FAST TRACK COMMUNICATION

Plasmon electron–hole resonance in epitaxial graphene

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Abstract

The quasiparticle dynamics of the sheet plasmons in epitaxially grown graphene layers on SiC(0001) has been studied systematically as a function of temperature, intrinsic defects, influence of multilayers and carrier density using electron energy loss spectroscopy with high energy and momentum resolution. The opening of an inter-band decay channel appears as an anomalous kink in the plasmon dispersion which we describe as a resonance effect in the formation of electron–hole pairs. Due to the inevitable strong coupling of plasmons with single particle excitations in reduced dimensions, such signatures are generally expected.

Interaction of light with matter is one of the key processes for many technical and even everyday applications, and metallic surfaces play a crucial role in this context. They not only reflect light, but, if proper momentum sources are available, allow coupling of light into collective electronic surface excitations, called surface plasmon-polaritons (SPP), which enable conversion of light into electronic signals [1].

The SPP excitation is a consequence of the finite crystal size. Although they are localized at the surface, they should be clearly discriminated from ‘true’ low-dimensional sheet or wire plasmons, which are the result of collective excitations of a one- (1d) or two-dimensional (2d) electron gas existing in partially occupied electronic surface states, in sheets with thicknesses in the monolayer range, such as graphene, or in ultra-thin wires, e.g. these materials exhibit an extremely flat and almost linear dispersion (group velocities around $10^6 \text{ m s}^{-1}$) [2, 3]. Thus much shorter wavelengths than in SPPs are involved, which allow confinement of the excitation down to the nanometer range and make them very attractive for nanoelectronic applications. On the other hand, due to the low conductance of 1d and 2d metallic systems, one has to cope with comparatively strong damping of plasmonic excitations and their sensitivity to defects on the atomic scale. Therefore, such studies require geometrically perfect and at the same time electronically flexible materials, i.e. in which the coupling and the chemical potential can be adjusted. Graphene turns out to be a perfect model system for this purpose.

Graphene, as a two-dimensional lattice of sp$^2$-hybridized carbon atoms has been shown to be a model system to study many fundamental aspects of 2d electron systems, e.g. their electronic correlations, collective phenomena, many-body interactions, dynamical processes and their interrelations [4–8]. The material itself has triggered intense research within recent years. Single layers can be synthesized by different techniques, e.g. exfoliation of graphite or decomposition of hydrocarbons on transition metal surfaces [4, 9, 10]. Well oriented graphene layers grown on SiC substrates by sublimation of Si allow detailed studies of the morphology, the interface, the electronic structure, and even of transport properties [11–16]. Coupling of energy into excited plasmonic states of graphene offers a new perspective in low-dimensional physics, but its exploration is still at its beginning [17, 19, 18].

Indeed, the present knowledge on 1d and 2d sheet plasmons is quite limited: as shown, e.g., in monolayers of Ag on Si(111) [20, 21], plasmon damping becomes dominant.
Figure 1. (a) Loss spectra (semi-log scale) for 1 ML graphene grown on H-etched SiC(0001) as a function of momentum transfer, $k$. The primary electron energy is 20 eV. Only the contribution of the 2d sheet plasmon to the loss spectrum is highlighted. (b) Details of the fitting model, shown exemplarily for $k = 0.05 \, \text{Å}^{-1}$, containing, apart from the main sheet plasmon peak (solid line (orange)), a Drude tail (dashed green), phonon and multiplasmon losses (dotted lines). For details of the fitting procedure see [18]. (c) LEED pattern of 1 ML of graphene grown on SiC(0001) ($E = 140$ eV). The first order spots of graphene and the substrate are marked by G(10) and SiC(10), respectively.

Once the plasmon dispersion curve intersects the single particle band leading to Landau damping by single particle intraband excitations (SPE$_{\text{intra}}$). Outside the Landau regime, this mechanism is still effective, but cannot be described without explicit consideration of correlations [22–24] or momentum transfer processes [18]. Energetically low lying valence band states are considered only in terms of a polarizable background causing a quasi-linear dispersion at long wavelengths [3]. Couplings to other particles have not been included in random phase based descriptions [22], and nor have signatures of resonant coupling seen so far in experiments. Only for hybrid systems, where plasmons interact with molecular orbitals or excitonic states [25], has a resonant coupling been recently reported.

In this report we show by detailed analysis with angle resolved high resolution electron energy loss spectroscopy (EELS) that for the 2d sheet plasmons (as well as for 1d plasmons) coupling of plasmonic excitations with various decay channels is crucial since this coupling has a direct influence on the sheet plasmon dispersion. As we will show, once inter-band transitions are allowed by energy and momentum conservation (SPE$_{\text{inter}}$), resonant coupling between the plasmon and the inter-band electron–hole (e–h) pair excitation (exciton), already previously identified as plexciton excitation [26], leads to pronounced de-tuning of the plasmon frequency around the Fermi energy and to enhanced damping. A complementary type of quasiparticle excitation involving plasmonic excitations in graphene, namely resonant coupling between the plasmon and the hole during photoemission, called plasmaron, was recently observed by Bostwick et al [27, 8]. Both excitation channels demonstrate the importance of resonant couplings for plasmonic decay.

The growth of graphene and the measurements were performed under ultra-high vacuum (UHV) condition. As substrate, Si-terminated 6H-SiC(0001) samples (n-doped, $\approx 10^{18}$ cm$^{-3}$ from SiCrystal AG) were used and graphene was grown by sublimation of Si while annealing the SiC substrate to approximately 1500 K. Further details can be found in [14, 18]. The plasmons were measured by using a combination of high resolution electron loss spectrometer (EELS) as electron source and a detector with a low energy electron diffraction system (LEED) providing simultaneously high energy and momentum ($k_\parallel$) resolution [28]. Typical operating parameters were 25 meV energy resolution at a $k_\parallel$ resolution of $1.3 \times 10^{-2} \, \text{Å}^{-1}$.

A sequence of EEL spectra of a monolayer (ML) of graphene taken at different $k_\parallel$ values along the $\Gamma$–K direction is shown in figure 1. The most intense loss peak (shaded peak in figures 1(a) and (b)) can unambiguously be attributed to the sheet plasmon in graphene [17, 18]. A detailed analysis of the loss peaks (see figure 1 and [18]) reveals that the loss spectra can be decomposed into the main plasmon loss, two low energy phonon losses at 70 and 150 meV without significant dispersion, and small contributions fromhigher excitations,(273,115),(726,789)
Interestingly, the existing theoretical models describe only sections of this dispersion. For example, the nearly free electron gas model (NFEG) with inclusion of first order non-local field effects, as derived by Stern [33], describes the experimental data well in the limit of large momentum transfer \((k > 0.1 \text{ Å}^{-1})\) assuming an electron density of \(N = 1 \times 10^{13} \text{ cm}^{-2}\) and an effective mass of \(m^* = 0.06 \pm 0.01 m_e\) (solid line in figure 2). These values are close to those deduced from photoemission [11]. Inclusion of dynamic screening for both electrons and holes (dashed–dotted line, [22]) shifts the dispersion to lower values and now yields a perfect match to experiment for small \(k\) up to 0.09 \text{ Å}^{-1}, but underestimates the plasmon energies in the SPE\text{\_inter} regime. Although e–h excitations are included in these RPA descriptions, the NFEG models do not contain effects like resonant energy transfer with corresponding \(k\)-dependent changes of lifetimes. As we will show below, the inclusion of resonant energy transfer at \(E_F\) due to opening of the inter-band e–h excitations channel allows a quantitative fit of the measured dispersion curve, now even within an extended NFEG model. It should be noted that, a \textit{priori}, interface states can also mediate such inter-band transitions. However, as the system presented here does not show relevant surface states in the considered energy range [34], an intrinsic inter-band transition due to the finite filling of the conduction bands is likely and will be discussed in the following.

In order to observe such resonance effects between excited states, a short, but still sufficiently high lifetime \(\tau_{\text{e–h}}\) at resonance is necessary in order to discriminate both types as separate excitations. As sketched in figure 3(b), the finite value of \(E_F\) above the Dirac point in pristine graphene enables inter-band transitions at finite \(k\)-values, which are shown as vertical transitions between shifted conduction and valence band states [35]. Indeed, we can describe the whole dispersion curve in every detail (see figure 3(a)) from the loss function \((\Im(1/e))\), using simply the Drude model of the dielectric function \(\epsilon = 1 - \omega_p^2/\omega(\omega + i\gamma)\), and the NFEG model of Stern assuming a resonance by opening the SPE\text{\_inter} channel. This results in a momentum-dependent dissipation \(\gamma(k)\) for the plasmons. The effective damping \(\gamma(k)\) is composed of a non-resonant term \(\gamma_{\text{non\_res}}\), which takes into account intra-band transitions and structural imperfections, and a resonant part \(\gamma_{\text{res}}\). Figure 3(c) shows the best fit result for \(\gamma\). While \(\gamma_{\text{non\_res}}\) increases linearly with momentum [18], \(\gamma_{\text{res}}\) has a pronounced
maximum around \( k_F \), as expected. The asymmetry in the damping curve demonstrates further that intra-band transitions at low energies contribute to the dynamic loss channel as well. This pronounced damping is clearly seen in the experiment (figure 3(d)), although the increase of FWHM is smaller than calculated. Finite \( k \)-resolution and the simultaneous excitations of, e.g., phonons, not considered here, may be possible reasons. Nevertheless, the resonant broadening is even seen in much broader spectra, e.g. in the presence of F4-TCNQ molecules acting as defect scatterers.

This purely phenomenological description of the dip can be rationalized by a simple two-oscillator model representing plasmon and e–h pair formation by inter-band transitions put on top of the non-resonant dynamic mechanisms. It yields a description fully consistent with the first approach. In order to see this de-tuning effect in the dispersion, the lifetimes, \( \tau \), of both oscillators need to be of same order at \( k_F \). If, further, the interaction strength \( 2\Delta \gg \hbar/\tau \), polaritons are expected in this regime of strong coupling. The upper and lower polariton states are given by \( E_{\text{UL}}(k) = 1/2(E_{\text{pl}}(k) + E_0) \pm 1/2\sqrt{(2\Delta)^2 + (E_{\text{pl}}(k) - E_0)^2} \), where \( E_{\text{pl}} \) and \( E_0 \) are the non-interacting plasmon mode and exciton energy, respectively [36, 37]. Here we set the sheet plasmon energy \( E_{\text{pl,sten}} \) for \( E_{\text{pl}} \) and the Fermi energy \( E_F \) for \( E_0 \), which is the lowest energy of inter-band e–h pair formation without additional momentum. \( 2\Delta \) measures the interaction between the quasiparticles. The best fit yields an interaction energy of only 100 meV, in qualitative agreement with [8]. Consistent with the strongly enhanced damping determined from the fits described above, the observation of separate Rabi split states is suppressed, and only the continuous transition from the lower (\( E_L \)) to the upper branch (\( E_U \)) can be observed. In fact, this model also fits the data quantitatively with values of damping close to those determined above. Formally, this model of plasmon electron–hole interaction is closely related to interacting plasmons located in spatially separated graphene layers [23], which show similar effects in the dispersion. However, since smooth single graphene sheets were used here, we conclude that the coupling to e–h oscillators is the dominant process.

Finally we show that the position of the dip is only influenced by the chemical potential rather than by structural parameters. For this purpose, we adsorbed a small amount of F4-TCNQ [38], which reduces the carrier density and hence shifts \( E_F \) downwards. Figure 4 shows the dispersion after adsorption of approximately 0.01 ML at 300 K. As expected, the dip shifts to lower \( k_F \)-values (\( \approx 0.03 \, \text{Å}^{-1} \)). This shift is also seen in the resonance of the FWHM. Since the added molecules act as scattering centers, the loss structure is further broadened so that the exact determination of \( k_F \) from the FWHM is more difficult. Remarkably, the average slope of the dispersion remains unchanged, although the electron density at \( E_F \) is reduced to \( 3 \times 10^{12} \, \text{cm}^{-2} \) due to adsorption of F4-TCNQ, which may have two possible reasons. Firstly, the effective mass may be reduced by approximately the same factor when reducing the filling of the bands above the Dirac point, leaving...
N m$^{-1}$ approximately constant. Secondly, the coupling of the plasmon mode with the loss channels, as evident from the large FWHM, leads to an effective integration over the electron density around $E_F$ with a width proportional to the measured FWHM of the plasmon mode. Both the dynamics of the single and the collective excitation modes are extremely short and on the same timescale, which results in mixing of collective and single particle excitations.

In summary, the detailed analysis of plasmon excitations and their decay mechanisms, using graphene as a 2d model system, yields ultra-short dynamics with lifetimes of the order of $\tau \approx 10^{-14}$ s. Both e–h pair excitations by intra- and inter-band transitions contribute significantly to the decay of plasmons. When the latter channel is opened at finite $k_F$, coupling between plasmons and e–h pair excitations is resonantly enhanced. As a consequence, characteristic modifications of the plasmon dispersion and effective integration over the density states at $E_F$ responsible for plasmon formation were found, thus widening the standard picture for plasmon excitations.

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Figure 4. Graphene plasmon dispersion before (O) and after (O) F4-TCNQ doping. Inset: corresponding changes of $k$-dependent FWHM. Upper inset: stereographic model of F4-TCNQ. Solid line: fit with the NFEG model without resonant damping.