate consists of only high-purity SiO_2 glass and single-crystalline Si, the layers are atomically bonded to each other, and the plate is subjected to temperatures as high as 1000 °C in the fabrication process.

In the oxidization process, 221 nm of the Si surface was converted into the 482-nm SiO_2 glass waveguide. This shows that the thickness of the SiO_2 glass waveguide (t_{WG}) is ~2.2 times that of the oxidized Si, which is consistent with previously reported results [17]. Since the thickness of the Si layer of the SOQ substrate is 440 nm, the relation between t_{WG} and the thickness of the Si reflecting layer (t_{RE}) can be expressed as:

$$t_{RE} = 440 \text{ nm} - t_{WG}/2.2 \, . \tag{1}$$

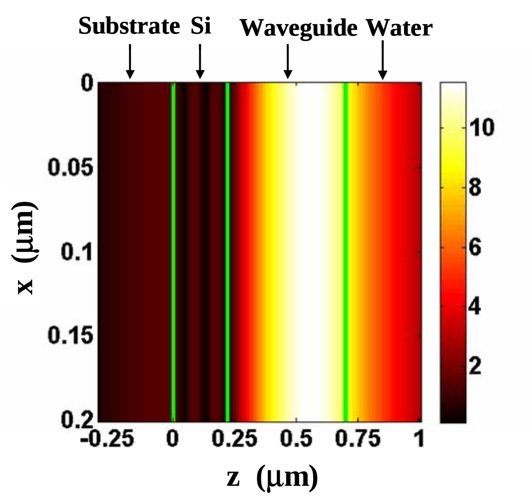

Fig. 6. Simulated amplitude of the electric field of the waveguide mode excited in the sensing plate consisting of a SiO_2 substrate, a 220-nm thick Si reflecting layer, and a 480-nm thick SiO_2 glass waveguide. The incident light is an S-polarized beam with a wavelength of 632.8 nm and irradiates the sensing plate through an isosceles SiO_2 glass prism with a vertex angle of 30°. The surface of the waveguide is assumed to be immersed in water. The incident angle corresponds to the angle at which the strongest resonance is observed. The illuminating plane wave propagates in the positive *z*-direction. The substrate, the reflecting layer, and the waveguide are lined from left to right. Each boundary is indicated by a green line. The strength of the field is indicated by the color bar.

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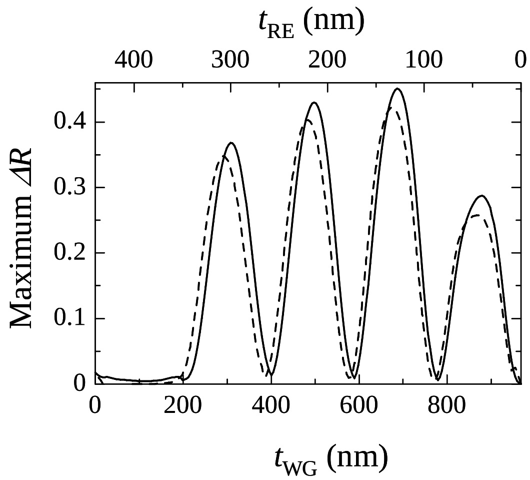

Fig. 7. Simulated correlation between the maximum ΔR obtained by a waveguide-mode sensor with a monolithic sensing plate that can be fabricated from the SOQ substrate and the values of t_{WG} and t_{RE}. The maximum ΔR was calculated by using the thin-film transfer-matrix technique for the case of a monolayer with n = 1.45 and a thickness of 5 nm adhering to the surface of the waveguide. The solid and the dotted curves represent the maximum positive and negative values of ΔR, respectively.

The value of t_{WG} is a function of the time and the temperature of the oxidization process and is controllable. Based on Eq. (1), we can analyze the correlation between the sensitivity of a waveguide-mode sensor with a monolithic sensing plate that can be fabricated from the SOQ substrate and the values of t_{WG} and t_{RE}. The sensitivity is evaluated by calculating the maximum ΔR by using the thin-film transfer-matrix technique for the case of a monolayer with n = 1.45 and a thickness of 5 nm adhering at the surface of the waveguide. The monolayer mimics the adsorption of streptavidin [18]. The result is shown in Fig. 7. The solid and the dotted curves represent, respectively, the maximum positive and negative values of ΔR as a function of t_{WG}. As can be seen, the value of t_{WG} must be more than 200 nm to obtain a good sensitivity. This shows that distinct waveguide modes are not excited if the value of t_{WG} is less than 200 nm, and that optimization of the values of t_{RE} and t_{WG} is very important to achieve a high sensitivity for the sensor. This is because these parameters strongly affect the excitation of the waveguide modes. The calculation shows that a waveguide with a t_{WG} of 686 nm gives the largest maximum ΔR of 0.451. It also shows that a sensor with a t_{WG} of 480 nm, corresponding to the experimental value, shows maximum positive and negative values of ΔR of 0.404 and −0.402, respectively, which are slightly better than those obtained by using the sensor that we fabricated, as shown in Fig. 3(b). The slightly poorer performance of the fabricated sensor compared with the ideal device may be due to nonhomogeneous modification of the waveguide surface with biotin and nonuniform adsorption of streptavidin on biotin. Nevertheless, it can be said that the fabricated sensor has fairly good sensitivity and its performance is close to that of the ideal device.

The correlation between t_{WG} and t_{RE} is restricted by the thickness of the Si layer of the SOQ substrate, as indicated by Eq. (1). Even better sensitivity can be realized by using an SOQ substrate with a Si layer of optimal thickness. Figure 8 shows the correlation between t_{RE} and the maximum ΔR induced by the adhesion of a monolayer with n = 1.45 and a thickness of 5 nm at the surface of the waveguide, as calculated by using the thin-film transfer-matrix technique. In this calculation, t_{WG} was fixed at 480 nm. The solid and the dotted curves represent the maximum positive and negative ΔR, respectively. The result shows that a t_{RE} of 302 nm gives the largest maximum ΔR of 0.451, indicating that an SOQ substrate with a Si

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layer with a thickness of ~520 nm forms a desirable monolithic sensing plate under the present oxidization conditions. This consideration shows that the sensitivity of a waveguide-mode sensor can be further improved by optimizing the thickness of the Si layer and the oxidization conditions.

Perforation of waveguides enhances the shift of the resonance positions in reflectivity, because molecules can penetrate into the waveguide to cause a stronger perturbation of the waveguide mode compared with the case of adsorption of molecules onto the surface only. The guided modes remain confined, as the diameters of the holes are too small to be resolved by the light. The light merely experiences the effective medium and not the perforated waveguide. However, in previous reports, waveguide surfaces were roughened as a result of the perforation process [5–7]. This roughening enhances radiation losses, decreases the resonance strength, and increases the resonance line width. These factors result in a lower achievable maximum value of ΔR and reduce the sensitivity, even if a large peak shift is achieved.

The perforation of the monolithic sensing plate effectively enhanced the sensitivity. As shown in Fig. 4, the shift in the peak position became 10 times larger as a result of the perforation. In addition, the depth of the dip was scarcely decreased by the presence of perforations in the present experiment. The width of the dip increased, but it remained less than twice the width for the unperforated waveguide. These remarkable improvements are due to the quality of the thermally grown SiO_2 glass. As shown in Fig. 5, because of the uniform and rigid structure of the thermally grown SiO_2 glass, the glass was scarcely damaged by the etching, and nanosized holes with a preferable size were created. The resultant uniform etching of the surface suppresses any degradation in reflectivity and, as a result, better sensitivity is obtained.

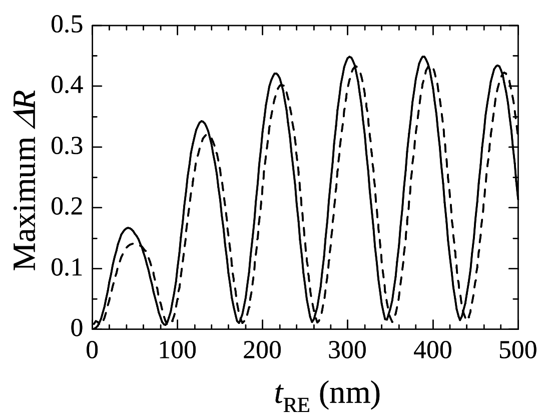

Fig. 8. Simulated correlation between t_{RE} and the maximum ΔR calculated by using the thin-film transfer-matrix technique for the case of a monolayer with n = 1.45 and a thickness of 5 nm adhering at the surface of the waveguide. The value of t_{WG} was fixed to be 480 nm. The solid and the dotted curves represent the maximum positive and negative values of ΔR, respectively.

5. Conclusions

We developed a monolithic sensing plate for a waveguide-mode sensor, fabricated by thermal oxidization of an SOQ substrate. The resulting waveguide consists of SiO_2 glass of high purity and high uniformity. The sensor shows a high sensitivity that is comparable or superior to that of previously reported waveguide-mode sensors. In addition, the developed sensing plate has superior stability. We also showed that the sensitivity can be effectively enhanced by perforating the waveguide by means of swift heavy-ion irradiation and subsequent etching. The monolithic sensing plate is expected to be useful for high-sensitivity detection of molecules in various fields of application, including medicine, pharmacology, biotechnology, and the life sciences.

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