

4. Results and discussion

4.1 Response of the LSPR to the SAM formation

One of the key factors for success of a sensor is the construction of highly effective recognition surface capable of fast and reliable interaction with the corresponding binding analyte of interest. It is important to create a robust sensor surface with specific binding properties and minimal background interference to improve the screening capabilities. Cleaning processes of silicon substrates typically use piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$, 3:1 by vol.) [20]. Anyway, we observed in our previous experiments that piranha solution damaged the gold nanodisks surfaces and changed slightly the LSPR peak of the gold nanostructure. For this reason, cleaning was carried out rinsing with isopropanol and DI water exclusively.

Figure 3 shows the transmission spectra before and after immersing the sample into the 3-ICTPS solution for 2 hours. The spectrum shows that the minimum in the transmission blue-shifted to 1.368 μm in relation to the initial sample resonance of 1.396 μm . This observed notable blue-shift of 28 nm can be explained by a small increase in the nanoparticle height due to exposure to the solvent [21]. The formed monolayer is deposited in such a way that it covers completely the silicon surface, including the regions closely surrounding the gold particles. Organosilane SAM formation is driven by strong covalent attachment of these molecules to the native silicon oxide on the silicon surface through Si-O-Si bonds. The resulting 2-3 nm thick monolayer forms a densely packed and very stable structure with the isocyanate functional group oriented more or less along the normal to the silicon surface. Here, it is important to note that silanes do not form multilayers on gold surface at room temperature [22] and the rinse and heating steps should remove most of the deposited silane molecules from the gold surface, minimizing in this way the possible non-specific adsorption interference. Anyway, either SAM molecules or amine molecules could remain on the metal surface. To ensure that the non-specific adsorption of amine molecules was negligible, the bare sample prior to functionalization was exposed to amine vapour for a sufficiently long time and an IR measurement was carried out. Here, a LSPR wavelength red-shift of only 4 nm was obtained, which is negligible compared to the shifts obtained during sensing experiments. This means that there is no need to block the gold surface in order to avoid the non-specific adsorption. Therefore, sensing experiments were performed with no previous blocking of the gold surface, reducing thus cost in the fabrication process. It can be also pointed out that if a previous blocking of the gold surface was performed, the partially covered gold sidewalls could restrict sterically the subsequent SAM formation on the silicon areas close to the sidewalls, where the near-field is strongly confined, which would decrease dramatically the sensitivity of the sensor.

4.2 Response of the LSPR to vapor exposure

In order to evaluate the sensing ability of the silicon-functionalized system, we used ethylenediamine as target analyte, even though this molecule does not exhibit the greatest binding affinity constant to isocyanate groups. Sensing experiments were firstly performed by heating the sample at 150 °C on a hotplate to regenerate the isocyanate functional groups. This treatment removes the moisture from the surface, leaving the isocyanate functional groups available for the subsequent amine binding reaction. Then, the sample was exposed to ethylenediamine vapour for several minutes at room temperature. Before the transmission measurements, the sample was rinsed with deionised water in order to remove the unbound molecules and dried under a flow of dry air. As shown in Fig. 4a, binding of ethylenediamine molecules to isocyanate groups leads to significant red-shifts in the resonant wavelength of the nanodisks. Initially, the silicon surface modified with a monolayer of 3-ICTPS showed a transmission minimum at 1.368 μm (black spectrum). After 5 min of exposure to ethylenediamine vapour we observed a wavelength red-shift to 1.392 μm . Increasing the exposure time to 15 and 25 min resulted in additional red-shifts to 1.403 μm and 1.406 μm ,

respectively. After this time the resonance remained constant because the saturation level was reached. The sensor response evolves as a function of the analyte exposure time because the ethylenediamine binding at the functionalized surface is strongly time-depending. Hence, binding of ethylenediamine molecules at the isocyanate functional groups needs a determined incubation time to take place. The sensor response saturation occurs when the dynamic equilibrium is established between the sorption and desorption of molecules from the substrate. The binding kinetics will mainly depend on both the amount of active sites on the silicon surface and the number of analyte molecules in vapour phase. For this test, the time constant of the ethylenediamine vapour binding process, τ , can be extracted from the characterization of the λ_{LSPR} shift, $\Delta\lambda_{\text{LSPR}}$, as a function of the analyte exposure time, as shown in Fig. 4b. The experimental data were fitted by a time-dependent equation based on the sorption/desorption kinetics presented by Langmuir [23], $\Delta\lambda_{\text{SPR}} = \Delta\lambda_{\text{max}} [1 - \exp(-t/\tau)]$, where $\Delta\lambda_{\text{max}} = 37.8$ nm was the sensor response corresponding to the saturation of the binding sites and the time constant $\tau = 5.16 \pm 0.4$ min. This time depends upon the affinity reaction between the analyte and the isocyanate active sites on the silicon surface. Thus, the relative resonance shift $\Delta\lambda_{\text{max}}/\lambda_0$, where λ_0 is the wavelength of the plasmonic resonance, can be determined in case of a complete saturation of the surface. A value $\Delta\lambda_{\text{max}}/\lambda_0 = 0.027$ was obtained when all the active sites were occupied by ethylenediamine molecules. Taking into account that only a small area of the silicon surface contributes strongly to the resonance shift, this approach provides a clear improvement in terms of sensitivity over other sensing techniques based on metal nanostructures [24].

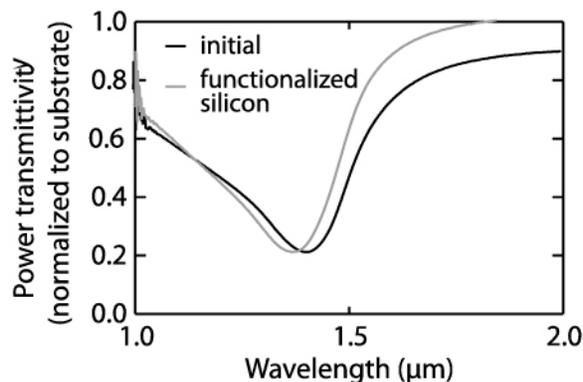


Fig. 3. Measured IR transmission spectra before and after chemical modification of the silicon surface.

4.3 Surface regeneration

One of the advantages of using isocyanate groups is that it allows an easy regeneration of the active sites, which is of key importance for the recycling of the same sensor platform [7]. Regeneration allows to reduce cost and to consume less time because of elimination of various preliminary steps like fabrication, calibration and standardization of the sensor surface. Moreover, multiple measurements with enhanced repeatability can be performed. Typically, surface regeneration is achieved by using chemical reactants such as HCl [25], NaOH [25,26], glycine-HCl [27] among others. They are in the pH range from highly acidic to basic and are used depending on the nature and extent of the binding. Anyway, these strong chemical reactants can affect the binding ability of the functionalized surface and could even damage the nanostructure by erosion of the metal, resulting in a general diminished lifetime of the chip. Our use of organosilane containing isocyanate as functional group has, however, the advantage of an easier and reliable regeneration of the active sites by a simple thermal step, avoiding the use of chemical reactants. Figure 5 shows how the heating of the sensor at 150°C regenerates the isocyanate, recovering approximately the signal corresponding to the functionalized sample. A subsequent sensing test was performed to check if the regenerated

surface was still active, obtaining a smaller redshift of 14 nm. This decrease in the resonance shift could possibly be caused by the damage to some active sites during the regeneration and handling of the sample.

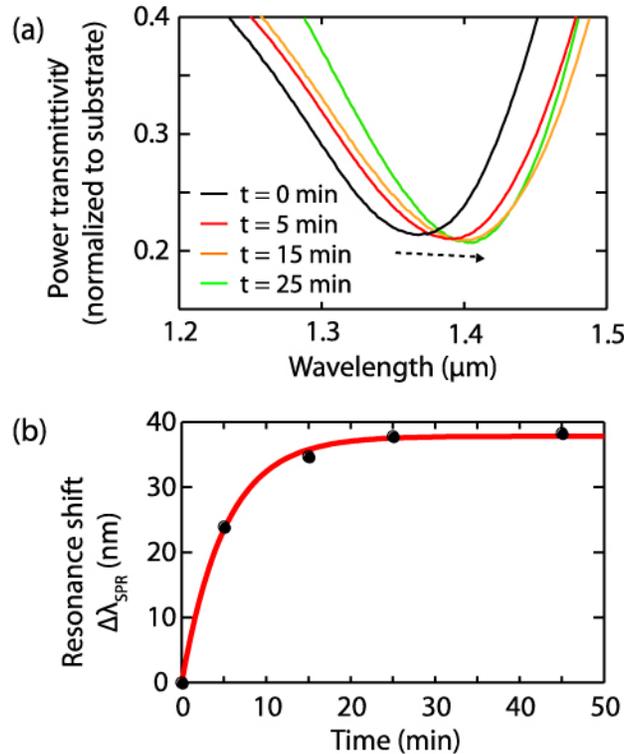


Fig. 4. (a) Transmission spectra at different exposure times to ethylenediamine vapour. (b) Saturation curve showing the resonance shift as a function of exposure time, and fitting to the Langmuir model. The spectrum at 45 min is not shown for the sake of clarity

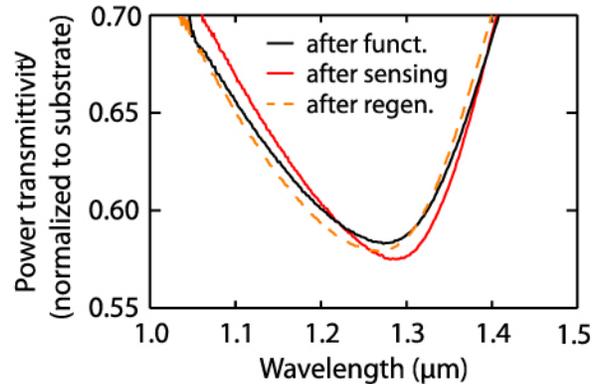


Fig. 5. Transmission spectra after the functionalization of the silicon surface (black curve), after sensing of ethylenediamine (red curve) and after heating at 150°C (dashed curve). Note that the power transmission levels differs from previous results due to the sample being from a different fabrication run.

5. Conclusions

In summary, we have demonstrated the use of LSPR of gold nanodisks on silicon in which we functionalized the silicon substrate surface for chemosensing purposes, unlike usual metal

functionalization. This is possible thanks to the electric field of the nanodisk resonance being strong at the silicon surface surrounding it. The sensor was designed to show a strong resonance in the infrared regime, showing a high sensitivity of the system to SAM formation and subsequent binding events. The silicon surface instead of the gold surface was functionalized with 3-(ICPTS) containing isocyanate as functional group. The sensing ability of the system was investigated exposing it to amine vapour. Isocyanate-amine binding events led to significant red-shifts in the resonant wavelength up to 37 nm when the saturation level was reached. This value corresponds to a relative resonance shift $\Delta\lambda_{\max}/\lambda_0 = 0.027$. Taking advantages of the thermally reversible interaction isocyanate-amine, we demonstrated that the surface was easily regenerated by heating of the sensor, avoiding in this way the use of chemical reactants which could damage the metallic nanostructures. Further work will include the optimization of the metallic nanoparticle in order to maximize the SPR red-shift displacement when applying the organic substances.

Acknowledgements

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