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Observation of interacting polaronic gas behavior in Ta-doped TiO₂ thin films via terahertz time-domain spectroscopy

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Transparent conductive oxides (TCOs) — materials that have the twin desirable features of high optical transmission and electrical conductivity, play an increasingly significant role in the fields of photovoltaics and information technology. As an excellent TCO, Ta-doped anatase TiO₂ shows great promise for a wide range of applications. Here, terahertz time-domain spectroscopy (THz-TDS) is used to study the complex optical conductivity $\tilde{\sigma}(\omega)$ of the TCO — heavily Ta-doped TiO₂ thin films with different Ta-doping concentrations, in the frequency range of 0.3–2.7 THz and temperature range of 10–300 K. Fitting the complex optical conductivity to a Drude-like behavior allows us to extract the temperature dependence of the effective mass, which suggests the existence of many-body large polarons. Moreover, the carrier scattering rate of Ta-doped TiO₂ with different carrier concentration agrees with the interacting polaron gas theory. Our results suggest that with increasing electron density in TiO₂, the interaction between polarons is larger and electron-phonon coupling is smaller, which is beneficial for achieving high mobility and conductivity in TiO₂.

In the past decade, the rapid development of information technology and consumer electronics has created huge demand for transparent conductive oxides (TCOs).¹ The most commonly-used TCO in large-scale application, indium tin oxide (ITO) thin film, suffers increasingly from the rarity of the post-transition metallic element indium.^{2,3} Also, one needs a variety of TCOs with different work functions and refractive indices for matching with other materials such as doped GaN in devices.³ Recently, Ta-doped anatase TiO₂ has been found to be a good TCO with carrier density and mobility values similar to those of ITO, thus showing great promise for various applications.^{4,5}

Due to the polar nature of TiO₂, polarons — phonon-dressed electrons — rather than bare electrons, are the carriers that determine the conductivity in Ta-doped TiO₂.⁵⁻⁷ The Fröhlich electron-phonon coupling constant (α) is used to classify polar materials: (1) in materials with relatively large α (> 6), the quasiparticles are small polarons and the conduction mechanism is hopping, which leads to a relatively low mobility; while in the case of weaker electron-phonon coupling ($\alpha < 6$), the quasiparticles are large polarons, which behave like free electrons but with effective mass still larger than free electron mass.⁶ Large polarons ($\alpha < 6$) have been observed by ARPES on pure anatase TiO₂ and by optical-pump THz-probe spectroscopy on pure rutile TiO₂, while a polaronic liquid has been observed in pure anatase TiO₂ using transport measurements.⁸⁻¹⁰ In doped-TiO₂, however, first-principles calculations predict the existence of small polarons ($\alpha > 6$) in Ta- and Nb-doped rutile and anatase TiO₂, while transport and transient absorption measurements suggest the presence of large and small polarons, respectively, in both Nb- and Ta-doped anatase TiO₂.^{5,11} In traditional theories, polarons are treated as quasiparticles which do not interact with one another.^{5-7,11,12} This assumption is valid in the case of low carrier densities. However, in heavily-doped semiconductors, such as Nb-doped SrTiO₃ and Ta-doped TiO₂, where the carrier density is very large ($\sim 10^{21}$ cm⁻³), the interaction between carriers cannot be ignored.¹³ In this paper, we present terahertz time-domain spectroscopy (THz-TDS) studies of Ta-doped TiO₂ thin films at different temperatures to study their frequency-dependent far-infrared conductivity. Our results reveal the existence of an interacting polaronic gas in these TCOs, and suggest that their large conductivity is caused by the combined effects of (1) a large carrier density, *and* (2) a small electron-phonon coupling constant, α , due to Ta doping.

Three Ta-doped TiO₂ thin films (labelled as sample A, sample B and sample C) are grown by pulsed laser deposition (PLD) on double side polished SrLaAlO₄ (SLAO) substrate with dimension 5 mm×5 mm×1 mm at temperature of 880 K, and at different oxygen partial pressures for different Ta-doping concentration. The thickness and Ta-doping concentration of each thin film is measured by Rutherford backscattering spectrometry (RBS). Ion channeling measurements indicate the Ta and Ti minimum yield to be of the order of 10 %, indicating an extremely high crystalline quality and substitutionality of the Ta at the Ti site. Hall measurements are performed to obtain the carrier density of each sample, and the temperature-independent results are consistent with previous research.⁵ XRD measurements are performed to confirm the anatase phase of our samples, and the

results suggest that only the component of the optical conductivity perpendicular to the optic axis of anatase (c-axis) is measured in this work. The details of sample characterization are in supplementary material. The carrier density, Ta-doping concentration, and thin film thickness of sample A, B, and C are shown in Tab. I.

THz-TDS is a non-contact far-infrared optical technique, that has been used to study the low-energy excitations of materials such as superconductors, topological insulators, and semiconductors.¹⁴ From the amplitude and phase of the transmitted complex THz electric field, we are able to extract the complex optical conductivity, $\tilde{\sigma}(\omega)$, without the need for Kramers-Kronig transformation.¹⁵ In particular THz-TDS has been used to study polaronic effects in semiconductors.^{9,16} The transmission THz spectrum of our samples are measured using a commercial THz-TDS system (TeraView TPS-3000), coupled with a Janis ST-100 FTIR cryostat and motorized vertical stage to move from sample to reference (see Ref. 15 for details). The THz wave is generated and detected by photoconductive antennas fabricated on low-temperature-grown GaAs films. The setup is well calibrated as shown in Fig. S1 in supplementary material where the vac-vac curve is the measurement of sample holder without sample and reference. Its transmission coefficient [$\tilde{T}(\omega) = \tilde{E}_{samp}(\omega)/\tilde{E}_{ref}(\omega)$] is within $100 \pm 1\%$ in 0.3—2.5 THz, which represents the trustable region of our measurements.

From the THz-TDS measurements, the time domain electric field signal of sample and reference is obtained [Fig. 1(a)]. Fig. 1(b) shows the transmission coefficient ($\tilde{T}$) of sample A (data of other samples are similar) at selected temperatures in the frequency domain. $\tilde{T}$ is obviously temperature-dependent for temperature >100 K, while it changes only a little at low temperature, which is consistent with DC measurements (Fig. 4). The smaller transmission coefficient at lower temperatures indicates stronger THz absorption and higher conductivity.

The complex refractive index [$\tilde{n}(\omega) = n(\omega) + ik(\omega)$] of the three samples at various temperatures can be extracted by numerically solving Eq. (1), which is a standard THz data analysis method:¹⁵

$$\tilde{T}(\omega) = \frac{2\tilde{n}(1 + \tilde{n}_{sub}) \exp\left[\frac{i\omega d(\tilde{n} - 1)}{c}\right] \exp\left[-\frac{i\omega \Delta L(\tilde{n}_{sub} - 1)}{c}\right]}{(1 + \tilde{n})(\tilde{n} + \tilde{n}_{sub}) + (\tilde{n} - 1)(\tilde{n}_{sub} - \tilde{n}) \exp\left(\frac{2i\omega d\tilde{n}}{c}\right)}. \quad (1)$$

Here $\tilde{n}$ and $\tilde{n}_{sub}$ are the complex refractive indices of Ta-doped TiO₂ thin film and substrate (SLAO), respectively, d is the thin film thickness, ΔL is the thickness difference between sample and reference substrates, and c is the light speed in vacuum. This equation takes into account multiple reflections in the Ta-doped TiO₂ thin film. However, because of the relatively large refractive index and thickness of SLAO [$\text{Re}(\tilde{n}_{sub}) > 4.1$, thickness ≈ 1 mm], the multiple reflections in the substrate is far from the main peak and excluded in our data analysis.

The extracted complex refractive index $\tilde{n}$ is then used to calculate the complex conductivity [$\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$] according to the relationship $\sigma_1 = 2\omega\epsilon_0nk$ and $\sigma_2 = \omega\epsilon_0(\epsilon_\infty - n^2 + k^2)$. Here ϵ_0 is the permittivity of free space and ϵ_∞ is the high-frequency dielectric constant, which is set to 1 initially, and will be a fitting parameter in the conductivity model discussed later.¹⁴ The obtained complex conductivity of all the samples as functions of frequency at different temperatures are shown in Fig. 2. The decrease in σ_1 and σ_2 with increasing temperature is consistent with the trend seen in the transmission coefficient [Fig. 2 (b)]. Compared to other TCOs such as ITO, our three samples display a stronger temperature dependence of the conductivity, suggesting a stronger electron-phonon interaction and consistent with a polaronic nature of the carriers in TiO₂.¹⁷

From Fig. 2 we see that $\tilde{\sigma}(\omega)$ exhibits a typical Drude response, where $\sigma_1(\omega)$ has a maximum at zero frequency and decreases with increasing frequency, while $\sigma_2(\omega)$ is zero at low frequency and increases with increasing frequency. Therefore, in order to understand the transport properties of our samples, the frequency-dependent complex conductivity is fitted by the Drude model:

$$\tilde{\sigma}(\omega) = \frac{e^2N}{m^*} \frac{1}{\gamma - i\omega} - i\epsilon_0\omega(\epsilon_\infty - 1), \quad (2)$$

where N , m^* and γ are the density, effective mass and scattering rate of carriers in the thin film, respectively. The fits of Eq. (2) to the complex optical conductivity obtained from THz data are very good at all temperatures, with selected fitting curves shown in Fig. 2(a). In the fits, the value of the carrier density (N) of sample A, B and C are set to 0.5 , 1.2 and $1.5 \times 10^{21} \text{ cm}^{-3}$ according to Hall measurements, and are temperature-independent shown in Fig. S4, which is consistent with the degenerated doping nature of our samples.¹⁸

From the fits, the parameters scattering rate (γ) and effective mass (m^*) of the three samples as functions of temperature are shown in Fig. 3. At low temperatures ($<100 \text{ K}$), the temperature independence of γ [Fig. 3(a)] suggests defect scattering to be the dominant scattering process.¹⁹ However, the strong increase of γ at higher temperatures suggests a very different mechanism. This temperature dependence can also be seen in Fig. 2(a), where the Drude peak narrows with decreasing temperature. The narrowing of the Drude peak at low temperatures was also observed in Nb-doped SrTiO₃ in Ref. 13 and 20, which the authors attributed to many-body polaronic effects. The effective mass m^* also shows a strong temperature dependence [Fig. (3b)], in contrast with that in normal metals such as silver and gold, where m^* is temperature independent.²¹

The standard Drude model above yielded good simultaneous fits to $\sigma_1(\omega)$ and $\sigma_2(\omega)$, and revealed a strong temperature dependence of γ (and m^*). However, the Drude model does not provide for a *microscopic origin* for this strong temperature

dependence, and for this, we present the interacting polaronic gas (IPG) model below.¹³ We offer the three justifications that Ta-doped TiO₂ is an IPG. First, angle-resolved photoemission data showed that with doping, anatase-TiO₂ can become a polaronic gas where the quasiparticles are large polaron;⁸ Second, due to the large carrier density ($\sim 10^{21} \text{ cm}^{-3}$ from Hall measurements, see the section I in supplementary material), the average electron-electron distance is smaller than 1 nm, which is on the order of the polaron radius ($\sim 1 \text{ nm}$, see Ref. 8) and the lattice constant of anatase TiO₂ ($a = b = 0.38 \text{ nm}$, $c = 0.95 \text{ nm}$).²² This increases the correlation between adjacent polarons and makes the notion of an interacting polaronic gas in this material plausible. The carrier density in our samples is greater than that in another doped perovskite system – Nb-doped SrTiO₃, where optical (THz to IR) spectroscopy data yielded a carrier density $n \sim 10^{20} \text{ cm}^{-3}$, which the authors attributed to the presence of an interacting polaronic gas.²⁰ Third, in the conventional perturbation theory for large polarons, the effective mass $m^* = m_b / (1 - \alpha/6)$ is taken to be temperature-independent.⁷ Even in the modified Feynman's polaron theory, m^* should not change by $\sim 10\%$ from 10 K to 300 K.²³ Therefore, the strong temperature dependence of m^* seen in our data suggests the presence of many-polaron effects. The same Nb-doped SrTiO₃ paper mentioned above [Ref. 20] showed a similar temperature-dependent effective mass, where the ratio of the effective mass at high to low temperatures is ~ 2.4 , which the authors attributed to the presence of a polaronic liquid.²⁰ In comparison, our data show an increasing $m^*(300 \text{ K})/m^*(10 \text{ K})$ ratio of 1.7, 1.9 and 2.3 in samples with increasing carrier density (samples A, B and C, respectively), suggesting a positive correlation between the strength of many-body effects and carrier density (doping concentration). Hence correlations between polarons are not insignificant in our samples.

We now turn to the mathematical formulation of the IPG model. Considering both electron-phonon and electron-electron interactions as well as the Fermi statistics of the polaron gas, the model yields a complex optical conductivity that is mathematically similar to that of the Drude model in Eq. (2), but with the real and frequency-independent scattering rate γ replaced by a *complex* and *frequency-dependent* scattering rate $\tilde{\gamma}_{IPG}(\omega)$,¹³

$$\tilde{\sigma}_{IPG}(\omega) = \frac{e^2 N}{m^*} \frac{1}{\tilde{\gamma}_{IPG}(\omega) - i\omega} - i\epsilon_0 \omega (\epsilon_\infty - 1), \quad (3)$$

where

$$\tilde{\gamma}_{IPG}(\omega) = \frac{i\tilde{\chi}(\omega)}{\omega}, \quad (4)$$

and $\tilde{\chi}(\omega)$ is the weighted sum of the contributions from different phonon modes:

$$\tilde{\chi}(\omega) = \sum_j \alpha_j \tilde{\chi}_j(\omega), \quad (5)$$

and the individual $\tilde{\chi}_j(\omega)$ given by:

$$\begin{aligned}\tilde{\chi}_j(\omega) = & \frac{\hbar\omega_{L,j}^2}{6\pi^2 N m_b} \left(\frac{\hbar}{2m_b\omega_{L,j}} \right)^{\frac{1}{2}} \int d\mathbf{q} \{ g(\mathbf{q}, \omega - \omega_{L,j}) \\ & + g^*(\mathbf{q}, -\omega - \omega_{L,j}) - g(\mathbf{q}, -\omega_{L,j}) - g^*(\mathbf{q}, -\omega_{L,j}) \\ & + \frac{1}{e^{\beta\hbar\omega_{L,j}} - 1} \{ G^R(\mathbf{q}, \omega - \omega_{L,j}) + [G^R(\mathbf{q}, \omega - \omega_{L,j})]^* \\ & - G^R(\mathbf{q}, -\omega_{L,j}) - [G^R(\mathbf{q}, -\omega_{L,j})]^* \} \}. \end{aligned} \quad (6)$$

Here $\omega_{L,j}$ and α_j are the phonon mode frequency and Fröhlich electron-phonon coupling constant, respectively, of the j^{th} LO phonon which is engaged in the polaron. g and G^R are the casual and retarded Green's functions (see the details in section II of supplementary material).

The total scattering rate $\tilde{\gamma}_{total}(\omega)$, which we fit to our data, is the sum of the real and temperature-independent contribution from defect scattering $\tilde{\gamma}_{defect}$,¹⁹ and the temperature-dependent and complex $\tilde{\gamma}_{IPG}$:

$$\tilde{\gamma}_{total}(\omega) = \gamma_{defect} + \tilde{\gamma}_{IPG}(\omega) = \gamma_{defect} + i \frac{\tilde{\chi}(\omega)}{\omega} = \gamma_{defect} + i \frac{\sum_j \alpha_j \tilde{\chi}_j(\omega)}{\omega}. \quad (7)$$

By performing the DFT calculation (see the section III in supplementary material), the LO phonon modes in Ta-doped TiO₂ at frequencies 6.0 THz (E_g), 7.1 THz (E_u), 13.0 THz (E_u), 15.3 THz (A_{1g}) and 18.6 THz (E_g), should participate in polaron formation.

We use Eq. (5) (see section II of supplementary material for details) to compute $\tilde{\chi}_j(\omega)$ for each phonon mode (Fig. S6). We notice that, at high temperatures and in our THz frequency range, $|\text{Im}[\tilde{\chi}_j(\omega)]| \gg |\text{Re}[\tilde{\chi}_j(\omega)]|$ and $\text{Im}[\tilde{\chi}_j(\omega)] \propto \omega$. Therefore, the quantity $i\tilde{\chi}_j(\omega)/\omega$ becomes a real and frequency-independent quantity, which we call $\gamma_{IPG,j}$. On the other hand, at low temperatures, both $\text{Re}[\tilde{\chi}_j(\omega)]$ and $\text{Im}[\tilde{\chi}_j(\omega)]$ are very small in magnitude, and so the main contribution to the experimental $\tilde{\gamma}_{total}(T)$ comes from the real and temperature-independent γ_{defect} . Hence, whether at low or high temperatures, the complex and frequency-dependent scattering rate $\tilde{\gamma}_{IPG}(\omega)$ in the IPG model [Eq. (2)] can therefore be replaced by a real and frequency-independent quantity $\gamma_{IPG,j}$. This effectively reduces the IPG model to the Drude model, and explains why both the IPG and Drude models fit the data equally well. However, we want to stress that the Drude model cannot give a microscopic explanation of the strong dependence of the scattering rate seen in our data, while the IPG model can. Our subsequent analysis using IPG thus assumes a real and frequency-independent $\gamma_{IPG,j}$, with the total scattering rate simplified from Eq. (6) to

$$\gamma_{total}(T) = \gamma_{defect} + \sum_j \alpha_j \gamma_{IPG,j}(T). \quad (8)$$

The Fröhlich electron-phonon coupling constant corresponding to each phonon mode (α_j) can then be obtained by fitting the experimental scattering rate to Eq. (7), and finally the value of effective Fröhlich coupling constant $\alpha_{\text{eff}} = \sum_j \alpha_j$, defined in Ref. 13 is obtained. The fitting results are given in Tab. 1, and the values of α_{eff} for all the samples are smaller than 6, which is consistent with the large-polaron scenario. From the fitting, we can see that at higher carrier density, the electron-phonon coupling (α_{eff}) is smaller, which is the result of screening effects arising from the higher electron density. This result is consistent with the observation that, as we go from sample A (smallest carrier concentration) to sample C (largest carrier concentration), the temperature dependence of $\gamma(T)$ is strongest for sample A and weakest for sample C.

Fig. 4(a) shows the DC resistivity $\rho_{DC}[1/\sigma_1(0.3 \text{ THz})]$ of the three samples as a function of temperature. Combined with transport measurements on more samples (more data are in Fig. S5 in supplementary material), the fitting to a power law $\rho_{DC} \sim T^\beta$ on the data (both THz and transport measurements) show the exponent evolving from $\beta \sim 3$ for low Ta-doping to $\beta \sim 2$ for high Ta-doping. This suggests that the system evolves from a e-ph scattering dominated^{5,24} regime at low Ta doping to an e-e/carrier-carrier scattering dominated regime. These results are consistent with our interacting polaronic gas analysis, where correlations between polarons are more significant at higher Ta doping.

In conclusion, THz-TDS technique is applied to study a Ta doped TiO₂ thin film. Utilizing the interacting polaron gas theory, the temperature dependence of scattering rate is explained by suggesting that the carriers in those samples are interacting polarons rather than bare electrons. Also, the Fröhlich coupling constant α is obtained, which is highly dependent on the carrier density. Therefore, the exceptional electronic performance of Ta-doped TiO₂ with higher doping concentrations is not only from its high carrier density, but also the reduced electron-phonon coupling (smaller α).

Supplementary Material

See the supplementary material for: (I) Experimental details and sample characterization; (II) Derivation of many-body polaron theory; (III) DFT calculation.

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FIG. 1. Experimental data of sample A at selected temperatures. (a) THz waveform that pass through the sample A and pure substrate (reference); (b) transmission coefficient of sample A in frequency domain, which shows obvious temperature-dependence. The data of samples B and C are similar.

FIG. 2. Real and imaginary conductivity of samples A, B, and C. Solid lines are fits to the Drude model [Eq. (2)].

FIG. 3. (a) Scattering rate obtained from experimental data, and the curve comes from the fitting to Eq. (8). (b) Temperature dependent effective mass of polarons in samples A, B, and C.

FIG. 4. (a) Temperature dependent DC resistivity of each samples (at 0.3 THz). The curves represent for the power law fitting ($\rho = \rho_0 + \rho_1 T^c$). (b) Exponent c from power law fitting as the function of carrier density.

TAB. I. Carrier density (from Hall measurements), Ta doping concentration (from RBS measurements), thin film thickness (from RBS measurements) and effective Fröhlich electron-phonon coupling constant α_{eff} (from IPG model), with different Ta doping concentrations.

Sample	Carrier density [10^{21} cm^{-3}]	Doping [a.t.%]	Thickness [nm]	α_{eff}
Pure anatase TiO_2^a	$\sim 10^{-2}$	–	–	~ 2.5
A	0.5	2.4	160.8	2.49
B	1.2	6.3	279.5	2.23
C	1.5	6.1	216.4	1.92

^a From Ref. 8.

Availability of data: the data that support the findings of this study are available from the corresponding author upon reasonable request.

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