

Photo-acoustic spectroscopy detects nanostructures against resonant and absorbing substrates

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Received 6 October 2025 / Accepted 20 November 2025

Abstract. Photo-acoustic spectroscopy is a powerful photo-thermal method for scattering-free, contactless and non-destructive measurements of absorption. In plasmonics and nano-photonics, it allows for characterization of light-matter interactions leading to non-radiative relaxation processes, which generate heat. Here, we address the issue of detecting absorption signal of periodically nanostructured layer of gold, sitting on a commercial, absorbing substrate. The nanostructured plasmonic layer alone exhibits resonant peaks in the near-infrared range due to a 2D array of elliptical nanoholes in Au. The substrate itself has cavity interference resonances in the same range, due to a layer of Si_3N_4 on Si wafer. Conventional optical techniques are influenced by scattering, which complicates the characterization of the nanostructures' absorption against the properties of the substrate. We apply photo-acoustic technique with a widely tunable laser source to measure the absorption spectra of these geometries, as well as on an Au-covered substrate without nanoholes and on a bare Si substrate. A microscope enabled us to differentiate the nanohole response from its surroundings, while the tunable modulation frequency allowed for studying different absorption depths. Complementary optical simulations reveal the spatial distribution of absorption, in good agreement with experimental results. A major potential of the proposed approach lies in monitoring and discriminating nanoscale structural changes in thin absorbing layers against the strongly absorbing substrate background, which is of great importance in situations involving sensing of low quantity of absorbing material placed on commercial wafers. Moreover, besides resonant plasmonic effects, this photo-acoustic set-up and modelling can be further adapted to study light coupling with plasmonic nanohole arrays in terms of incident light angle of incidence and polarization.

Keywords: Photo-acoustic spectroscopy, Plasmonics, Nanohole, Absorption.

Introduction

Absorbing materials convert absorbed electromagnetic wave energy into heat via non-radiative deexcitation, giving rise to photo-thermal effect. Photo-thermal techniques such as photo-acoustic [1–5], thermal lens [6–8] and photo-deflection [9] spectroscopies study various consequences of absorption-induced heating, allowing for non-destructive, contactless, sensitive and non-invasive characterization of optical and thermal properties of matter. In particular, photo-acoustic effect emerges when a material absorbs a modulated electromagnetic wave, heats up and cools down in cycles, and, consequently, creates a pressure wave, i.e., acoustic signal [10]. When the absorbing medium is closed in a photo-acoustic cell, the acoustic signal phase and

amplitude can be caught by a microphone at the modulation frequency, without any direct influence of the scattered light. This potentially allows for direct, scattering-free, sensitive, and low-cost measurement of spectral absorption properties of thin films and nanostructured surfaces, of great importance in modern plasmonics and nano-photonics.

Photo-acoustic spectroscopy (PAS) is efficiently applied to study optical properties of plasmonic nanostructures on transparent glass substrates: in ref. [11] it revealed plasmon-mediated absorption in a 2D array of nanoholes in Au, while in ref. [11] we reported on extrinsic chiral behavior of asymmetric Ag semishells. Issues arise in more complex environments – when nanostructures are grown on strongly absorbing or resonant substrates, where the resonant absorption of a thin nanostructured layer can be masked by the strong background PAS signal arising from the substrate. We previously solved this issue by increasing

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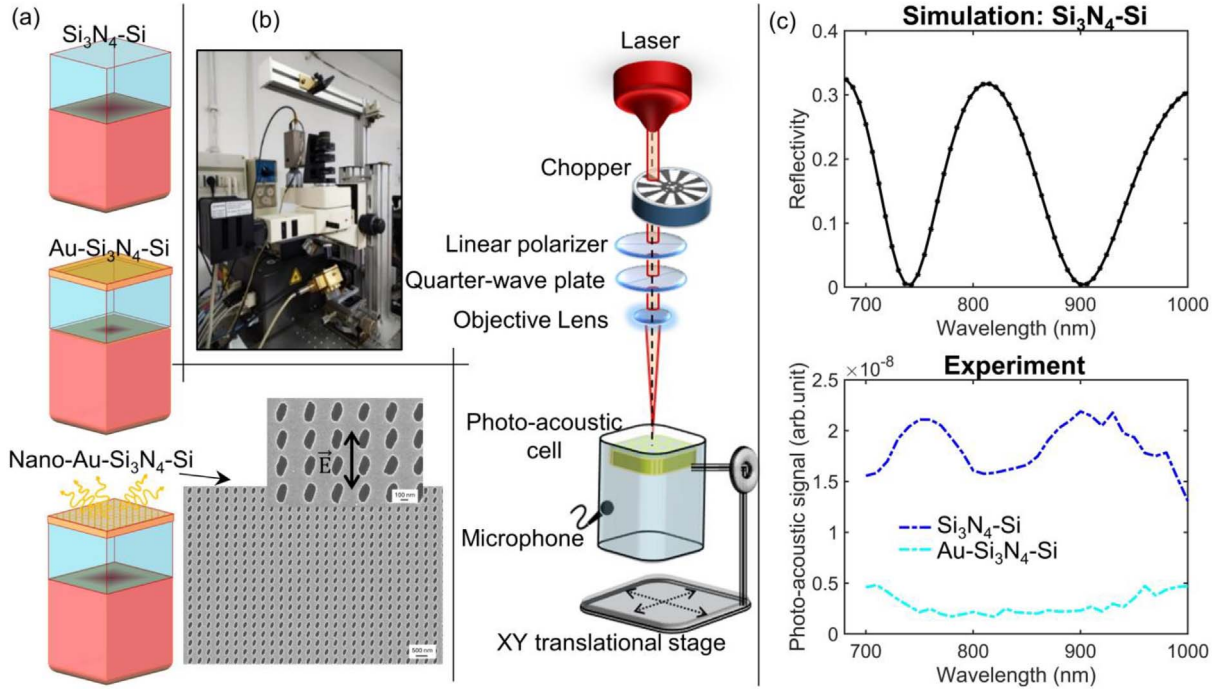


Figure 1. (a) Samples investigated are $\text{Si}_3\text{N}_4\text{-Si}$ (Si substrate with 1,022 Si_3N_4), $\text{Au-Si}_3\text{N}_4\text{-Si}$ (60 nm Au on the top of $\text{Si}_3\text{N}_4\text{-Si}$), and $\text{Nano-Au-Si}_3\text{N}_4\text{-Si}$ (elliptical nanohole array fabricated in Au on $\text{Si}_3\text{N}_4\text{-Si}$). (b) Photo-acoustic spectroscopy set-up, enriched with a microscope, allows for independent tuning of parameters: polarization, power, modulation frequency, excitation beam diameter and position; inset: photograph of the set-up. (c) Simulations and raw PAS amplitude spectra measured at 81 Hz for $\text{Si}_3\text{N}_4\text{-Si}$ and $\text{Au-Si}_3\text{N}_4\text{-Si}$: measured absorption peaks well agree with the calculated reflectivity dips.

the light modulation frequency f , as the thermal diffusion length scales with $1/\sqrt{f}$: contribution of the nanostructured upper part of the sample to the PAS absorption signal increases with the increase of f . In ref. [13] we studied $\sim 5 \mu\text{m}$ tall GaAs nanowires grown on Si, which couple light to strongly absorbing, resonant leaky waveguide modes. These modes were detected by increasing f from 25 Hz to 225 Hz. However, the overall PAS amplitude decreases with the increase of f [14, 15], hence modern PAS set-ups require the power tunability of the excitation light beam.

In this work, we explore the potential of widely tunable PAS to study the absorption properties of plasmonic nanostructures on absorbing and strongly resonant substrates. First, we consider a commercial Si- Si_3N_4 substrate, where $\sim 1 \mu\text{m}$ of Si_3N_4 forms a cavity with interference resonances in the near-infrared range. Next, we investigate the same substrate covered by a layer of Au, which dramatically decreases the absorption. Finally, we pattern Au into a 2D array of nanoholes and analyze the absorption differences with respect to the substrate exploiting PAS microscopy. We further employ optical numerical simulations to relate the electromagnetic behavior to the measured photo-thermal properties.

Material and methods

Figure 1a shows sketches of the three samples investigated. The first sample is a commercial substrate where Si is

covered with 1,022 nm of Si_3N_4 , i.e., $\text{Si}_3\text{N}_4\text{-Si}$, deposited by plasma enhanced chemical vapour deposition. The second sample has 60 nm of Au on the top of $\text{Si}_3\text{N}_4\text{-Si}$, i.e., $\text{Au-Si}_3\text{N}_4\text{-Si}$. The nanostructured sample, $\text{Nano-Au-Si}_3\text{N}_4\text{-Si}$, is a $100 \times 100 \mu\text{m}^2$ area of elliptical nanoholes in Au, fabricated by electron beam lithography (EBL). In detail, a negative resist (AN 7520.07) has been spincoated on a $\text{Si}_3\text{N}_4\text{-Si}$ substrate, and elliptical nanoholes have been patterned, with a periodicity of 400 nm. After development, 60 nm of Au has evaporated. A thin layer of Ti (5 nm) was used for better adhesion of Au to Si_3N_4 . After the lift-off process, performed in acetone for 60 h, the 2D array has been characterized by Scanning electron microscope (SEM), which a representative image can be seen in the inset; the black arrow represents the incidence polarization of the excitation under normal incidence. Figure 1b shows the photo-acoustic set-up positioned on a translation stage under normal incidence. It allows for tunable wavelength in the (680–1,000) nm range (including tunable power), tunable chopper frequency (up to 1,600Hz), and the precise adjustment of the laser position and focus by a microscope, as shown in the inset. In this work, the light is focused to 70 μm diameter. To gain “optical” insight into the absorption distribution in the investigated geometries, we further employ a commercial 3D electromagnetic solver based on finite-difference-time domain by Lumerical [16]. Nanoholes are modelled by including their ellipticity (major and minor axes diameters of 280 nm and 140 nm), and an in-plane tilt of 20°. Figure 1c shows great agreement between the

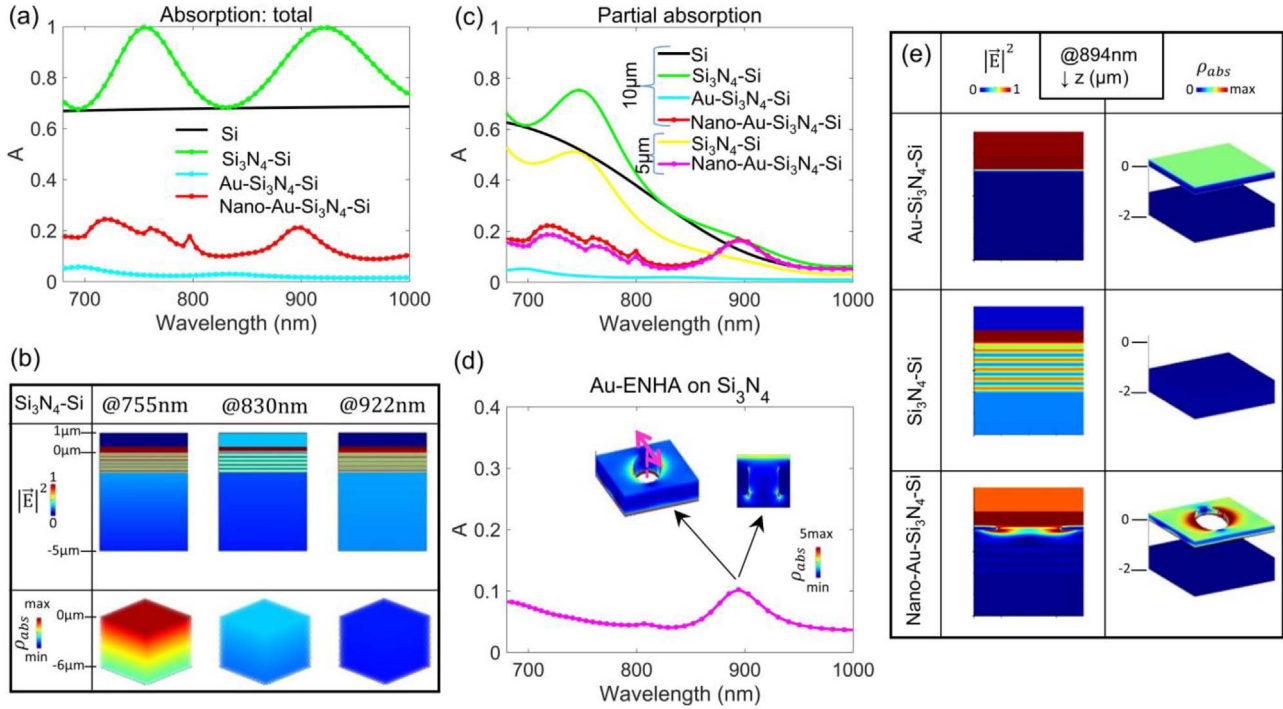


Figure 2. (a) Total absorption calculated as 1-reflectivity shows resonant modes in Si₃N₄-Si and overall lower absorption in the nanostructured sample. (b) Distribution of electric field intensity and absorption density in Si₃N₄-Si strongly depends on Si behavior at cavity resonant wavelengths. (c) Partial absorption is calculated by integrating absorption density over first 5 μ m or 10 μ m of Si in Si and Si₃N₄-Si, and adding the Au part for Au-Si₃N₄-Si and Nano-Au-Si₃N₄-Si. (d) Total absorption of Au ENHA on Si₃N₄ shows resonant absorption peak at 894 nm. (e) Electric field intensity and absorption density in the first 2 μ m of depth of the three samples.

reflectivity dips of the simulated Si₃N₄-Si with the PAS absorption peaks measured in the same sample. These initial measurements were performed at 81 Hz, and the raw PAS amplitude was normalized to the incident laser power. In comparison, the Au-Si₃N₄-Si sample showed very low absorption, as expected due to its high reflectivity. For further normalization, we also measured PAS signal from 600 μ m Si wafer.

Results and discussion

Where does the absorption take place at different wavelengths in geometries using Si₃N₄-Si as a substrate? As none of the incident power gets transmitted by our samples in the (680–1,000) nm investigated wavelength range, we first calculate the total absorption as 1-reflectivity. Figure 2a shows the resonant absorption peaks in the Si₃N₄-Si compared to a bare Si substrate, Nano-Au-Si₃N₄-Si overall absorbs less than Si₃N₄-Si due to large scattering. As expected, with respect to Au-Si₃N₄-Si the nanostructuring leads to the absorption enhancement. Figure 2b shows the confinement of the electric field intensity and absorption density at absorption peaks and dip wavelengths in Si₃N₄-Si; 0 μ m is the upper boundary of Si₃N₄, while the excitation comes from the top with the source position at 300 nm. At the two absorption peak

wavelengths, electric field is strongly confined in Si₃N₄, and reflection is suppressed. However, the Si absorption depth increases more than 5 times from 755 nm to 922 nm, leading to very different absorption density distribution in the first 5 μ m of propagation. We further integrate the absorption density over the volumes including first 10 μ m or 5 μ m of Si below Si₃N₄, including the nanostructured Au on the top, Figure 3c. Around 900 nm, the absorption of Nano-Au-Si₃N₄-Si does not depend on the volume of Si included, suggesting that the total absorbed signal comes from the nanostructured part involving 5/60 nm of Ti/Au. In this range, Nano-Au-Si₃N₄-Si has a absorption higher than its substrate for 5 μ m of depth. To check the influence of the Si₃N₄-Si background, we next investigate the optical properties of the elliptic nanohole array (ENHA) of the same geometric parameters on Si₃N₄, Figure 2d. At 894 nm, there is plasmonic resonant absorption peak resulting in confinement of the field between the ENHA and the substrate. We next visualize the electromagnetic distribution in the three samples at this wavelength, in the space from 1 μ m above until 1 μ m below Si₃N₄ layer, Figure 2e. Au-Si₃N₄-Si has negligible absorption on the Au border, while Si₃N₄-Si requires larger distances to absorb the wave. Finally, Nano-Au-Si₃N₄-Si confines the field on the plasmonic part, leading to an enhanced absorption [17].

We next employ PAS to characterize absorption in Si, Si₃N₄-Si and Nano-Au-Si₃N₄-Si at 54 Hz and 408 Hz.

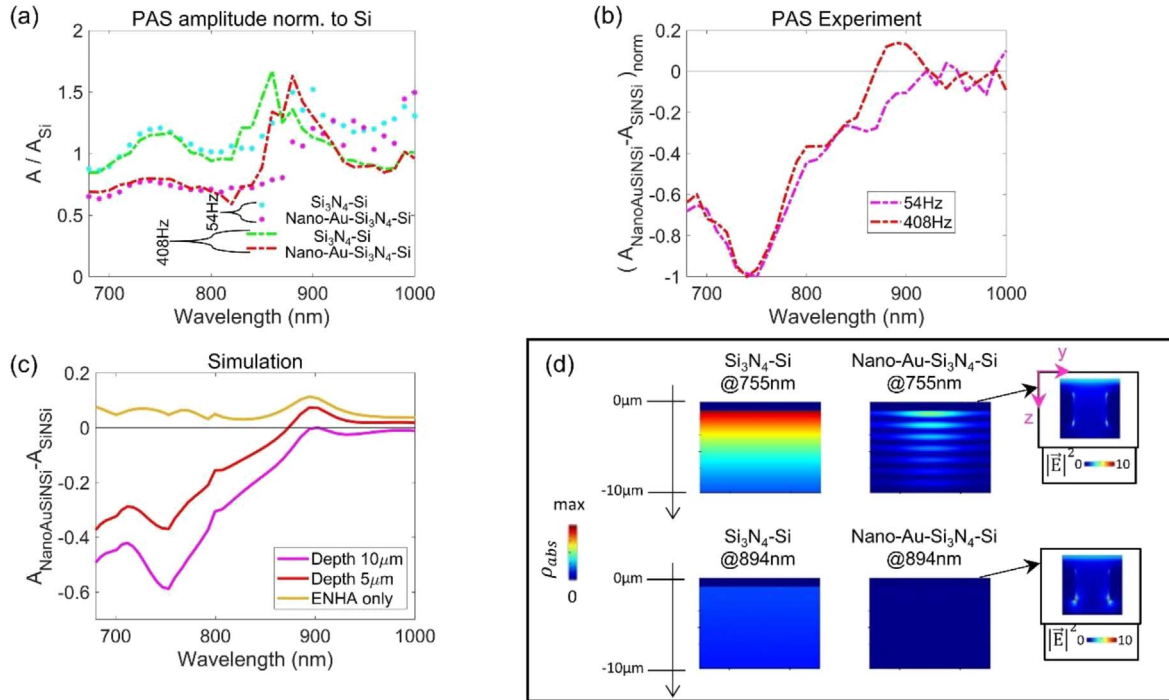


Figure 3. (a) Photo-acoustic spectra of $\text{Si}_3\text{N}_4\text{-Si}$ and $\text{Nano-Au-Si}_3\text{N}_4\text{-Si}$ at 54 Hz and 408 Hz, normalized to the bare Si spectra obtained at the same frequencies. (b) Experimental absorption difference between $\text{Nano-Au-Si}_3\text{N}_4\text{-Si}$ and $\text{Si}_3\text{N}_4\text{-Si}$, normalized to maximum, at 54 Hz and 408 Hz. (c) Simulations of absorption differences between $\text{Nano-Au-Si}_3\text{N}_4\text{-Si}$ and $\text{Si}_3\text{N}_4\text{-Si}$, where the partial absorption was integrated in over 10 μm or 5 μm of Si depth and including the upper plasmonic layers for the nanostructured sample. (d) Absorption confinement differences between $\text{Nano-Au-Si}_3\text{N}_4\text{-Si}$ and the substrate over first 10 μm of depth, at the absorption difference dip at 755 nm and peak at 894 nm. Insets plot the electric field intensity around nanohole.

Figure 3a shows PAS signals normalized to Si at the corresponding wavelengths. For $\text{Si}_3\text{N}_4\text{-Si}$, at both modulation frequencies absorption peaks with respect to Si following cavity resonant behavior. At 54 Hz, $\text{Nano-Au-Si}_3\text{N}_4\text{-Si}$ is lower than the $\text{Si}_3\text{N}_4\text{-Si}$ at almost all wavelengths. At 408 Hz, however, absorption is greater than that of Si and $\text{Si}_3\text{N}_4\text{-Si}$ around 900 nm. We further focus on the absorption difference between the nanostructure and its substrate. Figure 3b plots spectra of PAS signal difference between $\text{Nano-Au-Si}_3\text{N}_4\text{-Si}$ and $\text{Si}_3\text{N}_4\text{-Si}$, normalized to its maximum: $(A_{\text{NanoAuSi}_3\text{N}_4\text{Si}} - A_{\text{Si}_3\text{N}_4\text{Si}})_{\text{norm}} = (A_{\text{NanoAuSi}_3\text{N}_4\text{Si}} - A_{\text{Si}_3\text{N}_4\text{Si}}) / |\max(A_{\text{NanoAuSi}_3\text{N}_4\text{Si}} - A_{\text{Si}_3\text{N}_4\text{Si}})|$. Although PAS signal strongly decreases in amplitude from 54 Hz to 408 Hz, and the total absorption of $\text{Nano-Au-Si}_3\text{N}_4\text{-Si}$ around 900 nm is less than 20%, PAS is able to monitor spectral behavior of this difference. Optical simulations of this difference show great agreement with PAS when the partial absorption includes first 5 μm of Si below Si_3N_4 in both samples, Figure 3c. We finally plot the absorption density yz cross-section from the top until 10 μm of depth, Figure 3d. At 755 nm, strong substrate resonance leads to larger absorption with respect to $\text{Nano-Au-Si}_3\text{N}_4\text{-Si}$, while the absorption of the latter comes from both nanostructured part on the top, and Si, as seen from the periodic pattern decreasing in intensity. At 894 nm, all of the nanostructured absorption is confined in the plasmonic array, overcoming the Si absorption in the $\text{Si}_3\text{N}_4\text{-Si}$ case.

Conclusion

We have employed photo-acoustic spectroscopy and optical simulations to study absorption properties of nanostructures standing on resonant and absorbing substrates. Photo-acoustic signals were studied at low and high modulation frequencies to enhance the nanostructured layer contribution to the total PAS signal. Numerical investigation of absorption density at different substrate depths shows the importance of knowing the substrate behavior in detail, before the PAS modulation frequency gets tuned to access upper volumes of the sample. The differences between the nanostructured part and the substrate in the experiment agrees well with the absorption simulations in 5–10 μm . Further modelling of thermal responses, including different thermal boundaries, would be required to directly connect f with thermal diffusion length in nanostructured sample. In conclusion, PAS with multiple tunable parameters and a microscope can be used to study absorption in arrays of elliptical nanoholes, theoretically proposed for strong planar chirality [18, 19].

Acknowledgments

Alessandro Belardini and Emilija Petronijevic acknowledge LASAFEM Sapienza Università di Roma Infrastructure Project 2017 n. MA31715C8215A268 and PRIN 2022 PNRR Project INSPIRE n. P2022LETN5 founded by the European

Union – NextGenerationEU. Emilija Petronijevic acknowledges Sapienza Università di Roma project “Progetti di Ricerca Medi 2023 – n. protocollo RM123188F1CB517D” for supporting the collaboration. Sonia Freddi and Monica Bollani acknowledge Polifab, the micro and nanofabrication facility of Politecnico di Milano, for supporting the devices nanofabrication. L.A. acknowledges MUSA – Multilayered Urban Sustainability Action project, funded by the European Union – NextGenerationEU.

Funding

This research received no external funding.

Conflicts of interest

The authors have nothing to disclose.

Data availability statement

Data obtained in this work are not publicly available at this time but may be obtained from the authors upon reasonable request.

Author contribution statement

Conceptualization, E.P., L.C.A. and H.A.; Methodology, M.B., L.C.A. and A.B.; Software, E.P. and S.F.; Validation, A.B., L.C.A., M.B.; Formal Analysis, E.P. and L.C.A.; Investigation, E.P., H.A., S.F., L.A., R.S.; Resources, A.B.; Data Curation, E.P. and S.F.; Writing – Original Draft Preparation, E. P.; Writing – Review & Editing, A.B., S.F., M.B., L.A. and R.S.; Visualization, E.P. and S.F.; Supervision, M.B., R.S., L.C.A. and A.B.

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