Ultrathin Semiconductor Superabsorbers from the Visible to the Near-Infrared

Pau Molet, Juan Luis García-Pomar, Cristiano Matricardi, Miquel Garriga, Maria Isabel Alonso, and Agustín Mihi*

The design of ultrathin semiconducting materials that achieve broadband absorption is a long-sought-after goal of crucial importance for optoelectronic applications. To date, attempts to tackle this problem consisted either of the use of strong—but narrowband—or broader—but moderate—light-trapping mechanisms. Here, a strategy that achieves broadband optimal absorption in arbitrarily thin semiconductor materials for all energies above their bandgap is presented. This stems from the strong interplay between Brewster modes, sustained by judiciously nanostructured thin semiconductors on metal films, and photonic crystal modes. Broadband near-unity absorption in Ge ultrathin films is demonstrated, which extends from the visible to the Ge bandgap and is robust against angle of incidence variation. The strategy follows an easy and scalable fabrication route enabled by soft nano-imprinting lithography, a technique that allows seamless integration in many optoelectronic fabrication procedures.

The prospect of an efficient clean energy source and the need of converging light speed data transfer with current electronic systems push the scientific community into developing more economic and efficient ways to convert light into active electrons.[1] A first step to do so is to optimize the thickness of the active layer of the device to capture the maximum number of photons from the optical spectrum. In current crystalline silicon solar cells, thicknesses up to 300 µm provide the best performing devices.[2] However, not all materials can afford such widths due to low-mobility carriers[2,3] or expensive raw materials.[4] Diffusion lengths and recombination times limit the thickness and efficiency of many optoelectronic devices. A compromise between total absorption and conversion efficiency often needs to be reached.[5] Light-trapping schemes[5] play a major role in balancing out optimum thicknesses for charge extraction and efficient light absorption.[6] The ultimate goal of a light-trapping strategy is to achieve complete absorption of light in a broad spectral range while using the minimum amount of photoactive material. Traditional wafer-based technologies have extensively exploited light-trapping strategies up to a point where the classical limit of light trapping[7,8] is almost reached.[9] There is, however, an increasing interest in further decreasing the thickness of the active layer below the micron, where new properties appear for classic materials (such as flexibility for silicon[10]) and new materials like plastics[11] or nanocrystals[12,13] can be used at lower processing costs. Capturing light in such ultrathin devices requires redesigning the strategy, moving away from traditional ray optics approximations into the wave optics regime.[6] Many wave optics based designs are being currently investigated: photonic crystals (PhCs),[14,15] plasmonics,[16,17] and microresonators[18–20] provide new and exciting means of confining light in subwavelength thin films. Nevertheless, strong absorption enhancements are not restricted exclusively to the above-mentioned photonic architectures. Kats et al.[21] demonstrated flat nanometric films (up to 25 nm) of amorphous germanium (a-Ge) with 90% absorption in the visible range when deposited on optically thick gold films. Simply put, nanometric semiconductor coatings on metallic films act as Gires–Tournois interferometers[22,23] (a Fabry–Perot resonator where one of the interfaces is metallic). Such absorption comes from a strong interference effect originated by both the non-ideal behavior of the metal film at visible frequencies (allowing field penetration in the metal) and the high values of the complex refractive index of the semiconductor. In-depth analysis of these results revealed that this system sustains Fabry–Perot resonances (FPRs) coupled with Brewster modes[24] which are incident wave modes with no scattered wave that can be accessed from air. The excitation of this Brewster mode is possible at normal incidence and endows the system with omnidirectional strong absorption[25] (Figures S1 and S2, Supporting Information). The thickness of the semiconductor layer determines the position of the minimum in the reflectivity (maximum in absorption) of these resonances with the particularity that, because of the penetration depth in the metal, the resonant condition is below the classical λ/4 condition. Such...
a simple architecture is capable of exceeding the Yablonovitch classical limit\cite{7} for light trapping in thin films\cite{25} and has tremendous potential to boost performance in photovoltaics\cite{26}, photocatalysis\cite{27} and photodetection. However, the exploitation of these Brewster modes to improve light absorption is restricted to the visible regime, where the a-Ge film is strongly absorbing and the metal behavior is far from a perfect electric conductor (PEC). Therefore, this strategy fails to provide strong absorption peaks when the thickness of the semiconductor layer is increased, moving the resonant peaks into the NIR regime (Figure 1; Figure S3, Supporting Information). Hence, a light-trapping scheme that allows for a broadband absorption enhancement throughout the whole absorption region of germanium is still lacking. In this work, we demonstrate a broadband absorption in the semiconductor layer moving away from other broadband absorbers based on metamaterials\cite{28–30} where the main absorption is located in its metallic components, missing the generation of electron–hole pairs.

In our light-trapping photonic structure, incoming light is coupled to both Brewster modes and hybrid photonic–plasmonic modes leading to an unprecedented absorption enhancement from visible to the NIR (400–1500 nm) in a 70 nm thick germanium film. A germanium 2D square array of cylindrical holes is built on top of a gold film by means of soft lithography, a scalable technique compatible with reel to reel processing\cite{31–33}. In a cross-section of our a-Ge PhC, two a-Ge heights are differentiated, $t_1$ and $t_2$ (Figure 2): the overall layer of $t_2 = 70$ nm and the bottom part of $t_1 = 15$ nm inside the holes (55 nm depth). These two heights of a-Ge together with the

![Fabrication process of the nanostructure by nanoimprint lithography: a) the a-Ge layer deposition on gold by MBE (1), the photoresist spin coating (2), the nanoimprinting step (3), the reactive ion etching to expose the gold film underneath (4), the resist removal (5), and the second deposition of a-Ge (6). b) Top view and cross-sectional (inset) SEM images of a nanostructured 55 nm thick a-Ge layer with a square array of cylindrical holes on gold (step 5 in fabrication scheme). c) Top view and cross-sectional (inset) SEM images of a 70 nm thick a-Ge square array of cylindrical holes filled with 15 nm thick a-Ge (step 6 in fabrication scheme). d) Schematic depiction of the cross-section of the a-Ge photonic crystal on gold. Two distinct heights of a-Ge can be distinguished corresponding to $t_1 = 15$ nm and $t_2 = 70$ nm in the actual sample. e) Tilted SEM view of the final a-Ge photonic crystal. Inset: Photograph of four germanium photonic crystal structures on gold with $4 \times 4$ mm$^2$ patterned areas.](image-url)
metallic substrate allow the architecture to sustain simultaneously: (i) a Brewster mode in the visible range associated with $t_1$ and (ii) a suppression of backscattering in the NIR due to the coupling between the FPR of the thickness $t_2$ and the photonic–plasmonic modes of the nanostructure. The combination of the previous phenomena results in an integrated absorption in the a-Ge of 61% from 400 to 1500 nm. This represents an enhancement of 78% compared to the flat configuration with 70 nm germanium film on gold. The frequency range of absorption enhancement depends on structural parameters such as the radius, depth of the cylindrical cavities, and the center-to-center distance between them. Furthermore, the dispersion of the photonic architecture remains independent to the angle of incidence as proven by our finite difference time domain (FDTD) simulations, indicating that this structure is a formidable candidate for broadband angle independent light absorption.

The 2D PhC structure designed using FDTD simulations maximizes the absorption of the system from 400 to 1500 nm (see the Experimental Section). The square array was chosen over other geometries because of the more extensive set of reciprocal lattice vectors sustained by the photonic crystal, hence the higher number of resonant modes contributing to the absorption spectrum. Regarding the morphology of the photonic crystal slab, an air-hole array was preferred over a germanium pillar nanostructure due to its easier fabrication procedure, however analogous results can be obtained with a pillar array as illustrated in Figure S4 in the Supporting Information. The thickness of the a-Ge layer on gold determines the frequency range at which the FPRs appear (Figure 1). The photonic crystal profile with two differentiated heights (Figure 2d) allows to excite these resonances both at visible and NIR range. The filling fraction between both heights of a-Ge present in the photonic architecture determines the interplay between the absorption at visible versus NIR wavelengths. To achieve precise control over all the thicknesses involved in the structure, the a-Ge layer deposition took place in two steps as summarized in the fabrication procedure (Figure 2). In brief, a 55 nm a-Ge layer was deposited onto a gold-coated substrate by molecular beam epitaxy (MBE) (Figure 2a). After the soft nanoimprinting process, a dry etching step is performed to expose the gold substrate through the holes followed by the resist removal. At this stage of the process (Figure 2b), the structure, a 55 nm a-Ge PhC, exhibits a strongly enhanced absorption in the NIR range (Figure 3b). In order to amplify the absorption in the visible range, a second 15 nm Ge layer is deposited (Figure 2d). The resulting photonic structure consists of thin a-Ge layer $t_1$ deposited at the bottom of the hole array surrounded by a thicker a-Ge layer $t_2$ (Figure 2c–e). The final photonic architecture strongly absorbs visible wavelengths while exhibiting intense absorption peaks reaching almost 100% at the NIR range (Figure 3a). The absorption spectra of two flat a-Ge films on gold (Figure 3c,d) illustrate the FPR modes excited at each thickness. On one hand, a 15 nm thick a-Ge layer (Figure 3d) achieves a single almost total absorption peak at 760 nm. On the other hand, the absorption of the 70 nm flat a-Ge film on gold (Figure 3c) shifts toward the NIR, but falling below 50% at 1400 nm (Figure S3, Supporting Information). In comparison, the absorption measured in the final a-Ge photonic architecture is much more than the sum of the two radiative modes sustained by the different a-Ge thicknesses; there is an additional contribution to the absorption provided by the photonic crystal geometry, greatly improving the NIR response of the film.

We now investigate the role of the photonic crystal geometry in the enhancement in absorption, especially at the NIR frequencies where there are no Brewster modes to couple to. To elucidate the different resonant modes sustained by our photonic structure, the total absorption was calculated for architectures with a fixed radius $r = 300$ nm and thicknesses $t_1 = 15$ nm and $t_2 = 70$ nm, upon varying the lattice parameter $L$ (Figure 4a). The dashed line corresponds to a lattice parameter of $L = 700$ nm, corresponding to the photonic architecture under study in Figure 4b. The simulated total absorption accurately reproduces the position of the absorption peaks. From the fitting, it is also possible to extract the fraction of light absorbed by the a-Ge layer, being the rest of the absorbed light lost in the gold substrate (Figure 4b).

Next, we analyze the different resonances that originate the absorption peaks by looking at the spatial distribution of the electric field in the structure (Figure 4c) at the three wavelengths encircled in Figure 4a. In the visible spectrum, at a wavelength $\lambda = 600$ nm, the resonance (peak I) is due to the strong coupling of the incident light to the Brewster mode produced by the strong interference (FPR) in the $t_1$ slab (Figure 4c). This peak is very broad (from 500 to 900 nm) due to the high extinction of the semiconductor layer in the quasi-bound regime. The quasi-bound regime occurs when the real parts of the permittivities satisfy the relation $-\varepsilon'_{Ge} < \varepsilon'_{Au} < 0$. This condition leads to broad absorption peaks related to highly damped surface modes (Figure S2, Supporting Information).
The position of the Brewster resonance is not affected by the increase in lattice parameter $L$ (Figure 4a, visible regime), only a decrease in the magnitude of the absorption occurs when the filling fraction of $t_1$ decreases with respect to that of $t_2$. This mode (I) intersects with the first order of diffraction for $\lambda \approx L$ (in our example, $L = 700$ nm) that corresponds to the straight diagonal mode in Figure 4a. In sum, for short wavelengths the electromagnetic radiation is mostly enclosed within the thin a-Ge layer and diffracted modes of the architecture also appear.

The maps of the electric field distribution at longer wavelengths, $\lambda \approx 1170$ and 1370 nm, (Figure 4cII,III) indicate the confinement of the electric field in the overall layer $t_2$ of a-Ge. Here, the field distribution follows the geometrical modes of the inverse a-Ge photonic crystal. In this regime, the total absorption approaches 100% with 80% of the absorption attributed to the a-Ge. Moreover, this absorption spectrum is robust against changes in the angle of incidence as proven by FDTD simulations for the two polarizations (Figure S5, Supporting Information).

Regarding the nature of these resonances, it is useful to remember that a bidimensional grating accesses parallel wavevectors $k_\parallel$ larger than $k_\parallel = \frac{2\pi}{\lambda}$ inside the photonic crystal. The parallel wavevector $k_\parallel$ can be obtained from Equation (1)

$$k_\parallel = k_{\parallel 0} \pm b_{\parallel} \frac{2\pi}{L}$$  

(1)

where $b_{\parallel 0} = \sqrt{b_x^2 + b_y^2}$ and $b_x, b_y = 0, 1, 2...$ A combination of numbers $\{b_x, b_y\}$ gives the diffraction order inside the semiconductor layer. The bidimensional periodicity grants access to the photonic–plasmonic modes with $k$ larger than the air–light line, which are a hybridization of the bare plasmonic modes with the Bloch modes of the periodic array (Figure S5, Supporting Information). The position of the FPR is determined by the resonant condition associated with thickness $t_2$, as is shown by the confinement of the electric field in this layer (Figure S5c, Supporting information). The absorption exhibited by our nanostructure in the NIR is the result of the coupling between the photonic–plasmonic modes and the FPR. The excitation of these modes leads to a hybridization of two surface waves at the interfaces Ge/Au and air/Ge that show evanescent fields in both air and Au layers (Figure S6, Supporting Information). These excited modes present a flat dispersion relation, indicating an associated group velocity much smaller than $c$ (i.e., a large density of states), which amplifies any light–matter interaction phenomena such as light absorption.[35] Moreover, these hybrid modes show a confinement of both magnetic and electric fields similar to findings in previous works[36–38] in which the interference of magnetic and electric dipoles plays a major role in the angle-suppressed scattering. The slow group velocity and the large confinement entail that the light is coupled to hybridized radiative plasmonic Bloch modes.

In sum, a 2D Ge photonic crystal deposited on a gold film exhibits a broadband absorption from the visible to the NIR range exceeding that of a more traditional periodic structure. The presence of the metal substrate transforms a high-index 2D photonic crystal into a superabsorbing photonic structured surface exhibiting highly localized resonant modes. The dramatic effect of the gold substrate in the confinement of the electromagnetic fields is further evidenced in the Figure S7 in the Supporting Information.

The position of the absorption peaks can be tuned by changing the structural configuration of our architecture, defined by the parameters $t_1, t_2, r$, and $L$, as is shown in Figure 4.
Figure 4a for the lattice parameter \( L \) and studied at length for the other parameters in the Figures S8, S9, and S10 in the Supporting Information. In photonic structures with larger lattice parameters and higher \( t_f \), the NIR absorption peaks redshift. This is illustrated for photonic crystals with \( t_f = 80 \) nm and lattice parameters \( L = 700 \) and 1100 nm (black curves) in Figure 5a,b. In order to maintain a high absorption in the visible region, we deposited 100 nm of a lossless dielectric layer \( (\varepsilon_{\text{ARC}} = 1.47) \) on top of the photonic crystal as an antireflection coating (ARC). This ARC layer decreased the impedance mismatch of the semiconductor with air, boosting the absorption in the visible spectrum, and producing an almost perfect total absorption in these frequencies (Figure 5). In this way, the a-Ge photonic crystal on gold with an ARC exhibits an 81% of total integrated absorption from 400 to 1500 nm (Figure 5a). The fraction of light absorbed in the germanium rises to a total of 69%, which represents a 101% enhancement of the a-Ge absorption compared to that of a flat film with the same thickness.

In summary, we demonstrate an 81% of total integrated absorption (69% in the semiconductor) over a broad spectral range, from 400 to 1500 nm, in an 80 nm germanium photonic crystal built on a gold layer. The herein demonstrated broadband absorption comes from the synergy of coupling the impinging light to Fabry–Perot resonances hybridized with Brewster modes in the visible spectrum, and with photonic–plasmonic modes sustained by the architecture in the near-infrared range. The thickness of the a-Ge layer determines the spectral position of the radiative modes, whereas the geometry of the photonic crystal dictates the frequencies for the Bloch modes. Through a rational design of the architecture, the absorption in the active layer exceeds over 100% that of a flat 80 nm a-Ge film on gold. Furthermore, the high-refractive index of the semiconductor renders the absorption profile of the photonic structure independent to the angle of incidence.

The fabrication of these photonic structures follows a highly scalable nanoimprinting technique, which adds to the appeal of the enhanced optical properties described herein. We believe this photonic structure has a tremendous potential for light-harvesting applications such as photodetection, photocatalysis, and photovoltaics. In addition, a properly designed interplay between Brewster and photonic–plasmonic modes may result in many exciting optical properties extendable to other systems and materials.

**Experimental Section**

2D Photonic Crystal Fabrication: 2D germanium photonic crystals on gold were fabricated by nanoimprint lithography using polydimethylsiloxane molds with patterned areas of 16 mm². Polished silicon wafers 500 µm thick were used as substrates. A gold film of 150 nm was deposited onto the Si wafer at 300 °C. A thin Cr layer was used in order to increase the adhesion of the Au layer on the substrate. Next, 55 nm of a-Ge were deposited using an MBE system. The base pressure was below 5 × 10⁻¹⁰ mbar and the substrate temperature was 25 °C. The deposition rate was set to 0.45 Å s⁻¹ and the desired a-Ge layer thickness was obtained by controlling the deposition time. Then, 350 nm of Shipley 1813 resist was spin coated on the Ge-coated Au films. The initial resist was diluted at 1:1 (w/w) in 2-methoxy-1-methylethyl acetate and spin coated at 7000 rpm with a 1000 rpm s⁻¹ acceleration for 40 s. The nanoimprinting procedure took place after the resist deposition, during thermal treatment at 125 °C on a hotplate. Once the resist was imprinted, the pattern was transferred to the a-Ge by reactive ion etching (RIE). An initial etching step of the residual resist layer was realized with oxygen plasma at 20 mL min⁻¹, 75 mTorr, and a forward power of 110 W. Next, the a-Ge etching was performed with a SF₆/CHF₃/O₂ mixture at 30/12/10 mL min⁻¹, 100 mTorr, and a forward power of 100 W. Any resist residue was removed with acetone rinsing. Eventually, 15 nm of a-Ge were deposited on the patterned sample following the initial MBE recipe. The 100 nm ARC coating was deposited on the completed samples by spin coating of a 1:6 (w/w) solution of hydroxypropyl cellulose (Aldrich) at 6000 rpm for 120 s.

**FDTD Design:** The numerical calculations were performed using Lumerical FDTD solutions (www.lumerical.com) and verified with the Wave Optics module of COSMOL Multiphysics (www.cosmol.com). The dispersion model of Au was taken from Johnson and Christy (69) and the a-Ge data was obtained from spectroscopic ellipsometric analysis. The simulated architecture reproduced the schematic shown in Figure 2a with the geometrical parameters extracted from SEM micrographs of
the actual samples. A linearly polarized plane wave source impinging a unit cell was modeled with a wavelength ranging from 400 to 2000 nm, providing a good agreement with experimental results.

Far-Field Reflection Measurements: An FTIR spectrophotometer attached to an optical microscope (Vertex 70 and Hyperion, Bruker) was used to obtain the far-field reflection measurements in the 400–2200 nm range. The background reflection spectrum was set with a silver mirror that exhibits a 96% reflectivity in the tested range of wavelengths. Reflected light was collected through a 4x objective with a 2×2 mm spatial aperture.

Scanning Electron Microscopy (SEM): The used SEM QUANTA FEI 200 FEG-ESEM with a field emission gun source. All the images were taken using a 15 kV beam to generate the secondary electrons in a high-vacuum regime (10–3 Pa).

Ellipsometry Measurements: The optical constants, thickness and roughness of the a-G layer were measured with ellipsometry (Figure S11, Supporting Information). A SOPRALAB GESSE rotating polarizer ellipsometer was used to take the measurements. The examined spectral range went from 250 to 1030 nm and several incidence angles were used (55°, 65°, 75°, and 77°). An in-house code was used for the data analysis and a Cody–Lorentz dispersion model[40] utilized to parameterize the optical constants in and beyond the range of the used ellipsometer.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors thank the Spanish Ministry of Economy and Competitiveness (MINECO) for its support through Grant MAT2016-79053-P. A.M. was funded by a Ramón y Cajal fellowship (RYC-2014-16444). The work at ICMM was carried out under the auspices of the Spanish Severo Ochoa Centre of Excellence programme (Grant No. SEV-2015-0496). This project has received funding from the European Research Council (ERC ENLIGMENT) under the European Union’s Horizon 2020 research and innovation programme (Grant No. 637116).

Conflict of Interest
The authors declare no conflict of interest.

Keywords
broadband absorption, nanostructuring, photonic crystal, soft lithography

Received: October 9, 2017
Revised: November 22, 2017
Published online: