Interaction of single-layer CVD graphene with a metasurface of terahertz split-ring resonators

Federico Valmorra[a], Giacomo Scalari[a], Curdin Maissen[a], Wangyang Fu[b], Christian Schönenberger[b], Jong Won Choi[c], Hyung Gyu Park[c], Mattias Beck[a] and Jérôme Faist[a]

[a]ETH Zurich, Institute for Quantum Electronics, Wolfgang-Pauli-Strasse 16, CH-8093 Zurich, Switzerland;
[b]Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland;
[c]ETH Zurich, Institute of Energy Technology, Sonneggstrasse 3, CH-8092 Zurich, Switzerland

ABSTRACT

The interaction of large-area single-layer CVD-graphene with a metasurface constituted by THz split-ring resonators was studied via THz Time-Domain Spectroscopy in the frequency range 250 GHz÷2.75 THz. Transmission measurements showed that the presence of the graphene shifts the resonances of the THz-metasurface towards lower energies and increases the transmittance, mainly at resonance. A comparison between two possible configuration is here presented revealing a much stronger interaction for the case of split-ring resonators evaporated directly onto the CVD-graphene layer with respect to the opposite configuration. From the recent literature the presented system is a good candidate for THz modulators with possible use also in cavity-QED experiments.

Keywords: TeraHertz, CVD graphene, split-ring resonator, metamaterial, TDS

1. INTRODUCTION

The TeraHertz (THz) region of the electro-magnetic spectrum, between 100 GHz and 10 THz, has attracted in the last decades increasing attention for its technological potential.[1] In fact, since several solid-state systems have characteristics and processes belonging to the THz energy region, THz technology is important for spectroscopy and investigation of molecular bonds, material structures and carrier dynamics.[2] On the other hand the THz region is of fundamental scientific importance, being this the bridge between optics and electronics. Such situation is challenging from the technological point of view because the concepts stemming from one of these fields used for building sources, detectors and modulators are pushed at their limits towards the opposite one, resulting in poorer performances with respect to pure electronic/optic devices. Because of such situation, this frequency region is often referred to as *THz gap*.

Graphene emerged in the last decade as one of the most interesting electronic materials.[3] A single layer of Carbon atoms arranged in a honeycomb pattern revealed extremely high charge carrier mobility up to tens of thousands cm^2/Vs, also at room temperature, becoming one of the most studied solid state systems in electronics.[4] More recently, studies on the plasmonic and optical properties of graphene have been and are being pursued.[5,6] In particular, a cut-off energy of twice the Fermi energy (typically some hundreds meV, infrared spectral region) makes inter-band transitions dominant at THz frequencies.[7] These combined electro-optic characteristics reveal graphene as a promising material for optoelectronic and plasmonic applications.[8] In the quest for decreasing the THz gap, useful applications of graphene reside particularly in detectors[9] and modulators.[10]

Further author information: (Send correspondence to F.V.)
F.V.: E-mail: valmorrf@ethz.ch, Telephone: +41446333867
G.S.: E-mail: scalari@phys.ethz.ch, Telephone: +41446333928

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In the THz spectral region the most common semiconductors are transparent and it is therefore difficult to manipulate the radiation efficiently. One of the best ways to deal with such problem is with the use of metamaterials.[11,12] Metamaterials are sub-wavelength-structured artificial materials that respond homogeneously to the radiation displaying an effective dielectric permittivity ϵ_e and magnetic permeability μ_e, that can then be tailored at will.[13,14] A second fundamental property of metamaterials is the ability of confining electro-magnetic fields into highly sub-wavelength volumes, increasing in such a way the strength of interaction between field and material. This is of great importance first when dealing with graphene at THz frequencies where radiation with wavelength of 30 μm÷1 mm interacts with a nominally 0.334 nm thick layer. Secondly, this fact is a key factor for entering the field of quantum electro-dynamics, where strong interaction is needed to access the (ultra-)strong coupling regime.[15]

2. MATERIALS AND SAMPLE

Two different samples configurations were investigated and are here presented. A first configuration (from here on *Sample A*) consists of a THz metasurface produced on semi-insulating GaAs substrate. The CVD-graphene layer was subsequently transferred onto the sample. Aiming for stronger interaction, a second configuration (*Sample B*) was then tested. The CVD-graphene layer was first transferred onto a SiO_2/Si substrate and afterwards was the THz metasurface evaporated on top of this. The two different substrates were used for sample-production convenience but do not affect the present discussion, being their effect excluded by normalization procedures (see Sec. 3). Details on the graphene production and transfer and on the metamaterial properties and realization are given in the following subsections.

2.1 Graphene

Graphene single layer was grown by Chemical Vapour Deposition (CVD) technique on standard 25 μm copper foil at 1000°C for 10 minutes from a mixture of H_2/CH_4 with fluxes of 10/25 sccm, respectively. Subsequently the graphene-on-Cu was spin-coated with PMMA and put onto a Cu-etching solution constituted by ammonium-persulfate (Sigma-Aldrich) in water with proportion in weight $(HN_4)_2S_2O_8 : H_2O = 2 : 100$. After few hours the Cu is completely dissolved and the PMMA-graphene is rinsed in fresh water, collected with the substrate and dried.[16] The PMMA is removed with warm aceton and the graphene layer checked via Raman spectroscopy, confirming that a single layer was produced with a negligible D peak as shown exemplary in the spectrum of Fig. 1 taken on Sample B. The area of the used graphene layer was about 6x8 mm^2. No electrical characterization was carried out on the CVD-graphene layer but such layers are typically p-doped with Fermi energy few hundreds of meV into the valence-band.

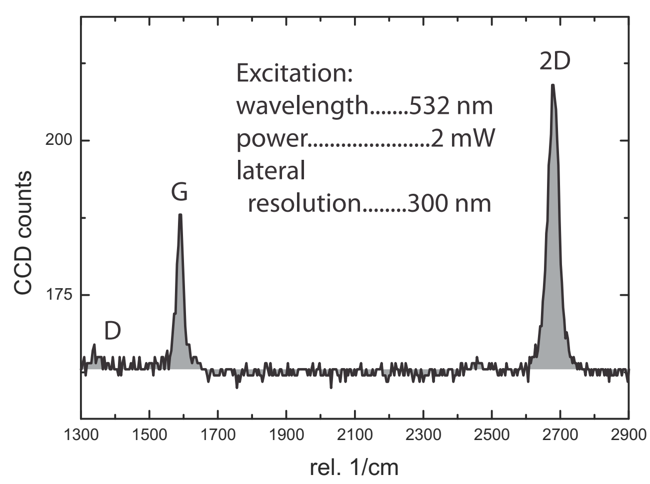

Figure 1. Examplary typical Raman spectrum of transferred graphene on SiO_2 taken on Sample B. The high 2D peak with respect to the G peak and the very small D peak confirm the goodness of the CVD-graphene monolayer. The characteristics of the Raman setup are given into the figure.

2.2 TeraHertz Metasurface

The basic unit cell of a metasurface is constituted by a C-shaped gold wire constituting the split-ring resonator (SRR). The slit of the SRR can be considered as a capacitor's gap whereas the metallic wire accounts for resistance and inductance, altogether fulfilling the RLC-series circuital description.[17] For the presented samples a more complex SRR design[18, 19] was chosen displaying two concatenated single-C-shaped wires, resulting in the unit cells for the THz metasurfaces displayed in Fig. 2. The unit cell was then reproduced in a square array covering a total surface of 2.5x2.5 mm^2, defined onto the samples with standard lithographic techniques and produced by e-beam evaporation of Ti/Au with thickness 4/200 nm and warm aceton lift-off. The SRR used for Sample A has resonant modes at 880 GHz and 2.33 THz and was deposited on semi-insulating GaAs substrate and covered with graphene. The SRR used for Sample B has resonant modes at 609 GHz and 2.37 THz and was deposited directly onto the graphene on SiO_2/Si. Reference samples with the respective THz metasurface on the corresponding substrate but without graphene were also fabricated.

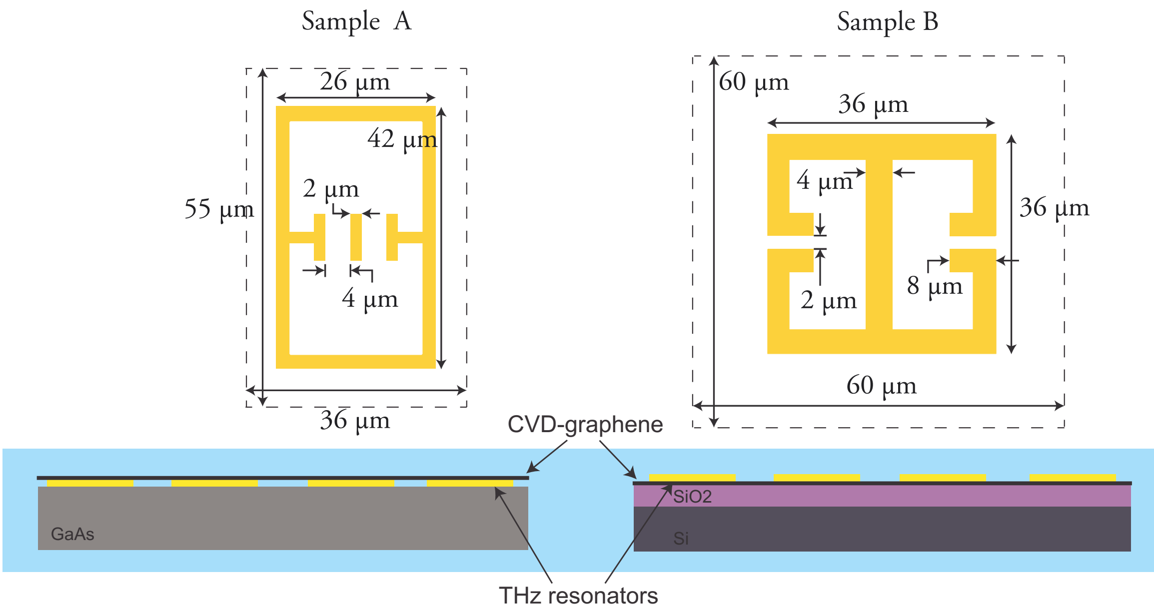

Figure 2. Sketch with dimensions of the THz split-ring resonators into the respective unit cells (dashed rectangles) and sample configuration highlighting the opposite relative position of the THz metasurface with respect to the CVD-graphene layer.

3. SETUP AND MEASUREMENTS

Transmission measurements were performed with a THz Time Domain Spectroscopy (TDS) setup. In the setup, a Ti/Sapphire laser (Maitai, SpectraPhysics) produces light with wavelength of 800 nm in pulses with a length of 75 fs at a repetition rate of 80 MHz. The initial beam gets split into two, one of which impinges onto an interdigitated switch (TERASED, Gigaoptics) at an average power of 400 mW after going through a delay-line. The THz radiation is produced by the switch, biased at 16 V with frequency 15.5 kHz and 50% duty cycle, and is focused onto the sample and re-collected from it by an arrangement of confocal parabolic mirrors. The Thz beam is then aligned with the second part of the initial infrared beam and focused onto a 110-oriented ZnTe crystal where electro-optical sampling takes place. The resulting beam is then detected in a balanced scheme by photodiodes. Varying the delay between the THz and the sampling beams allows the time-domain measurement of the transmitted electric field amplitude. The THz beam travels continuously into a nitrogen purged environment to avoid water vapour absorption. The setup works in the bandwidth 250 GHz÷2.75 THz with a frequency resolution of 60 GHz and a maximum beam waist on the sample of 2.5 mm.

Transmission measurements were performed on Samples A and B, as well as on the respective reference samples not containing the graphene and the respective substrates (GaAs for Sample A and SiO_2/Si for Sample B).

The measurements for the two samples and the corresponding reference samples, normalized to the substrate, are shown in Fig. 3 in blue and black, respectively. The plotted transmittance is therefore representative of the CVD-graphene/THz metasurface paired-system, independently of the backing substrate. The strong oscillations in some of the spectra at the edges of the setup bandwidth are due to the normalization procedure. The overall wiggling is instead due to the Fourier transformation of a finite-extent time-varying signal without apodization, but with the use of zero-padding. The baseline of the reference spectra (black in Fig. 3) is expected to be at unity: the slight deviation seen is possibly the result of a non-identical alignment in the measurements of sample and reference.

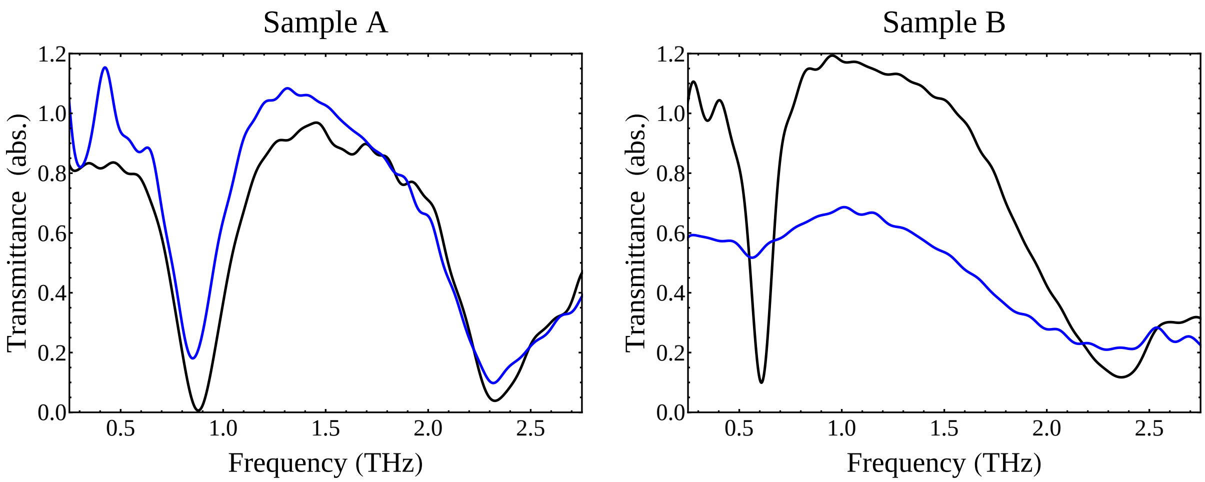

Figure 3. Transmission spectra for Sample A and B (blue) and the relative references (black), normalized to the substrate. The interaction with the graphene red-shifts the resonant frequencies and varies the transmitted intensity (discussion in the main text).

3.1 Discussion and Conclusions

Considering the spectra in Fig. 3, the first striking feature is the difference in the overall transmittance of the samples containing graphene (blue) with respect to the ones without graphene (black). For Sample A, where graphene was transferred onto the THz metasurface, the transmittance shows that graphene affects the metasurface resonances by slightly increasing the overall transmission and red-shifting their frequencies. Specifically the transmittance at resonance in presence of graphene has a variation of $\Delta T_1 = 17.5\%$ and $\Delta T_2 = 5.8\%$ for the two resonances, respectively. On the other hand, in the spectral regions out-of-resonance, it remains approximately unchanged at an average value of 90%.

When the metasurface is instead directly evaporated onto the graphene layer, as for Sample B, the paired-system transmittance is strongly changed over most of the investigated spectrum. The transmittance is increased in correspondence to the resonant modes, with a much bigger effect for the first one with the transmittance varying from 9.7% to 51.7% ($\Delta T = 42\%$). The second mode becomes also much broader implying a difficult minimum frequency estimation. For the spectral region out-of-resonance, instead, the transmittance, that should be approximately 100% for both the graphene layer and the THz-metasurface when considered singly, has an average value of 60%. It is therefore possible to affirm that there is a stronger interaction between the CVD-graphene layer and the THz-metasurface in the case of Sample B, possibly because of better electrical contact. The shift of the resonant frequencies has also in this case negative sign, confirming it as a *red*-shift. Also for this effect, a bigger change is measured for Sample B than for Sample A: 7.2% with respect to 3.3%. The resonant frequencies of the graphene-metasurface system are collected in Table 1. The measured red-shifts of the THz metasurface resonances in presence of graphene agree with what reported in the literature for several different types of systems, whose spectral response was modified/manipulated with graphene.[20–24]

A	1^{st} mode (GHz)	2^{nd} mode (THz)
Sample	851	2.319
Reference	880	2.326
$\Delta\nu$	-29	-0.007
$\Delta\nu/\nu_R$	-3.30%	-0.30%

B	1^{st} mode (GHz)	2^{nd} mode (THz)
Sample	565	2.344*
Reference	609	2.366
$\Delta\nu$	-44	-0.022*
$\Delta\nu/\nu_R$	-7.20%	-0.93%*

Table 1. Resonant frequencies of the two modes of the investigated THZ metasurfaces for Sample A and B and the correspondent reference samples. The absolute frequency shift is calculated as $\Delta\nu = \nu_S - \nu_R$. Values marked by (*) are of difficult estimation because of the very broad resonance at the edge of the setup bandwidth.

In conclusion we presented transmission measurement investigating the interaction of single-layer CVD-graphene with a THz metasurface. A comparison between two possible configuration was analysed revealing a much stronger interaction for the case of split-ring resonators evaporated directly onto the CVD-graphene layer. Such interaction was measured as change in sample transmittance up to 42% and red-shift of the THz-metaserface resonances up to 7.2% for the first mode. From the recent literature[21–24] and as an outlook it is expected that gating the CVD-graphene layer will lead to an active control of the sample transmission, making of the presented system a good candidate for THz modulators. In addition, increased light-matter coupling put the system forward for cavity QED experiments, and following recent theoretical calculations,[25] investigations in the magnetic field might reveal strong coupling between the cyclotron transition in the CVD-graphene and the photonic modes of the THz-metasurface.

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