

Quantum of optical absorption in two-dimensional semiconductors

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The optical absorption properties of free-standing InAs nanomembranes of thicknesses ranging from 3 nm to 19 nm are investigated by Fourier transform infrared spectroscopy. Stepwise absorption at room temperature is observed, arising from the interband transitions between the subbands of 2D InAs nanomembranes. Interestingly, the absorbance associated with each step is measured to be ~1.6%, independent of thickness of the membranes. The experimental results are consistent with the theoretically predicted absorbance quantum, $A_Q = \pi\alpha/n_c$ for each set of interband transitions in a 2D semiconductor, where α is the fine structure constant and n_c is an optical local field correction factor. Absorbance quantization appears to be universal in 2D systems including III–V quantum wells and graphene.

The optical properties of heterostructure quantum wells (QWs) have been extensively studied since the 1970s, in GaAs/AlGaAs (1), GaInAs/AlInAs (2, 3), InGaAs/InP (4), and HgCdTe/CdTe (5). Here we do a careful quantitative examination of the intrinsic absorption properties of free-standing 2D semiconductor thin films, which has previously been done only for layered structures, such as MoS₂ (6). (The criterion of real two-dimensionality is that the material thickness be smaller than the electron Bohr radius.)

Previous work has shown that graphene, a 2D semimetal, has a universal value of light absorption, namely $\pi\alpha$, where α is the fine structure constant (7). Here, we use free-standing InAs membranes with exceptionally small thickness as a model material system to accurately probe the absorption properties of 2D semiconductors as a function of thickness. We demonstrate that the magnitude of the light absorption is an integer product of a quantum of absorbance. Specifically, each set of interband transitions between the 2D subbands results in a quantum unit of absorbance of $A_Q \sim \pi\alpha/n_c$, where n_c is the optical local field correction factor. The total absorbance for the first several sets of interband transitions is simply given as $A = MA_Q$, where M is the integer number of allowed transitions for a given photon energy. The result here appears to be universal, except for small correction factors associated with higher bands.

Recently, there has been a high level of interest in exploring the fundamental science (6–10) and associated devices (11–20) of free-standing (i.e., attached to a substrate by van der Waals or other weak forces) 2D semiconductors. Two-dimensional layered semiconductors [e.g., MoS₂ (11), WSe₂ (15), GaSe (16), Bi₂Sr₂CaCu₂O_x (17), Bi₂Se₃ (18), and Bi₂Te₃ (19) or diamond/zinc-blend structures InAs (12) and InGaSb (20)] can be readily mounted on virtually any support substrate, thereby enabling a wide range of novel device concepts and practical applications. In one example system, InAs quantum membranes (QMs) with adjustable thicknesses down to a few atomic layers have been realized by a layer transfer process onto a user-defined substrate (12). The approach enables the direct optical absorption studies of fully relaxed (i.e., unstrained) (21) 2D III–V semiconductors by using transparent substrates, without the constraints of the original growth substrate (10). Here, we use InAs membranes of thickness $L_z \sim 3$ –19 nm on CaF₂ support substrates as a model

material system for examining the absorption properties of 2D semiconductors. Given the large Bohr radius of ~ 34 nm (22) in bulk InAs, strong quantum confinement of carriers is readily obtained for sub-20-nm quantum membrane thicknesses. Note that there are only ~ 5 unit cells in a 3-nm-thick InAs QM, given its lattice constant of ~ 0.6 nm (23). In such a quantum mechanically confined 2D system, there is electronic band dispersion in the two unconfined directions, with discrete energy subband edges at values determined by quantum confinement (24) in the third direction. In our case, the InAs QMs can be effectively treated as infinitely deep potential wells, because they are confined by air on one side and by a wide band-gap (25) CaF₂ substrate on the other side. Fig. 1A shows the optical microscope image of a periodic array of ~ 5 - μ m-wide InAs strips (of ~ 3 nm thickness), on a CaF₂ crystal substrate produced by the layer transfer process (SI Text). CaF₂ was chosen as the support substrate as it is optically transparent for the wavelength range of interest. From visual appearance (Fig. 1A), it is evident that ultrathin InAs QMs exhibit strong optical contrast, thereby allowing for the detailed optical characterization even for the films consisting of a few atomic layers in thickness.

Fig. 1B shows the calculated energy levels of a 9-nm InAs QM with CaF₂ and air boundaries. The molecular beam epitaxy-grown InAs samples are not intentionally doped, eliminating band filling (the Fermi level was calculated from an estimated bulk electron density of 2×10^{16} /cm³) (26). Here, the effects of surface accumulation layers due to surface defects are ignored (see Fig. S1 for surface accumulation layer effects). Fig. 1C depicts the qualitative band structure of a 2D InAs QM, with vertical arrows indicating the interband transitions from the n th heavy hole (hh)/light hole (lh) subband to the n th electron (e) subband. Here we define e_n – hh_n and e_n – lh_n as the n th set of interband transitions. Due to spatial matching of electron/hole wave functions in different energy subbands, interband transitions in quantum wells are favored when $\Delta n = n' - n = 0$, where n' and n are the subband indexes for electrons and holes, respectively (27). Consequently, there are two allowed transitions to each electron subband: one from the corresponding hh subband and the other from lh subband.

We use Fourier transform infrared (FTIR) microspectroscopy (Fig. 2) to probe optical interband transitions (in the range 0.3 eV $< h\nu < 1.2$ eV) in InAs QMs at room temperature (SI Text). Transmittance and reflectance spectra were collected in the range of $2,414$ – $9,656$ cm^{–1} (0.30 – 1.20 eV) over an aperture size of $\sim 50 \times 50$ μ m², with 8 cm^{–1} (1 meV) resolution and 512

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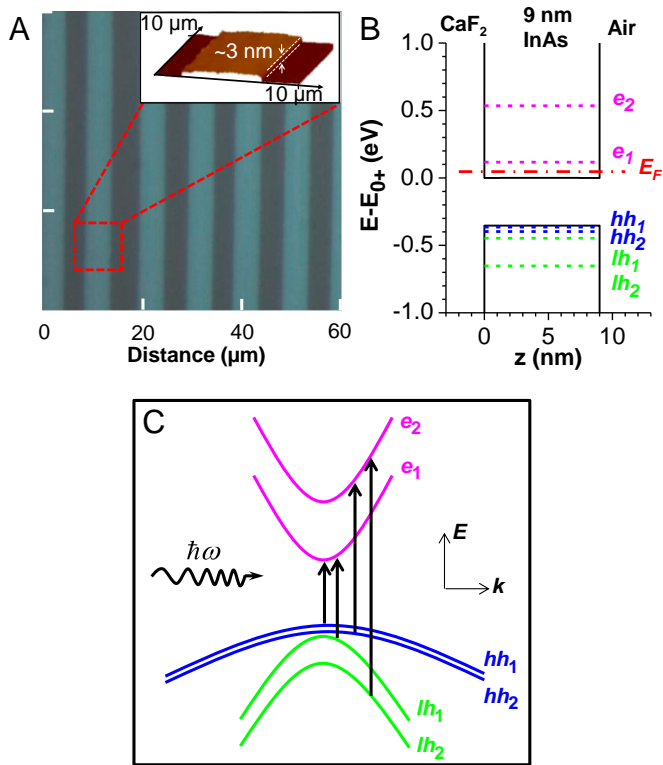


Fig. 1. (A) Optical microscope image of InAs 2D strips (~3 nm thick) on a CaF₂ substrate. (Inset) The atomic force microscope image of a single InAs strip. (B) CaF₂/InAs (9 nm)/air quantum well band diagram with energy referring to E(z = 0⁺), abbreviated as E₀₊. E_F shows the quasi-Fermi level, whereas e₁, e₂, hh₁, hh₂, lh₁, and lh₂ are the indexes for the conduction and valence subbands. Note that only the first two conduction/valence subband edges are shown. (C) Qualitative band structure schematic of a 2D InAs QM, with arrows indicating the allowed optical interband transitions between valence and conduction subbands.

averages for all samples with different thicknesses. Atmospheric H₂O and CO₂ effects were removed using OMNIC 8.2 software (Thermo Scientific). The absorption spectra of InAs QMs for each thickness were obtained by subtracting the transmittance and reflectance from a normalized 100% spectrum, yielding Fig. 3. The final spectra were generated by dividing the measured spectra by the fractional area fill factor of the InAs strips. Fig. 4 shows the overlaid absorbance (A) spectra of InAs QMs with L_z ~ 3 nm, 6 nm, 9 nm, 14 nm, and 19 nm. Clear step-like features are observed in the absorbance spectra arising from the quantized interband transitions between the 2D subbands (10). The

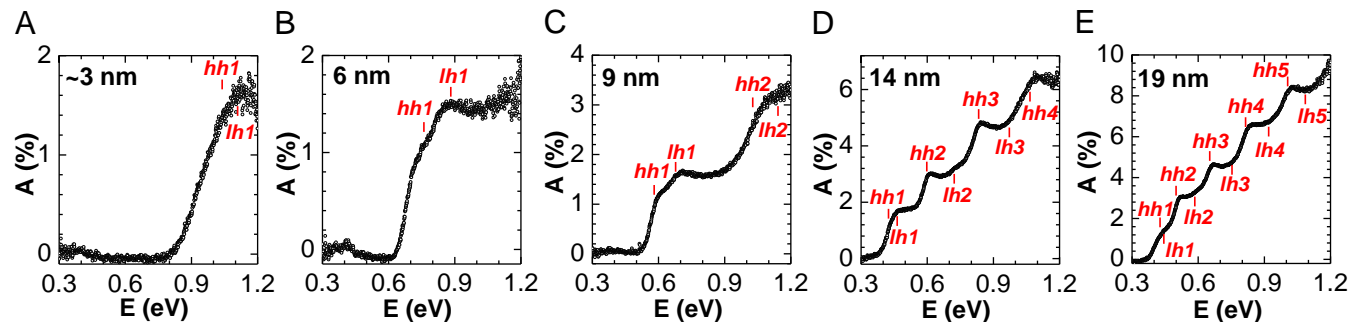


Fig. 3. Absorbance for (A) 3-nm, (B) 6-nm, (C) 9-nm, (D) 14-nm, and (E) 19-nm InAs quantum membranes. The absorbance spectra are corrected by dividing by the surface area fill factor of InAs.

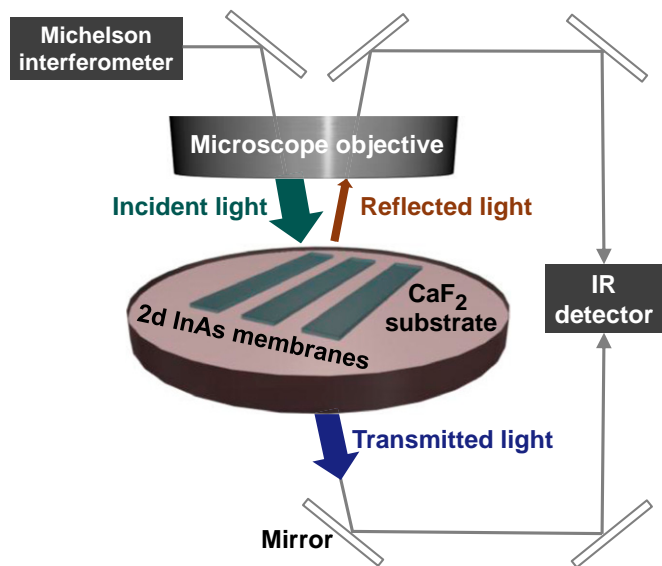


Fig. 2. Schematic illustration of the FTIR microspectroscopy setup used for the absorption measurements. The absorption spectrum is obtained from the measured transmission and reflection spectra. The incident light angle was actually perpendicular to the membrane.

spacings between the measured absorbance steps are in quantitative agreement with the calculated interband energy spacings (see Fig. S2 for the detailed analysis). Note that intersubband transitions are negligible due to our transverse electric (TE) polarization. The experimental finding here is that the individual absorbance steps plateau at $1.6 \pm 0.2\%$ (SD) for all samples, regardless of the QM thickness. The result was reproducible for multiple samples and measurements.

To shed light on this observed absorption behavior, the electron-photon interaction in a semiconductor material is theoretically evaluated from Fermi's golden rule. If a light wave with electric field \vec{E} , polarization vector \hat{e} , and frequency ω is incident perpendicular to a direct band-gap semiconductor membrane with a thickness L_z, in an infinitely deep potential well model (28), the optical absorption coefficient is

$$\alpha'(\omega) = \frac{e^2}{n_r c \epsilon_0 m_0^2 \omega} \frac{1}{L_z \hbar^2} \frac{1}{m_{en}^* + 1/m_{hm}^*} |\hat{e} \cdot \vec{p}_{cv}|^2, \quad [1]$$

which is a step function for each interband transition, where e is the electron charge, n_r is the real part of surrounding refractive index, c is the speed of light, ε₀ is the vacuum permittivity, m₀ is the free electron mass, ħ is Planck's constant, m_{en}^{*} and m_{hm}^{*} are

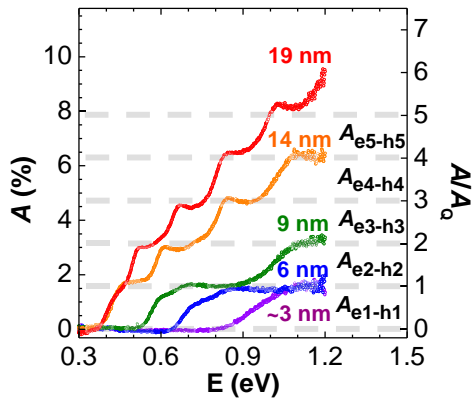


Fig. 4. Absorbance spectra of InAs QMs with thickness of $L_z \sim 3$ nm, 6 nm, 9 nm, 14 nm, and 19 nm at room temperature, showing universal absorbance steps of $A_Q \sim 1.6\%$ in magnitude. Dashed lines indicate each 1.6% of absorbance. The $A_{e_n-h_n}$ represent the absorbance from the corresponding interband transitions, e_n-h_h and e_n-h_n .

the effective mass for electrons and holes of the n th conduction and valence subbands present from the 2D density-of-states, and $|\hat{e} \cdot \vec{p}_{cv}|^2$ is the momentum matrix element describing the electron-photon interaction. Eq. 1 arises from Fermi's Golden Rule, with optical perturbation $i\vec{A} \cdot \vec{p}_{cv}/m_o$, where \vec{A} is the vector potential related to the optical electric field as $\vec{E} = j\omega\vec{A}$.

The reciprocal effective masses $1/m_c$ and $1/m_h$ arise in k - p perturbation theory (29) from a similar perturbation $\hbar|\vec{k} \cdot \vec{p}_{cv}/m_o$. The reduced effective mass produced by this repulsion of conduction and valence bands in second-order k - p perturbation theory is $1/m_{cn}^* + 1/m_{hn}^* = 4|p_{cv}/m_o|^2/E_{cv}$, where $E_{cv} = \hbar\omega$ is the interband transition energy.

Thus, k - p perturbation theory puts $|p_{cv}|^2$ in the denominator of Eq. 1, whereas the optical perturbation puts $|p_{cv}|^2$ in the numerator of Eq. 1. Thus, the momentum matrix element $|p_{cv}|^2$ cancels. Many of the other terms in Eq. 1 cancel as well, leaving behind the dimensionless absorbance $\alpha' L_z = \pi(e^2/4\pi\epsilon_o\hbar c)/n_r$. Aside from π , and a correction for the surrounding refractive index n_r , the absorbance per 2D sublevel is $(e^2/4\pi\epsilon_o\hbar c)$, a group of fundamental constants known as the fine structure constant $(e^2/4\pi\epsilon_o\hbar c) = \alpha = 1/137$.

The prime on the absorption coefficient α' is meant to distinguish it from the fine structure constant α . Because $\alpha' L_z$ is dimensionless, it is somewhat inevitable that it would be related to α , the dimensionless parameter in opto-electronics and quantum physics. Indeed, optical absorption depends on electric charge, and α is actually electric charge squared (in fundamental units where $\hbar = 1$, $c = 1$, $4\pi\epsilon_o = 1$).

The simplified calculation above is vindicated by Szkopek's detailed calculations (30, 31), which multiply the step function by a Sommerfeld Coulomb correction factor

$$S(\omega) = \frac{2}{1 + \exp\{-2\pi\sqrt{Ry}/(\hbar\omega - E_{cv})\}},$$

where Ry is the electron-hole Rydberg binding energy. This puts a sharp, narrow, double-height spike, right at the step function,

whose width is related to the typical millivolt hydrogenic binding energy. In the experiment (Fig. 4) the double-height spikes are washed out, and hardly seen, leaving only small vestigial peaks at each step.

There is an additional correction. The dimensionless absorption steps that we observe at $\sim 1.6\%$ are actually smaller than $\pi\alpha = 2.3\%$. This is due to a local optical electric field correction factor, which we call n_c . In a surrounding refractive index n_r , $n_c = n_r$, as is clear from Eq. 1. When the quantum membrane film is mounted on a substrate of refractive index n , it experiences both the incident electric field, E_o , and the Fresnel reflected electric field $\{(1-n)/(1+n)\}E_o$. Superposing the incident and reflected fields, that local optical electric field at the quantum membrane is weaker by $\{2/(1+n)\}E_o$, which reduces the optical absorption by $\{2/(1+n)\}^2$, and the local field correction factor becomes $n_c = \{(n+1)/2\}^2$, yielding the corrected step absorption A_Q :

$$A_Q \equiv \alpha'_n(\omega)L_z = \frac{\pi\alpha}{n_c} = \pi\alpha \left(\frac{2}{1+n} \right)^2.$$

In our case the refractive index of CaF_2 is $n = 1.43$, changing the optical local field correction factor n_c to $\{(1+n)/2\}^2 = 1.48$, reducing the absorption step height to $\sim 1.58\%$, in close agreement with our observed step height in Fig. 4.

Thus, we have shown experimentally and theoretically that light absorption in 2D semiconductors is independent of specific material parameters, such as band gap, effective mass, and thickness. The simplification of $A = M \cdot A_Q$ holds true over a broad range of photon energy, given that the considerable confinement energy shifts with M .

The measured absorbance values for previously reported III-V and II-VI heterostructure QWs are in the range of 0.6–1.1% per QW for the first step (1–5), slightly smaller than the A_Q value presented in this work. This is expected due to an optical local field correction factor $n_c \sim 3.5$, appropriate to a quantum well grown and embedded in high-index material, rather than to our case of free-standing quantum membrane on a low-index substrate. On the other hand, the result here is also consistent with the reported absorbance for graphene (7), $A \sim \pi\alpha$, which is for a totally suspended membrane with vacuum on either side.

In summary, light absorption in near-ideal 2D semiconductors is experimentally examined by using free-standing InAs QMs as a model material system. The absorbance of 2D InAs is found to be an integer multiple of the quantum absorbance, A_Q , governed only by the fundamental physical constant α . Besides its significance in the basic understanding of electron-photon interactions in quantum confined semiconductors, this result provides a unique insight toward the use of 2D semiconductors for novel photonic and optoelectronic devices. Future work should focus on experimental studies of the absorbance magnitude of other 2D material systems.

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