Electron-Hole Droplet Formation in Direct-Gap Semiconductors Observed by Mid-Infrared Pump-Probe Spectroscopy

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Mid-infrared pump-probe measurements with subpicosecond time resolution reveal the existence of a metastable condensed phase of the electron-hole ensemble in a direct-gap semiconductor CuCl. High-density electrons and holes are directly created in a low-temperature state by the resonant femtosecond excitation of excitons above the Mott transition density. Strong metallic reflection with a plasma frequency $\hbar\omega_p \approx 0.5$ eV builds up within 0.3 ps. Within a few picoseconds, the mid-infrared reflection spectrum is transformed from metalliclike into colloidlike. The observed resonance feature at $\hbar\omega_p/\sqrt{3}$ allows us to obtain the carrier density in the metastable electron-hole droplets of 2×10^{20} cm^{-3}.

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Photoexcited semiconductors may constitute a unique playground to investigate quantum many-body phenomena driven by the long-range Coulombic forces. In particular, if the exchange- and correlation-induced attractions among the high-density photogenerated carriers are strong enough to overcome the fermionic repulsive pressure and to reduce the chemical potential below the exciton energy, the fermionic condensate in the form of the electron-hole liquid drops (EHD) appears as the first order phase transition [1]. The investigation of the properties and formation dynamics of EHD can provide an opportunity to understand new aspects on the quantum many-body effects. However, excessive heating that accompanies photoexcitation often prevents the EHD formation.

This difficulty may be avoided in indirect-gap semiconductors, in which electron-hole system can reach quasiequilibrium during the relatively long carrier relaxation time. In direct-gap semiconductors, the situation is more complicated because the system cannot reach quasiequilibrium during carrier lifetime. The nonequilibrium many-body dynamics were investigated by measuring the transient gain and emission spectra [2–6], although photon-mediated effects influence the radiation processes and therefore make interpretation of the experimental data difficult. Correspondingly, no clear evidence of EHD has been reported yet even though the possibility of the existence of EHD has been discussed extensively [7].

In order to observe EHD in direct-gap semiconductors, it is necessary to create the electron-hole ensemble at low temperature, which would allow the system to reach quasiequilibrium within the carrier lifetime and to develop a method to probe the collective intraband motion of carriers. In this paper we propose to study the many-body dynamics by measuring reflectivity in the vicinity of the plasma frequency, where the optical response of the electrons and holes is determined by intraband transitions. This method provides direct access to the photoexcited carriers, which modify the dielectric constant ϵ_b of a semiconductor as follows:

$$\epsilon_M = \epsilon_b\left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\right), \tag{1}$$

where $\omega_p = \sqrt{4\pi n e^2/\epsilon_b m}$ is the plasma frequency, n, m, and e are the carriers' effective density, mass, and electric charge, respectively, and γ is the plasma damping. At $\omega \ll \omega_p$, the reflectivity of the homogeneous medium with dielectric constant (1) tends to 1 for any ϵ_b [8,9] [see Fig. 1-(2)]. However, if the spatial distribution of the photoexcited carriers is inhomogeneous, the shape of the transient reflectivity spectrum changes dramatically. When the characteristic size of the ionized areas is smaller than the wavelength and the volume fraction f of the ionized component is low, $f \ll 1$, the effective dielectric constant, ϵ_{eff}, is the following [10]:

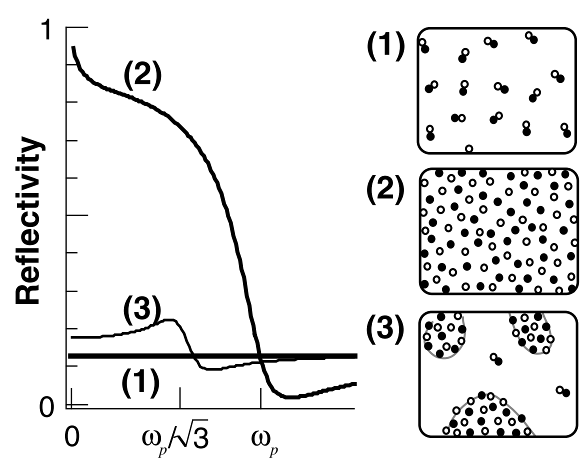

FIG. 1. Reflectivity around plasma frequency $\hbar\omega_p$ at different situations of electron-hole: (1) dilute exciton gas, (2) homogeneous plasma, and (3) EHD with $f = 0.1$ of volume fraction. In the spectra of (2) and (3), plasma damping is set at $0.1\hbar\omega_p$.

$$\epsilon_{\mathrm{eff}} = \epsilon_b \left(1 + 3f \frac{\epsilon_M - \epsilon_b}{\epsilon_M + 2\epsilon_b} \right). \qquad (2)$$

By using Eq. (1), one can show that there is a resonance feature of ϵ_{eff} at the frequency $\omega_p/\sqrt{3}$. Resonance EHD absorption at this frequency was observed in Ge [11]. It follows from Eq. (2) that at $\omega \ll \omega_p$ the reflectivity of the medium with dielectric constant ϵ_{eff} does not tend to 1 at nonzero f.

To examine low-temperature states of the electron-hole system, one needs to prevent carriers from overheating, which occurs under band-to-band excitation due to the band-gap reduction and the lack of an efficient cooling mechanism [3,6,12]. This excess heating can be reduced by excitations with ultrashort light pulses tuned to the exciton resonance [13,14]. In such a case excitons become ionized due to the screening of the Coulomb attraction between electrons and holes at the critical density of the excitonic Mott transition, while the band-gap reduction is nearly compensated by the reduction of exciton binding energy E_{ex} [15]. Correspondingly, this excitation scheme effectively prevents the overheating of carriers in materials with large E_{ex}.

CuCl is a typical direct-gap semiconductor that has a stable exciton state $Z_3 - 1s$, with large binding energy ($E_{\mathrm{ex}} = 212$ meV). The plasma frequency can be scaled with the exciton binding energy, $\hbar\omega_p = \sqrt{12/r_s^3}\,E_{\mathrm{ex}}$, where $r_s = \sqrt[3]{3/4\pi n a_B^3}$ [1]. In CuCl, ω_p for the degenerate plasma above the Mott transition density ($r_s^{\mathrm{Mott}} = \sqrt[3]{48/\pi} \approx 2.5$) is in the mid-infrared (mid-IR) region ($\hbar\omega_p^{\mathrm{Mott}} = \sqrt{\pi/4}\,E_{\mathrm{ex}} \approx 0.19$ eV), which is far below the band gap ($E_G = 3.416$ eV) and well above the LO phonon energy ($E_{\mathrm{LO}} = 25.9$ meV). Thus, the measurement of the photoinduced reflectivity change in the mid-IR region is suitable for probing the intraband motion of the photoexcited carriers in CuCl. Although coexistence of the exciton gas and EHD has been theoretically predicted in CuCl at low temperature [16], no experimental evidence of the phase separation has yet been reported. In this paper, by using mid-IR pump-probe reflectivity measurements, we show that the below-gap excitation effectively prevents the carriers overheating and results in the formation of EHD in CuCl.

The measurements are performed on a high-purity single crystal CuCl (thickness 37 μm). Pump and probe pulses are provided by a system based on an amplified mode-locked Ti:sapphire laser (775 nm center wavelength, 0.2 ps pulse duration, and 1 kHz repetition rate) and an optical parametric generator (OPG). The OPG fourth harmonics is tuned at 382 nm center wavelength, which is 170 meV below the band gap and slightly above the $Z_3 - 1s$ resonance, and used for photoexcitation. The absorption coefficient at this wavelength is about 2×10^3 cm^{-1}. The excitation pulse is focused (a spot size is 300 μm) on the sample kept at 10 K in the cryostat. The probe pulse is obtained by difference frequency generation in the $AgGaS_2$ crystal using the signal and idler beams of another OPG and focused on the sample with a spot size of 150 μm. The differential reflection signal is measured with a liquid-nitrogen-cooled HgCdTe mid-IR detector and a boxcar integrator synchronized with laser pulses. Spectral resolution is about 30 meV, limited by the spectral width of probe pulses. The interband emission is simultaneously measured using a spectrometer with a focal length of 50 cm equipped with a cooled CCD camera.

Without excitation, the crystal reflectivity, R_0, is about 0.14 within the spectral range from 1 to 10 μm. Figure 2 shows the temporal evolution of the normalized reflectivity change $\Delta R/R_0$ for the excitation density 4.3 mJ/cm^2 [Fig. 2(a)] and 0.6 mJ/cm^2 [Fig. 2(b)]. The inset of Fig. 2 shows relevant time-integrated emission spectra. At the excitation density of 4.3 mJ/cm^2, a broad plasma emission band [12] appears at the lower-energy side. At the lower excitation density, a narrow X-band emission [17] centered at 392.7 nm (slightly lower than the biexciton emission lines) appears. By using time-resolved emission measurements, we have shown [14] that this band is associated with the emission of cold plasma. One can observe from Fig. 2 that the pump-induced reflectivity change consists of instantaneous (within our temporal resolution) and decaying parts. At the excitation density of 4.3 (0.6) mJ/cm^2, the instantaneous reflectivity change is $\Delta R/R_0 = 4$ (0.7) at 10 μm and $\Delta R/R_0 = -0.7$ (-0.2) at 1.8 μm. The sign of $\Delta R/R_0$ at 4.0 μm changes from positive to negative at 8 and 3 ps for excitation densities 4.3 and 0.6 mJ/cm^2, respectively. At the excitation density of 0.1 mJ/cm^2, which is lower than the critical excitation density (0.4 mJ/cm^2 [14]) for excitonic Mott transition, no prominent change

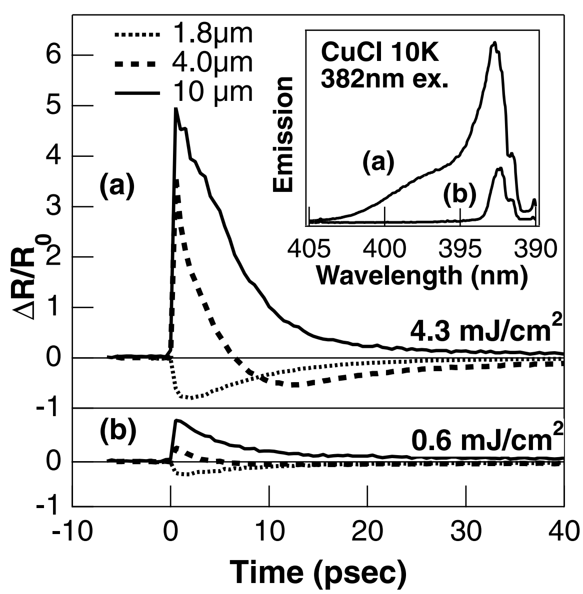

FIG. 2. The temporal evolution of normalized reflectivity change $\Delta R/R_0$ at 1.8, 4, and 10 μm at excitation densities of 4.3 mJ/cm^2 (a) and 0.6 mJ/cm^2 (b). The inset is the emission spectra at the excitation densities of (a) and (b).

in the mid-IR reflectivity associated with plasma was observed.

Figures 3(a) and 3(b) show the differential reflectivity spectra for 1, 10, and 30 ps pump-probe delay at excitation densities of 4.3 and 0.6 mJ/cm^2, respectively, along with the absolute reflectivity, shown on the right ordinate. At 4.3 mJ/cm^2, $\Delta R/R_0$ shows typical plasma behavior by increasing at the low-energy side and decreasing at the high-energy side, while the magnitude of the reflectivity clearly indicates that strong metallic reflection (reflectivity is 80% at 10 μm and 3% at 1.8 μm) appears at 1 ps delay. The spectra in Fig. 3 have two prominent features. The first is that the spectral position of the zero-cross point of $\Delta R/R_0$, E_0, decreases from 0.5 to 0.21 eV with the increase of the delay time. The second feature is the decrease of $\Delta R/R_0$ at 10 μm with the increase of the time delay and/or decrease of the excitation densities. Since condition $E_0 > 0.20$ eV always holds, we can exclude the effects associated with the $1s$-$2p$ excitonic transition with energy of about 0.17 eV. This allows us to analyze the transient reflectivity spectra by using the model discussed above. In this model, E_0, which corresponds to the spectral anomaly of the medium dielectric constant, is determined by the photoinduced carriers' density. As we have

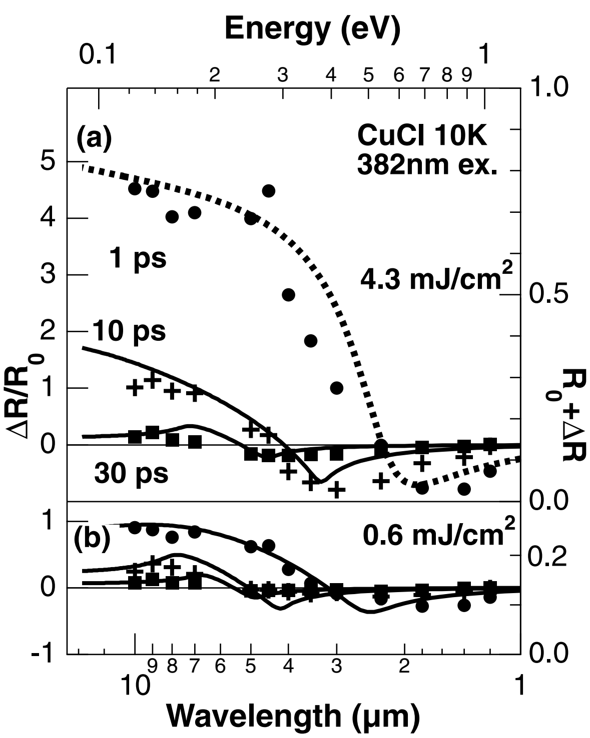

FIG. 3. The temporal evolution of the transient reflectivity spectra $\Delta R/R_0$ at 1, 10, and 30 ps at the excitation densities of (a) 4.3 mJ/cm^2 and (b) 0.6 mJ/cm^2. The right axis corresponds to absolute reflectivity $R_0 + \Delta R$. The dashed curve of (a) at 1 ps is the assumption of homogeneous plasma ($n = 3.8 \times 10^{20}$ cm^{-3}, $\gamma = 0.22$ eV). The solid curves represent the theory of the metallic mixture model (the parameters of Fig. 4 and $\gamma = 0.008$ eV).

shown above, $E_0 \approx \hbar\omega_p$ in the homogeneous limit, while in the inhomogeneous limit $E_0 \approx \hbar\omega_p/\sqrt{3}$ holds. Our experimental finding $E_0 > 0.20$ eV leads to the constraint $\hbar\omega_p > 0.20 \text{ eV} > \hbar\omega_p^{\text{Mott}}$, which implies that the density of free carriers is always above the Mott density. Therefore, we arrive at the conclusion that free carriers exist for all time delays in Fig. 3. We also observe a gradual reduction of $\Delta R/R_0$ with the increase of the time delay at the low-energy side and always negative $\Delta R/R_0$ at the high-energy side. Such a temporal evolution of the reflectivity clearly indicates the departure from the homogeneous carrier distribution, because the latter implies nearly 100% reflectivity below $\hbar\omega_p$.

The experimental results further imply that the carrier distribution splits into high-density plasma and low-density exciton gas parts. The free carriers occupy a finite volume fraction of the excited region, and this fraction increases with the increase in the excitation density. In particular, at the excitation density of 4.3 mJ/cm^2, one may expect that free carriers occupy nearly the whole excited region at 1 ps pump-probe delay [Fig. 3(a)] when the reflectivity is higher than 80% at 10 μm. In such a case, the zero-cross point is close to the plasma frequency, $E_0 \approx \hbar\omega_p \approx 0.53$ eV, and, correspondingly, the plasma density is $n \approx 4 \times 10^{20}$ cm^{-3}. The reduction of the reflectivity at the low-energy side down to 25% at 10 ps and 5% at 30 ps implies the ionized volume decreases for longer delays between pump and probe pulses.

In order to explain the experimental reflectivity spectra shown in Fig. 3, we model the excited region as a composite medium consisting of spherical particles with the dielectric coefficient ϵ_M given by Eq. (1) and volume fraction f, and dielectric particles with dielectric coefficient ϵ_b. Strictly speaking, we should take into account the exponential decrease in the carrier density caused by the linear absorption. In our experiment the penetration length is 5 μm, which is smaller than the sample thickness and comparable with the probe wavelength. However, it can be shown [8] that the exponential profile of the carrier density does not strongly affect E_0 or mid-IR reflectivity in our experimental condition. Therefore, for the sake of simplicity we neglect the carrier density profile of the surface. The effective dielectric coefficient of such a medium, ϵ_{eff}, is given by the following equation [18]:

$$f\,\frac{\epsilon_M - \epsilon_{\text{eff}}}{\epsilon_M + 2\epsilon_{\text{eff}}} + (1 - f)\,\frac{\epsilon_b - \epsilon_{\text{eff}}}{\epsilon_b + 2\epsilon_{\text{eff}}} = 0\,, \qquad (3)$$

which is reduced to Eq. (2) at $f \ll 1$. Since at small damping ($\gamma \ll \hbar\omega_p$) the reflectivity at the low-energy side is determined by the volume fraction, Eq. (3) allows us to estimate f from the experimental spectra. Equation (3) and the dependence of E_0 on the pump-probe delay also allow us to estimate the temporal evolution of the free carriers' density in the ionized parts. By using material parameters for CuCl we arrive at the following equation: $E_0/\hbar\omega_p \approx 1/\sqrt{3} + 0.55f$. This equation, along

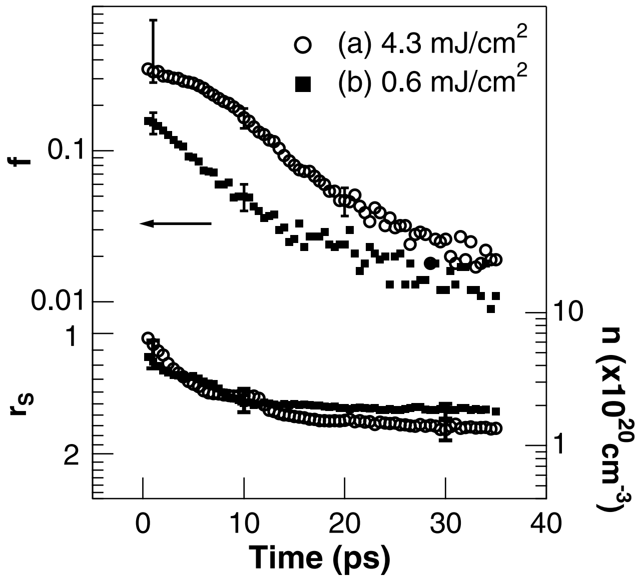

FIG. 4. Temporal evolution of volume fractions and densities of plasma estimated from Fig. 3 using Eq (3).

with spectra from Fig. 3, gives us the temporal evolution of f and the carrier density n shown in Fig. 4. Since $\Delta R/R_0$ is insensitive to f at $f > 0.5$, the obtained volume fraction of the ionized medium for the excitation density of 4.3 $\mathrm{mJ/cm^2}$ at the time delay 1 ps is underestimated, whereas n is overestimated. Figure 4 indicates that, although the initial value of f depends on the excitation density, the decay constant does not. Temporal evolution of n is also almost excitation independent. The calculated reflection spectra, which are presented in Fig. 3 as solid curves, well reproduce the overall features of the experimental ones. Figure 4 shows that n rapidly decreases from $4 \times 10^{20}\ \mathrm{cm^{-3}}$ to $2 \times 10^{20}\ \mathrm{cm^{-3}}$ within 10 ps after excitation and hardly changes at longer pump-probe delays, while f decreases monotonously. This indicates that the electron-hole system reaches a metastable EHD state within 10 ps. The obtained carrier density in the EHD corresponds to $r_s = 1.7$, which is in good agreement with the theoretical prediction in direct-gap semiconductors ($r_s \approx 1.7$ in CdS [19] and $r_s \approx 1.8$ in CuCl [16]). The above interpretation of the transient reflectivity spectra is also supported by the results of the time-resolved emission measurements. Specifically, we have shown [14] that with the excitation density of 3.5 $\mathrm{mJ/cm^2}$, the emission line shape is continuously transformed within 10 ps from a broadband characteristic to plasma into a narrower X band originated for the EHD.

In conclusion, we create a high-density electron-hole system at a temperature low enough to reach the quantum degenerate regime by resonant excitation of excitons below the band gap. We employ mid-IR pump-probe reflectivity measurements, which allow us to probe intraband collective carriers' motion and obtain clear evidence of the EHD formation in CuCl. By combining the results of the mid-IR reflectivity and ultraviolet emission measurements, we conclude that X-band emission originates from EHD. From the colloidlike spectral profile of reflection, we obtain carrier density in the metastable EHD of about $2 \times 10^{20}\ \mathrm{cm^{-3}}$.

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