Generalized Brewster-Angle Effect in Thin-Film Optical Absorbers and its Application for Graphene Hydrogen Sensing

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ABSTRACT

Generalized Brewster angle (GBA) is the incidence angle at polarization by reflection for $p$- or $s$-polarized light takes place. Realizing $s$-polarization Brewster effect requires a material with magnetic response which is challenging at optical frequencies since the magnetic response of materials at these frequencies is extremely weak. Here, we experimentally realize GBA effect in the visible using a thin-film absorber system consisting of a dielectric film on an absorbing substrate. Polarization by reflection is realized for both $p$- and $s$-polarized light at different angles of incidence and multiple wavelengths. We provide a theoretical framework for the generalized Brewster effect in thin-film light absorbers. We demonstrate hydrogen gas sensing using a single layer graphene film transferred on a thin-film absorber at the GBA with $\sim$1 fg/mm$^2$ aerial mass sensitivity. The ultrahigh sensitivity stems from the strong phase sensitivity near point-of-darkness, particularly at the GBA, and the strong light-matter interaction in planar nanocavities. These findings depart from the traditional domain of thin-films as mere interference optical coatings and highlight its many potential applications including gas sensing and biosensing.

KEYWORDS: Brewster-angle effect, thin film optics, perfect absorbers, visible frequencies, graphene, gas sensing
The Brewster angle, $\theta_B$, is commonly defined as the angle at which the Fresnel’s reflection coefficients for $p$-polarized light vanishes\(^1\). For a given medium, the sum of the incident angle $\theta_i$ and transmitted angle $\theta_t$ is $\pi/2$ when $\theta_i = \theta_t$. The orthogonality condition draws a simple picture for realizing the Brewster angle effect. Light incident on a medium at $\theta_B$ induces electron oscillations in the direction of the electric field which give rise to reflected wavelets. The oscillating electrons, however, do not produce a field at points on the axis of oscillation. When $\theta_i + \theta_t = \pi/2$, the oscillation axis is in the direction of the reflected wave, hence, no reflection takes place. The Brewster effect is widely used in different applications, e.g., reducing glare of sun reflecting off horizontal surfaces and in laser physics in gain media, cavity mirrors, and in prisms to minimize reflection losses, as well as in high performance terahertz modulators\(^2\). Furthermore, Brewster angle microscopes rely on the enhanced phase sensitivity near the Brewster angle and can image monolayers at the air-liquid interface\(^3\). However, the phase sensitivity at the Brewster angle is thought to be insufficient for sensing applications as the local electric fields for dielectric substrates are small\(^4\).

The aforementioned common definition of the Brewster angle, however, assumes that the reflection occurs from a plane wave incident on a homogenous, non-magnetic, achiral, and isotropic material. The Brewster effect can take place for either $p$- or $s$-polarized light if one of these assumptions is violated. For example, it is known that a Brewster angle for $s$-polarized light exists in a magnetic material with permeability $\mu \neq 1$. In magnetic materials, there exists an angle where the reflected $s$-polarized light vanishes $\theta^*_{\mu}$, and another angle where the reflected $p$-polarized light vanishes $\theta^*_{\mu}$, such that $\theta^*_{\mu} \neq \theta^*_{\mu}$ for non-normal incidence\(^5\). For a magnetic medium, the sum of the incident angle and the GBAs $\theta^*_{\mu}$ does not need to be $\pi/2$ as long as
total destructive interference between the magnetic and electric dipoles takes place at \( \theta^{\mu\cdot\nu} \). Accordingly, the Brewster effect can take place even when the oscillation axis is not parallel to the wave reflection direction and the wavelets produced by individual oscillating electrons do not vanish at the reflection direction. What is necessary, however, is that the vector sum of the radiated field vanishes in the reflection due to destructive interference\(^6\). The Brewster angle, in its most general form, is the angle where only a single polarization is reflected due to the destructive interference between radiating electric and/or magnetic dipoles for the orthogonal polarization.

Realizing generalized Brewster effect at optical frequencies is challenging since the magnetic response of materials at these frequencies is very weak, i.e., \( \mu \sim 1 \). Metamaterials, however, can support negative permeability, thus a magnetic response is possible\(^7\)\(^-\)\(^9\). The generalized Brewster effect was realized experimentally using split ring resonators in the microwave region\(^10\)\(^-\)\(^11\). In the optical regime, GBA effect was demonstrated using all-dielectric metamaterials\(^12\). In addition to the intense lithography required to fabricate a metamaterial with a magnetic response, the Brewster angle demonstrated did not realize complete polarization of the reflected light in the visible frequencies, particularly for \( s \)-polarized light\(^12\). Strictly speaking, however, this demonstration did not exhibit true Brewster effect, rather showed unequal reflection for \( s \)- and \( p \)-polarizations which is a natural consequence of the Fresnel equations even in the absence of any magnetic response. On the other hand, \( s \)-polarized Brewster effect was shown in stratified metal-dielectric metamaterials due to changes in the effective magnetic permeability of the thin-film stack\(^13\). In addition, for nonmagnetic media, the \( s \)-polarized Brewster effect was demonstrated by adding a two-dimensional material at the interface between two media when the conditions for total internal reflection are satisfied such that reflected \( s \)-polarized light is absorbed.
fully by the graphene layer\textsuperscript{14}. Furthermore, GBA was demonstrated in anisotropic materials\textsuperscript{15} and chiral materials\textsuperscript{16}.

The assumption that the reflection occurs from a homogenous medium can also be violated by creating a multilayer structure where either the $s$- or the $p$- polarized light is reflected and the other polarization is extinguished\textsuperscript{17}. The generalized Brewster conditions of lithography-free planar stack of thin-films have been theoretically investigated where the inhomogeneity is due to stacking different materials\textsuperscript{18-24}. In this case, the GBA corresponds to an angle where electric dipoles in the inhomogeneous stack of materials destructively interfere. An experimental realization of GBA effect of a transparent film on an absorbing substrate, however, has not been demonstrated. Furthermore, the realization of the generalized Brewster effect can be used for sensing applications providing that it is associated with strong field localization.

In this letter, we investigate theoretically and experimentally the generalized ($p$- and $s$-polarization) Brewster conditions of a lossless dielectric film on an absorptive substrate at multiple wavelengths in the visible spectral region. By demonstrating, thin-film interference based perfect light absorption of a single polarization, the Brewster effect, i.e., polarization by reflection, is realized for both $s$- and $p$- polarized light at different angles of incidence. We further demonstrate hydrogen sensing using a hybrid platform of single layer graphene and the thin-film absorber. The realization of phase singularity in the ellipsometry phase parameter at the GBA accompanied by strong field confinement within the graphene layer in the thin-film cavity enabled ultrahigh hydrogen sensitivities of \( \sim 1 \) fg/mm\(^2\) with cheap materials and scalable fabrication process.

**Theory of Generalized Brewster effect in thin-film light absorbers**

We investigate the proposed design, i.e., a lossless dielectric film on a substrate with optical losses. Our system consists of a superstrate (refractive index $n_0$), a dielectric layer (refractive Index $n_d$, ...
thickness d), and a lossy substrate (refractive index $n_s + i k_s$). Using transfer matrix theory\textsuperscript{25}, we obtain expressions for the conditions necessary to realize the GBA effect for $p$- and $s$- polarized light in terms of the incidence angle $\theta_0$ and the phase thickness of the dielectric layer $\Phi_d \equiv 2\pi d \lambda^{-1} \sqrt{n_d^2 - n_0^2 \sin^2(\theta_0)}$ (see Supporting Information for detailed derivation).

(i) $p$-polarization:

$$\theta_0 \approx \tan^{-1} \left[ \frac{n_s}{n_0} \left( 1 + \frac{1}{2} k_s^2 \left( \frac{n_0^2(n_0^2 - 3n_d^2)}{(n_0^2 - n_d^2)n_s^4} + \frac{2(n_0^2(2n_d^2 - 3n_s^2) + n_s^4)}{n_s^2(n_0^2 - n_d^2)(n_s^2 - n_d^2)} \right) \right) \right],$$

$$\tan(\Phi_d) \approx \frac{n_d^2 k_s(n_s^2 - n_0^2) \sqrt{n_0^2(n_d^2 - n_s^2) + n_d^2 n_s^2}}{(n_0^2 - n_d^2)n_s^3(n_s^2 - n_d^2)}.$$

The first condition above defines a unique GBA $\theta_0$ at which $p$-polarized reflection is zero. Note that when $k_s \to 0$ it reduces to the standard Brewster angle, $\theta_0 \to \tan^{-1}(n_s/n_0)$. For finite $k_s$ with the materials we use, the correction due to a lossy substrate is quite small, so $\theta_0$ remains close to the conventional Brewster angle. The $\tan(\Phi_d)$ condition can be solved to find a set of dielectric layer thicknesses $d$ that will give zero reflection (there is more than one possibility since $\tan(\Phi_d + m\pi) = \tan(\Phi_d)$ for any integer $m$. Note that when $k_s \to 0$, this condition reduces to $\tan(\Phi_d) = 0$. In this case, one possible solution is $d = 0$, the conventional case where no dielectric layer is present. In addition, the conventional Brewster effect ($\theta_0 = \tan^{-1}(n_s/n_0)$) is realized for other $d$ values that satisfy the $\tan(\Phi_d) = 0$. However, when $k_s > 0$ we need a finite $d > 0$ to achieve zero reflection, i.e., there is no Brewster angle for a dielectric with optical losses unless we add an additional lossless dielectric with finite thickness.

(ii) $s$-polarization:
To get zero reflection for s-polarization, the real parts of the refractive indices must satisfy \( n_0 n_s > n_d \). Additionally, to get compact expressions, we assume \( n_s > n_d > n_0 \). The conditions are then given by:

\[
\theta_0 \approx \tan^{-1}\left[ \frac{n_0^2 n_s^2 - n_d^4}{(n_0^2 - n_d^2)^2} \left( 1 + k_s^2 \frac{n_0^2 (n_d^4 - (n_0^2 - 2n_d^2)n_s^2 - 2n_s^4)}{2(n_d^2 - n_s^2)^2(n_d^2 - n_0^2 n_s^2)} \right) \right] \quad (2)
\]

\[
\tan(\Phi_d) \approx \frac{(n_d^2 - n_s^2)^2}{n_s k_s \sqrt{(n_0^2 - n_d^2)(n_d^2 - n_s^2)}}
\]

As with s-polarization, the presence of \( k_s \) makes only minor corrections to the angle and thickness results. In the limit \( k_s \to 0 \) we find \( \theta_0 \to \tan^{-1}\sqrt{(n_0^2 n_s^2 - n_d^2)/(n_0^2 - n_d^2)^2} \) and \( \tan(\Phi_d) \to \infty \). The latter implies that \( \Phi_d \) in the lossless case must be equal to \((2m + 1)\pi/2\) for \( m = 0, 1, 2, \ldots \). Now \( d = 0 \) is no longer a valid solution, so one needs a dielectric layer to get zero reflection even when \( k_s = 0 \). When \( k_s > 0 \) the value of \( \Phi_d \) is shifted slightly away from these odd multiples of \( \pi/2 \), and hence \( \tan(\Phi_d) < \infty \).

**Experimental verification using methyl methacrylate coated silicon substrate**

To experimentally show that a transparent dielectric film on an absorbing substrate exhibits GBA effect in the visible, we spin coated methyl methacrylate (MMA) layer with thickness \( t = 500 \text{ nm} \) on a silicon (Si) substrate which demonstrates \( p \)-polarized Brewster effect (Figure 1a), and \( s \)-polarized Brewster effect (Figure 1b), at different wavelengths and angles of incidence. We measured the reflectance spectra as a function of wavelength (350 nm to 800 nm) and angle of incidence (40° to 85°) using a spectroscopic ellipsometer, see Supporting Information. The false color 2D plot of measured reflectance spectra of \( p \)- and \( s \)-polarization is shown in Figure 1c and Figure 1d, respectively. In particular, \( p \)-polarization exhibits low reflection above incidence angle.
60° and all angle minimum reflection is obtained for s-polarization. However, zero reflection is only possible for a single wavelength and at the Brewster angle for both polarizations. Accordingly, the thin film absorber supports GBA for multiple wavelengths (Supporting Information Figure S2). The rectangulated regions refer to wavelength and angle pairs where the generalized Brewster effect occurs for p-polarized light (solid squares) and s-polarized light (dashed squares). Clearly, the thin-film absorber supports two modes in the wavelength range of interest for both p- and s-polarizations.

To further clarify the generalized Brewster effect, we performed reflectance measurements as a function of incidence angle by selecting the wavelength in which zero reflection obtained for both polarizations. We note that since the substrates used in experiments are opaque, absorptance (A) is complimentary to reflectance (R), i.e., $A = 1 - R$. Accordingly, when $R \to 0$, the structure exhibits perfect light absorption. For p-polarization, zero reflection is obtained at 378 nm and 552 nm as shown in Figure 1e and Figure 1f, respectively. The recorded Brewster angle for p-polarization at 378 nm and 552 nm is 81° and 76°, respectively. For s-polarization, zero reflection is obtained at 450 nm and 752 nm as shown in Figure 1g and Figure 1h, respectively. The obtained Brewster angle for s-polarization at 450 nm and 752 nm is 73° and 68°, respectively. The calculated p- and s-polarization angular reflection was obtained using transfer matrix method (Supporting Information Figure S3). In the model, we solved the Fresnel’s equations for a three-layer system (air-MMA (500 nm)-Si) and experimentally obtained refractive indices of MMA were used26-27. It is important to note that Brewster angle increases with decreasing the incident wavelength for both polarizations in order to satisfy the amplitude condition for total destructive interference i.e., the amplitude of the out-of-phase partially reflected waves from all interfaces must be equal in magnitude28. This is because at lower wavelengths, the reflectance from Si is
significantly high. Accordingly, to satisfy the amplitude condition, the reflection from MMA must increase which is only possible at high incidence angles. We simulated the field distribution of the MMA/Si system at the Brewster angles (Supporting Information Figure S4). We have also experimentally investigated the GBA effect in MMA-Ge-glass system and confirmed that this system shows similar Brewster angles, however the incident wavelengths were the effect is observed are slightly red shifted (Supporting Information Figure S5 and Figure S6).

Figure 1. Generalized Brewster effect in a thin-film dielectric on lossy substrate system. A schematic of the MMA (500nm)-Si light absorber exhibiting (a) p-polarized Brewster effect, and (b) s-polarized Brewster effect. The measured angular reflectivity spectra for (c) p-polarized and (d) s-polarized reflectance spectrum of the thin film absorber. The rectangulated regions refer to wavelength and angle pairs where the generalized Brewster effect occurs for p-polarized light.
(solid squares) and $s$-polarized light (dashed squares). Measured angular reflectance is shown for $p$-polarization at (e) 378 nm, and (f) 552 nm, and for $s$-polarization at (g) 450 nm, and (h) 752 nm.

Note that the system still exhibits the GBA effect even when the lossy substrate is a layer of finite thickness. The mathematical conditions for zero reflectance no longer have tractable analytical forms, but the infinite substrate theory in Eqs. (1-2) remains a reasonable approximation even when the lossy layer thickness is comparable to the wavelength of the incident light. We can see this in Figure 2, which shows incidence angle (top row) and dielectric layer thickness $d$ (bottom row) needed to ensure zero reflectance for each polarization. The oscillation in GBA as a function of thickness is due to additional Fabry-Perot interference effects due to the finite thickness of Si. Figure 2 was calculated for an MMA layer of thickness $d$ on top of an Si layer of thickness $d_{Si}$ on top of glass and is plotted as a function of $d_{Si}/\lambda$, where $\lambda$ is the incident wavelength. The dashed lines represent the predictions of the theory for infinite Si. One can see that as $d_{Si}$ gets larger the results converge to the theory predictions. The deviations increase as $d_{Si}$ approaches $\lambda$, but within this range are still typically less than 10%.
**Figure 2.** Numerical transfer matrix theory results showing the conditions needed to achieve the generalized Brewster angle effect when the lossy substrate layer has a finite thickness. The system consists of: an MMA layer of thickness $d$, an Si layer of thickness $d_{Si}$ on glass. The top row shows the incidence angle needed to realize the Brewster effect as a function of $d_{Si} / \lambda$ for (a) $p$-polarization, incident wavelength $\lambda = 552$ nm; (b) $s$-polarization, incident wavelength $\lambda = 450$ nm. The bottom row (c-d) shows the corresponding MMA layer thickness $d$ that is required as an additional condition. The dashed lines correspond to the theoretical predictions for an infinite Si layer, described in Eqs. (1-2) of the main text.

**Experimental verification using light absorbing thin-film metasurface**

Perfect light absorption can occur in ultrathin dielectrics with $t \ll \lambda$, i.e., the dielectric coating does not need to satisfy the anti-reflection coating condition of $t = \lambda / 4 \, n$. This takes place in a
two-layer system with a dielectric coating and a substrate, when the destructive interference phase condition is satisfied due to the existence of an abrupt phase change, i.e., the phase is either 0 or π, at the air/dielectric or the dielectric/substrate interfaces. Because the perfect light absorption in ultrathin films rely on acquiring a phase and not propagating in a refractive medium, these thin-film light absorbers are considered metasurfaces.

**Figure 3.** Generalized Brewster angle effect (s-polarized) using light absorbing thin-film metasurface. Angular reflectivity spectra. Measured (a) p-polarized and (b) s-polarized reflectance spectrum.

Figure 3 shows the angular reflectance spectrum for an ultrathin perfect light absorber consisting of a 60 nm TiO₂ film on a 100 nm Ni substrate. For p-polarized light, perfect light absorption does not occur at any angle or wavelength (Figure 3a). On the other hand, the Brewster angle occur at 750 nm and 68° for s-polarized light (Figure 3b). The refractive index of TiO₂ at 750 nm is ~ 2.5, i.e., \( t = \lambda / 5 \).
Experimental verification of singular phase at the GBAs

Ellipsometry measures the complex reflectance of a system, \( \rho \) which is parametrized by the amplitude component \( \Psi \) and the phase difference \( \Delta \), such that \( \tan \Psi = \frac{|r_p|}{|r_s|} \) and \( \Delta = \delta_{\text{outgoing}} - \delta_{\text{incoming}} \), where \( \delta \) is the phase difference between the \( p \)-polarized and \( s \)-polarized light, such that \( \rho = \frac{r_p}{r_s} = \tan \Psi \ e^{i\Delta} \). Accordingly, ellipsometry parameters \((\Psi, \Delta)\) have unique characteristics at the Brewster angle. In particular, \( \Psi \) reaches a minimum (maximum) at the Brewster angle for \( p \)-polarized \((s \)-polarized\) light. Furthermore, beyond the Brewster angle, the reflection phase undergoes \( \sim \pi \) phase shift. Accordingly, we can obtain a singular phase (phase difference between \( p \)- and \( s \)-polarization) of the reflected light at the zero-reflection wavelength and angle. We show that the lossless dielectric-absorbing substrate system provides singular phase at the Brewster angles of both \( p \)- and \( s \)-polarizations.

We experimentally measure the ellipsometry parameters \( \Psi \) and \( \Delta \) using a variable angle high-resolution spectroscopic ellipsometer. The experimentally obtained \( \Psi \) and \( \Delta \) spectra of transparent film-absorbing substrate system for wavelengths 378 nm, 552 nm, 450 nm and 752 nm are shown in Figure 4a, 4b, 4c and 4d, respectively. Note that \( \Psi \) can vary from 0 to 90° and \( \Delta \) ranges from 0 to 360° (or -180° to +180°). It is clear that minimum/maximum \( \Psi \) value and singular \( \Delta \) phase are obtained at the GBAs. For 378 nm and 552 nm wavelengths (Figure 4a and 4b), minimum \( \Psi \) is corresponding to Brewster angle for \( p \)-polarized light. On the other hand, maximum \( \Psi \) is obtained at 450 nm and 752 nm (Figure 4c and 4d) corresponding to Brewster angle for \( s \)-polarized light.
**Figure 4.** Measured pair of ellipsometry parameters ($\psi$ and $\Delta$). (a) at 378 nm, and (b) at 552 nm, (c) at 450 nm, and (d) at 752 nm. Singular phase is obtained at GBAs in which $\psi$ is minimum/maximum values.

**Hydrogen sensing with single layer graphene transferred on thin-film optical absorbers**

At ambient pressure and temperature, hydrogen is colorless, tasteless and highly flammable\textsuperscript{31}. Hydrogen is flammable at concentrations ranging from 4%-75% with low ignition energy. Accordingly, hydrogen sensing is largely used in industries where it is a necessary component or a byproduct to monitor and control the hydrogen partial pressure for safety purposes. Hydrogen is also produced by certain bacteria and hydrogen sensors are used in food industry and have possible medical applications\textsuperscript{32-35}. Furthermore, hydrogen sensing is important for fuel cell applications to investigate the loading or unloading kinetics of hydrogen in nanostructured materials.
Various electrical hydrogen sensors based on semiconductors, protonic conductors, and platinum wires have been proposed. However, these systems show enhanced sensitivity only at higher temperatures, which is a major safety issue. In contrast to electrical detection of hydrogen, optical detection techniques offer higher sensitivity in ambient environments, fast response times, and low power consumption. Furthermore, elimination of electric currents and possible sparks in hydrogen rich environments minimizes the risk of explosion. Many approaches for optical hydrogen sensing have been demonstrated using palladium-based optical systems. However, most of the palladium-based optical hydrogen sensors reported to date rely on intense lithography techniques.

Here, we exploit the singular phase behavior of our devices at the GBA to detect changes in the optical properties of the thin-film device for hydrogen sensing. Accordingly, we use a transferred graphene layer on the lossless dielectric-lossy substrate light absorber to detect low hydrogen concentrations. The device functions as a lithography-free, large area and inexpensive hydrogen sensor. Graphene is particularly attractive as it can reversibly react with atomic hydrogen. Upon hydrogenation, graphene changes its optical properties as it transitions from a semi-metal to an insulator. Furthermore, it was shown that the light-matter interaction of ultra-thin films can enhance drastically based on a strong interference effect in thin-film light absorbers which overcome the limitation between the optical absorption and film thickness. The strong field confinement inside the graphene layer results in ultrahigh sensitivity to the graphene optical properties which we exploit for high sensitivity hydrogen sensing.

Figure 5a is a schematic of the device showing the incoming and outgoing beams undergoing polarization dependent change in amplitude and phase. A CVD grown single layer graphene was transferred on an MMA-Si system using the conventional graphene transfer process.
The red curve in Figure 5b shows the Raman spectrum of graphene measured on the fabricated sample. The relative intensity of G and 2D peaks confirm that the transferred graphene is a single layer. Experimentally obtained $p$-polarized reflectance spectrum at 73° incidence angle is shown in Figure 5c. Adding a single layer graphene red-shifts the absorption modes, however, perfect light absorption is exclusively realized for $p$-polarized light at 625 nm wavelength and 73° angle of incidence. The red shift in the absorption modes is due to the high complex refractive index of graphene in the visible spectrum\cite{46} (Supporting Information Figure S8 and Figure S9). The addition of graphene further modifies the reflection phase, and ellipsometry parameters of the entire system (Supporting Information Figure S10 and Figure S11). The sensitivity of the mode location on the graphene layer implies that graphene surface chemistry can be effectively studied using the Brewster angle concept. We consider this mode to demonstrate phase-sensitive hydrogen sensing as described below.

The measured ellipsometry parameters $\Psi$ and $\Delta$ of the graphene-MMA-Si system at 625 nm are shown as black curve in Figure 5d and Figure 5e, respectively. One can see that singular phase is obtained at the Brewster angle (73°), where the $\Psi$ value is a minimum. To demonstrate ultra-high sensitivity of the thin-film optical absorber for hydrogen sensing, we used a plasma hydrogenation procedure. In particular, graphene-MMA-Si sample was exposed to different concentrations of atomic hydrogen by controlling the hydrogenation time. As a first step, we studied the Raman spectral features using hydrogenated samples. The hydrogenated graphene shows an additional sharp Raman D peak at about 1340 cm$^{-1}$, which is activated by defects\cite{43-44}. In Figure 5b, we show the emergence of Raman D peak around 1340 cm$^{-1}$ after hydrogenation of the sample (blue curve), which shows the chemical reaction of atomic hydrogen with graphene.
(Supporting Information Figure S12). On the other hand, the D peak does not exist for graphene with no hydrogenation.

The measured $\psi$ and $\Delta$ spectrum of the sample with different hydrogenation times (1-5 min) are shown in Figure 5d and Figure 5e. The marginal $\psi$ and $\Delta$ shifts at the Brewster angle ($73^\circ$) with respect to unhydrogenated graphene-MMA-Si sample are shown in Figure 5f. The variation in $\psi$ and $\Delta$ increased with increasing hydrogenation time. However, a drastic change in $\Delta$ is obtained at the Brewster angle compared to $\psi$ change. By considering the phase change obtained for 1 min hydrogenation time ($34^\circ$) and phase resolution of the instrument ($<1^\circ$), an areal mass sensitivity of the order of 1 fg/mm$^2$ can be achieved using the proposed platform. To put in context, GBA graphene gas sensor provides $\delta\psi=1^\circ$ and $\delta\Delta=34^\circ$ after 1 minute of hydrogen exposure and $\delta\psi=4.5^\circ$ and $\delta\Delta=75^\circ$ after 5 minutes of hydrogen exposure as compared to the singular phase plasmonic-graphene hydrogen sensor which provided $\delta\psi=2^\circ$ and $\delta\Delta=50^\circ$ after 20 minutes of hydrogen exposure$^4$. Furthermore, we calculated the power dissipation density (W/m$^2$) in the graphene-MMA-Si structure using finite difference time domain (FDTD) method. Figure 5g shows the calculated power dissipation density (W/m$^2$) in the graphene-MMA-Si structure as a function of wavelength at normal incidence (also see Supporting Information Figure S13). Surprisingly, the power dissipation density is an order of magnitude higher inside the graphene layer compared to the Si substrate. Enhanced light absorption in graphene was previously shown in the UV range using coherent light absorption in multilayer thin film structure$^{47}$, and in the visible and NIR wavelength ranges using a grating consisting of multilayer graphene-dielectric stack$^{48}$. Accordingly, the obtained ultrahigh sensitivity is due to the strong phase sensitivity at the Brewster angle and the strong light-matter interaction at the graphene film. We note here that upon extended hydrogenation, graphene absorption is quenched in the UV, visible, and IR frequencies$^{49}$. 
Since the sample required to anneal above 200°C for reversible hydrogenation\textsuperscript{43-44}, the demonstration of reversible hydrogenation is not possible using the MMA-based thin-film optical absorbers. Nevertheless, the proposed platform can be used to demonstrate reversible hydrogenation by replacing MMA with dielectrics such as SiO\textsubscript{2}. We show the reversible hydrogenation, however, by measuring the resistance of graphene which indicates its transition from semi-metal to insulator upon hydrogenation, and back to a semi-metal upon annealing (Supporting Information Figure S14).

**Figure 5.** Experimental demonstration of hydrogen sensing using graphene-MMA-Si system. (a) Schematic of fabricated graphene-MMA-Si system. (b) Raman spectrum of bare graphene and hydrogenated graphene acquired from the fabricated structure. The excitation wavelength was 633 nm. (c) Measured $p$-polarized reflectance spectrum of graphene-MMA-Si system at 73°. The measured (d) $\psi$ and (e) $\Delta$ spectrum of graphene-MMA-Si and hydrogenated graphene-MMA-Si for different times at 625 nm. The maximum $\psi$ and $\Delta$ change is obtained at the Brewster angle. (f)
The marginal ψ and Δ shifts with different hydrogenation times. (g) FDTD calculation of the power dissipation density inside the graphene-MMA-Si structure at normal incidence showing an order of magnitude higher power dissipation in the graphene layer.

In summary, we developed a formalism for generalized Brewster effect in the context of thin-film light absorbers. The experimental demonstrations confirm the existence of a Brewster angle for both s- and p-polarized light where the light is polarized by reflection due to polarization dependent perfect light absorption. Furthermore, by using an ultrathin lossless dielectric film on a lossy substrate, we realized the s-polarized Brewster effect using thin-film based metasurface which can act as an effective medium with a tunable Brewster angle. The high phase sensitivity near the GBA, it is possible to monitor slight changes in the electromagnetic environment of the thin-film device which enables a lithography-free ultrasensitive platform. In particular, we showed a hydrogen sensor with readily available and cheap materials, namely, Si, MMA, and graphene without any nanofabrication and without the need to couple graphene to a surface plasmon based sensor to indirectly probe the changes in graphene or other 2D material’s optical properties\textsuperscript{50}. The device can also function as a platform for other graphene-based sensors, in particular, for the development of cost-effective apta-biosensor platforms\textsuperscript{51}. The effect can be used to realize polarizers for both s- and p-polarizations, as well as for ultrafast polarization switches\textsuperscript{52}. Furthermore, it can be used for the Brewster window in gas lasers, and the optical broadband angular selectivity\textsuperscript{14} as well as for Brewster angle microscopy\textsuperscript{3}.

ASSOCIATED CONTENT

Supporting Information
Sample fabrication and characterizations; angular reflection measurements; spectroscopic ellipsometry characterizations; hydrogenation of graphene-based thin-film absorbers, and additional experimental and simulation results.

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Notes

The authors declare no competing financial interests.

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