A direct measurement method of quantum relaxation time

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ABSTRACT

The quantum relaxation time of electrons in condensed matters is an important physical property, but its direct measurement has been elusive for a century. Here, we report a breakthrough that allows direct determination of quantum relaxation time at zero and non-zero frequencies using optical measurement. Through dielectric loss function, we connect bound electron effects to the physical parameters of plasma resonance and find an extra term of quantum relaxation time from inelastic scattering between bound electrons and conduction electrons at non-zero frequencies. We demonstrate here that the frequency-dependent inelastic polarization effect of bound electrons is the dominant contribution to quantum relaxation time of conduction electrons at optical frequencies, and the elastic polarization effect of bound electrons also dramatically changes the plasma resonance frequency through effective screening to charge carriers.

Keywords: quantum relaxation time, plasma resonance, dielectric loss function

INTRODUCTION

Quantum relaxation time ($\tau$) is an important physical property affecting some of the most critical electron transport parameters in advance materials, such as electrical conductivity and carrier mobility in metals and semiconductors, the pseudo-gap and critical temperature of superconductors \cite{1}, and the propagation distance of an electron carrying encoded information in quantum computation materials and devices \cite{2,3}. It also relates to the weak localization effect of topological materials \cite{4,5} and the coupling of multi-degrees of freedom in strongly correlated systems \cite{6}. In optical-driven electronic devices \cite{7–9}, $\tau$ under an electromagnetic (EM) field is a critical factor in determining the information exchange between electrons and photons.

Measurement of $\tau$ has never been a straightforward task. Conventionally, $\tau$ can only be determined indirectly under a static field by the equation: $\tau = \mu m^*/\epsilon$. While the carrier mobility ($\mu$) is identified by joint measurements of DC conductivity and Hall effect using electrical-contact methods, the effective mass ($m^*$) is obtained by magnetic oscillation experiments under an ultra-high magnetic field and ultra-low temperature. A method for direct measurement of quantum relaxation time is a constant pursuit for physicists, especially at non-zero frequencies.

In 1900, Drude proposed a theory describing the interaction between photons and conduction electrons \cite{10}, which paved the way towards an optical solution for quantum relaxation time measurement. The Drude model predicts the resonance of conducting electrons in a material under optical radiation at plasma frequency $\omega_p$. The Drude model was later modified \cite{11} with quantum theory by Sommerfeld and others, resulting in a universal expression of the Drude–Sommerfeld complex dielectric function for all conductive materials, that is the response of a free electron gas to an optical radiation derived from the Maxwell equation \cite{12}:

\begin{equation}
\varepsilon^D(\omega) = \varepsilon_{\infty}^D + i\varepsilon_1^D = \left(\varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + 1/\tau_D^2}\right) + i\frac{\omega_p^2}{\omega\tau_D\left(\omega^2 + 1/\tau_D^2\right)},
\end{equation}

where

\begin{equation}
\omega_p^2 = \frac{4\pi n_e\epsilon^2}{m^*}.
\end{equation}
and \( \tau_D \) is the Drude quantum relaxation time (reciprocal of the electron scattering rate), which is considered frequency-independent and thus can be determined under DC field; \( \varepsilon_r \), the background dielectric polarizability [13] equals unity in the original model; \( n_s \), the number of conduction electrons (around the Fermi surface) per unit volume; and \( m^* \) the effective mass of conduction electrons.

Via introduction of effective mass, the background lattice effect to the conduction electrons can be partly accounted for in Equations (1) and (2) and the plasma frequency is rewritten [14] with a re-definition of electron mass by band structure effective mass of quasi-particles. Subsequently, the single quantum relaxation time of all conduction electrons hypothesized by Drude is naturally explained by single Fermi energy as per Fermi-Dirac statistics for all conductive electrons. This has been proven valid even for a highly correlated heavy-fermion system [6].

In more recent works [15–18], a constant \( \varepsilon_r = 1 + 4\pi n\alpha \) is introduced to resolve the discrepancies between the model and experimental values of plasma frequency, where \( \alpha \), a constant, is the ionic polarizability coefficient, and \( n \) is the atomic density. As a result, the resonance is expected to occur where \( \varepsilon_r(\omega) \) vanishes at the so-called screened plasma frequency \( \omega_s \) [19], instead of \( \omega_p \), to account for the frequency shift from screening of conduction electrons, where

\[
\omega_s^2 = \frac{\omega_p^2}{\varepsilon_r} - \frac{1}{\tau_D}.
\] (3)

Here, the background dielectric polarizability \( \varepsilon_r \) for different materials is obtained by fitting the plot of \( \varepsilon_r^D \) vs \( 1/\omega^2 \) over wide range frequencies [15–18] with the assumption that \( \omega \gg 1/\tau_D \):

\[
\varepsilon_r^D(\omega) \approx \varepsilon_r - \frac{\omega_p^2}{\omega^2}.
\] (4)

The slope and intercept of the plot correspond to \( \omega_p^2 \) and \( \varepsilon_r \), respectively.

However, problems remain. Firstly, a constant value of \( \varepsilon_r > 1 \) is not physical, as when \( \omega \to \infty \), \( \varepsilon_r \) should equal unity from both theoretical and experimental points of view. Secondly, as fitting with experimental data in different frequency ranges yields varied slopes with \( 1/\omega^2 \), the resulting \( \varepsilon_r \) cannot be uniquely determined (differing by several times). As shown in Fig. 1(A), the fits of Ag based on Equation (4) in different wavelength ranges would give varied fitting results. Moreover, the screened plasma wavelengths do not match the experimentally determined resonance frequencies. For Ag and Au, \( \lambda_1 = \frac{2\pi}{\omega_1} \) are calculated to be 267 and 329 nm based on Equations (3) and (4) using reported data [20], which are 21–47% smaller than the observed resonance frequencies of 323 and 485 nm, respectively. Notably, deviations in fitting greatly increase in the alkali metals (Cs), as shown in Fig. 1(B).

The relaxation time \( \tau_D \) can also be deduced by applying the same assumption to the imaginary part of Equation (1) [22,23] as

\[
\varepsilon_r^D(\omega) \cdot \omega \approx \frac{\omega_p^2}{\omega^2} \cdot \frac{1}{\tau_D}.
\] (5)

Théye [22] obtained the quantum relaxation time of Au films from Equation (5) using dielectric constant data over a wide frequency range, and found that \( 1/\tau_D \) is, to a certain extent, frequency-dependent. Nagel and Schnatterly [24] proposed a two-carrier model emphasizing the contribution from conduction electrons scattering and disordering in grain boundaries. However, the reciprocal relaxation time from the disorder effect increases only slightly (< 10%) with frequency for annealed samples, far from being sufficient to account for the experimentally observed 5-fold increase in \( 1/\tau_D \) at plasma resonance [17,18,20,21,25].

Thus, as shown in the above examples, there exists a large deficiency for the Drude–Sommerfeld model to explain the experimental data. The dielectric function is a consequence of the primary effect from interaction between the EM field and free electrons correctly described by the Drude model, characterized by the bare plasma frequency \( \omega_p \) and the frequency-independent quantum relaxation time \( \tau_D \); it is also a consequence of the primary effect from interaction between the EM field and bound electrons, resulting from excitations or transitions from the valence band to the conduction band. We believe that a secondary effect, which results from interaction between conducting electron oscillation and bound electron oscillation, accounts for these discrepancies.

Figure 1. The fits of (A) Ag and (B) Cs in different ranges: the experimental data (black square) [20,21] and fitting results based on Equation (4). The fitting processes for Ag are in the range from 210 nm to 1305 nm (blue curve in (A)) and from 1350 nm to 2480 nm (orange curve in (A)); Cs are in the range from 310 nm to 1050 nm (blue curve in (B)) and from 1100 nm to 2200 nm (orange curve in (B)), respectively.

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Figure 2. (A) Comparison of experimental and calculated values of $\epsilon_r(\omega), k(\omega)$ for aluminum: experimental data [28] (black solid line), Drude results based on Equation (1) by Ordal et al. [27] (blue dashed line) and Drude model modified with a square-frequency dependence of reciprocal relaxation time by Markovic and Rakic [26] (pink dotted line). (B) Experimental data [26] (black solid line) and Drude model (parameters in Table 1) combined with DFT calculations (green dash-dotted line).

for the large deficiency between the description of the Drude model and optical data.

Therefore, the bound electron effect must be included in the model analysis. With this in mind, the total complex dielectric function should be written as [12,19]:

$$\epsilon(\omega) = \epsilon^D(\omega) + \epsilon^B(\omega),$$

where $\epsilon^B(\omega) = \epsilon^B(\omega) + i\epsilon^B(\omega)$ describes the elastic and inelastic deformation of the bound electron polarization effect and can be calculated according to Fermi’s golden rule through density functional theory. The Lorentz simple harmonic oscillator model was used to approximate $\epsilon^B(\omega)$ [12,19], but success was limited. In another attempt, Markovic and Rakic [26] proposed inclusion of a frequency-dependent ‘electron re-radiation’ effect in the Drude–Sommerfeld model, related to response to the EM wave from both conduction and bound electrons, and causing a change of phase speed of EM radiation. By replacing $1/\tau_0$ with $1/\tau(\omega) = 1/\tau_0 + \omega^2$, the complex refractive index $[n(\omega) \text{ and } k(\omega)]$ of Al is fitted as shown in Fig. 2(A). Not only does the fitted plasma frequency ($\sim$94 nm) deviate from the experimental data (83 nm) more than that obtained from the simple Drude–Sommerfeld model [27], but also the reciprocal relaxation time (1590 cm$^{-1}$) at the plasma resonance frequency is three times the DC value of $\sim$550 cm$^{-1}$ (from DC resistivity [28] and $\omega_p$ by $\frac{1}{\tau_0} = \frac{\omega_p^2}{\pi^2 \rho_{dc}}$, dramatically deviating from the experimental results.

It comes to our realization that $\epsilon^B(\omega)$ is a very complex and sample-dependent term, which requires a more complex function of superposition of multiple harmonic oscillators. In Fig. 2(B), we calculate the $n(\omega)$ and $k(\omega)$ of Al based on Equation (6) with $\epsilon^B(\omega)$ obtained by density functional theory (DFT) [29], which takes into account all possible band transitions and appropriate quantum statistics. Compared with the data in Fig. 2(A), a significant improvement is achieved with a more suitable bound electron term on the dielectric function. This proves that for the model to match with the optical data, a complex form must be used to describe the bound electron effect with sufficient detail.

In this work, we propose a new measuring method accounting for contributions of both conduction (Drude term) and bound electrons to determine frequency-dependent quantum relaxation times. We subsequently analyze the complex bound electron effects with experimental data through multi-parameter fitting of dielectric loss function. The results clearly prove that bound electrons play a dominant role in quantum relaxation at optical frequencies.

RESULTS

To understand the impact of the bound electron term $\epsilon^B(\omega)$ on the damping effect to conduction electrons at plasma resonance, we hereby propose adopting an approach used for electron scattering loss analysis [12]. First, we choose to utilize the dielectric loss function (DLF, defined as the inverse of the dielectric function)

$$\frac{1}{\epsilon(\omega)} = \frac{\epsilon_r(\omega) - i\epsilon_i(\omega)}{\epsilon^D(\omega) + \epsilon^r(\omega)}. $$

If only considering the interaction with free electrons $\epsilon^D(\omega)$, the real and imaginary parts of DLF $\frac{1}{\epsilon(\omega)}$ are given by Dressel and Gruner [12] as

$$\text{Re} \left\{ \frac{1}{\epsilon(\omega)} \right\}_D = 1 + \frac{(\omega^2 - \omega_p^2)^2}{(\omega^2 - \omega_p^2)^2 + \omega^2 \tau_D^2},$$

and

$$\text{Im} \left\{ \frac{1}{\epsilon(\omega)} \right\}_D = \frac{\omega^2 \alpha \tau_D}{(\omega^2 - \omega_p^2)^2 + \omega^2 \tau_D^2},$$

respectively. As shown in Fig. 3, the Drude term $\text{Im} \left\{ \frac{1}{\epsilon(\omega)} \right\}_D$ has a very sharp symmetric plasma resonance peak at $\omega_p$, with a maxima of $\omega_p \tau_D$, and full width at half maximum (FWHM) of $1/\tau_D$. Considering the secondary scattering effect between conducting and bound electrons, we include the bound electron effect described by $\epsilon^B(\omega)$ in the DLF. The resonance frequency shifts from $\omega_p$ to the screened plasma frequency $\omega_s$, given by

$$\omega_s^2 = \frac{\omega_p^2}{\epsilon_r(\omega_s)} - \frac{1}{\tau_D}.$$
where the term $\frac{1}{\tau_{AC}(\omega)} = \varepsilon^B(\omega_s)\omega_s/\varepsilon(\omega_s)$ turns the sharp symmetric resonance peak into a broadened asymmetric resonance peak as a result of inelastic scattering of conduction electrons by bound electrons, as shown in Fig. 3. Hence, measurement of the FWHM of the dielectric loss peak could provide a direct means to identify the quantum relaxation time at a given non-zero frequency (i.e. the plasma frequency).

For a real material, we can first determine $\omega_s$, $\varepsilon_s(\omega_s)$, and $\tau_s(\omega_s)$ with the measured peak position, peak value and FWHM of plasma resonance, and then $\varepsilon^B(\omega)$ and $\tau_p$ by fitting the asymmetric function of $-\text{Im}\left(\frac{1}{\varepsilon(\omega)}\right)$ with optical data, as well as $\omega_p$ based on Equation (9) (for details of the data processing procedure, see Supplementary data S1).

To manifest the Drude term, we make an axis transformation to eliminate the contribution of bound electrons (black dot and line in Figs 3 and 4), including two parts: the first is the screening of conduction carrier density, resulting in the change in plasma frequency; the second is the asymmetric broadening of the plasma resonance peak.

It is important to note that the quantum relaxation time obtained by our method is the only direct measurement to our knowledge. It is also important to note that, in addition to phonon-electron, impurity-electron and electron-electron scattering, we find, for the first time, an additional scattering mechanism for the quantum relaxation time of conduction electrons in solids at non-zero frequencies.

Using $\varepsilon_s(\omega) = 0$ in Equation (11), we deduce the peak value of the dielectric loss spectrum at $\omega_s$:

\[
-\text{Im}\left\{\frac{1}{\varepsilon(\omega_s)}\right\} = \frac{1}{\varepsilon_s(\omega_s)} = \frac{\alpha_s}{\tau_s(\omega_s)} = \frac{\alpha_s}{\tau_s(\omega_s)}\frac{\tau_{AC}(\omega_s)}{\varepsilon(\omega_s)}.
\]

Letting Equation (12) be $\frac{\alpha_s}{\varepsilon(\omega_s)}$ $\tau_s(\omega_s)$, we obtain an equivalent optical quantum relaxation time $\tau_s(\omega_s)$ and the corresponding FWHM of this new resonance to be

\[
\frac{1}{\tau_s(\omega_s)} = \frac{1}{\tau_D} + \frac{1}{\tau_{AC}(\omega_s)}.
\]
and nickel. The corresponding fitted parameters are shown in Table 1. Data of (A) potassium, (B) rubidium, (C) silver, (D) gold, (E) cesium and (F) nickel. The imaginary parts of dielectric function of Rb, Ag, Au are also treated as constant around \( \omega \), and, therefore, we can assume a constant value for the fitting purpose. The \( \varepsilon_i^B(\omega_i) \) of Al, K, Ag, Au are also treated as constant around \( \omega_i \). In contrast, the data for Cs [21] follow a straight line, and, thus, we fit the data with a linear function \( \varepsilon_i^B(\omega) = a + b\omega \) to yield \( a = 0.56, b = -1.28 \times 10^{-5} \) cm, and the values of \( \varepsilon_i^B(\omega) = 0.25 \) and \( 1/(2\pi \tau_{D}) = 2230 \pm 100 \) cm\(^{-1}\). If a constant \( \varepsilon_i^B(\omega) \) is used instead of a linear function for Cs, the fitting error of \( 1/(2\pi \tau_D) \) would increase significantly from <10% to 50%. For Ni, a linear and parabolic function \( \varepsilon_i^B(\omega) = a + b\cdot\omega + c\cdot \omega^2 \) \( (a = 15.75, b = -3.25 \times 10^{-4}, c = 1.86 \times 10^{-6}) \) is used for fitting the experimental data around plasma resonance. If a linear function \( \varepsilon_i^B(\omega) \) is utilized for Ni, the fitting results cannot be self-consistent.

Table 1 summarizes the parameters \( \tau_D, \omega_p, \omega_s, \varepsilon_i(\omega_s), \varepsilon_i(\omega_i), \varepsilon_i^B(\omega_i) \) obtained by DLF-BE analysis and the zero-frequency relaxation time (\( \tau_D \)) deduced from resistivity data for metals K, Rb, Ag, Au, Cs, Al and Ni. The comparative \( \omega_p \) and \( \varepsilon_i^B(\omega) \) results from DFT calculations using the Vienna Ab initio Simulation Package [31–33] and \( \varepsilon_i^B(\omega) \) calculated from \( \varepsilon_i^B(\omega) \) by Kramers-Kronig relations are also listed in Table 1.

As shown in Table 1, the screened plasma wavelength \( \lambda_s \) values obtained with the DLF-BE method agree perfectly with the experimental values. In the meantime, \( \lambda_p \) values from DLF-BE match well with the DFT calculations, in contrast to the previously reported discrepancies with the Drude model [19]. This confirms that the screening effect of bound electrons is well represented by a proper expression obtained from DLF-BE analysis. The zero frequency relaxation time (\( \tau_D \)) from DLF-BE analysis is generally in good agreement with the results from DC electrical measurement [28] at room temperature for all the metals. However, for Cs, the \( 1/\tau_D \) obtained through DLF-BE analysis is significantly larger than the DC one, presumably because of differences in the sample impurity levels of Cs [21]. The DFT calculated \( \varepsilon_i(\omega_s) \) and \( \varepsilon_i^B(\omega) \) are also consistent with the parameters derived from experimental data. We noted that for alkali metals, while the elastic polarization effects are relatively small (\( \omega_p/\omega_s \sim 1.1–1.2 \)), the inelastic polarization effects are very large, that is \( 1/\tau_{AC} \) values are 10–15 times higher than \( 1/\tau_D \). For transition metals Ag, Au and Ni, the elastic polarization effects are much larger (2–4 times), while the inelastic polarization effects are moderately larger (\sim 4 times). In short, the \( 1/\tau_{AC} \) term contributes significantly more than \( 1/\tau_D \) in \( \tau_s(\omega) \) in all cases here. This suggests that the bound electron effect has a dominant contribution for electron quantum relaxation in the UV-visible optical frequency range, and also induces large changes in plasma resonance frequencies. On the other hand, the results also indicate that the historical assumption of frequency-independent quantum relaxation time in the Drude term cannot describe the optical response correctly. This is the first time that bound
Table 1. Drude’s parameters of different metals obtained from various methods.

| Method   | K [17] | Rb [18] | Cs [21] | Ag [20] | Au [20] | Al [25] | Ni [30] |
|----------|--------|---------|---------|---------|---------|---------|---------|
| Drude    | 139 ± 5 | 202 ± 10 | 2230 ± 100 | 166 ± 50 | 236 ± 50 | 545 ± 50 | 523 ± 150 |
| DC       | 139 | 199 | ∼ | 144 | 188 | 520 | 398 |
| DLF-BE   | 1346 | 2734 | 4860 | 804 | 854 | 3836 | 98 566 |
| DFT      | 34 048 | 30 817 | 24 752 | 74 627 | 75 188 | 106 383 | 64 103 |
| Drude     | 30 899 | 27 778 | 24 108 | 31 006 | 20 325 | 121 007 | 75 820 |
| DFT      | 29 977 | 27 345 | 22 410 | 31 056 | 23 810 | 123 457 | 70 789 |
| λp (nm)  | 291 | 321 | 356 | 139 | 143 | 93 | 111 |
| DFT      | 294 | 324 | 404 | 134 | 133 | 94 | 156 |
| Drude     | 283 | 313 | 352 | 139 | 138 | 79 | — |
| DFT      | 324 | 360 | 415 | 323 | 492 | 82 | 132 |
| Drude     | 334 | 366 | 446 | 322 | 420 | 81 | 141 |
| DFT      | 334 | 366 | 446 | 322 | 420 | 81 | 141 |
| λs (nm)  | 324 [17] | 359 [18] | 413 [21] | 323 [23] | — | 83 [25] | — |
| ε1 (ωp) | 1.24 ± 0.005 | 1.26 ± 0.005 | 1.24 ± 0.03 | 5.4 ± 0.1 | 11.9 ± 0.1 | 0.78 ± 0.02 | 14 ± 0.1 |
| DFT      | 1.27 | 1.22 | 5.79 | 9.97 | 0.74 | 0.82 |
| ε∥ (ωp) | 0.54 ± 0.001 | 0.124 ± 0.001 | 0.25 ± 0.05 | 0.1 ± 0.02 | 0.1 ± 0.05 | 0.028 ± 0.002 | 1.82 ± 0.05 |
| DFT      | 0.06 | 0.13 | 0.32 | 0.3 | 0.57 | 0.03 | 2.1 |

DLF-BE: optical data processed with DLF analysis; DFT: modeled by DFT method; Drude: optical data fitted by Drude model; and DC: derived from \( \frac{1}{\tau_p} = \frac{\rho}{\beta} \) using resistivity data [28] and DFT calculated \( \omega_p \).

Figure 6. (A) DLF-BE analysis of ITO at 303 K. (B) Comparison of resistivity \( \rho_\beta(T) \) from the optical method and four-point probe method.

The electron polarization effect has been used to determine quasi-particle effective properties—carrier density and quantum relaxation time—of conduction electrons.

We further explore application of DLF-BE analysis to non-metals. To test the validity of this method to conducting semiconductors, a 176 nm thick indium-tin oxide (ITO) film sample was measured by ellipsometry at 303 K. The resistivity \( \rho_D \) obtained by DLF-BE in Fig. 6(A) is 101.9 \( \mu \Omega \cdot \text{cm} \), matching well with the DC four-point probe measurement of 100.4 \( \mu \Omega \cdot \text{cm} \) at similar temperature. This result proves that the method can be applied successfully in semiconducting materials with conduction electrons.

According to Matthiessen’s rule, \( \frac{1}{\tau_D} \) is composed of two terms:

\[
\frac{1}{\tau_D} = \frac{1}{\tau_{\epsilon-i}} + \frac{1}{\tau_{\epsilon-p}}(T). \tag{14}
\]

Here \( \frac{1}{\tau_{\epsilon-i}} \) represents the scattering rate of electron-impurity (extrinsic) and \( \frac{1}{\tau_{\epsilon-p}}(T) \), the scattering rate of electron-phonon (intrinsic), which is temperature-dependent.

To further separate the two terms, temperature-dependent measurements of dielectric constants were required. Ellipsometry measurement was carried out on ITO film from 303 K to 378 K at 15 K intervals. The results of DLF-BE analysis are given in Table 2. The sheet resistance was also measured from 297.3 K to 388.8 K at \( \sim 15 \) K intervals by four-point probe. Figure 6(B) compares the resistivity of the ITO sample obtained with DLF-BE analysis of optical data with the four-point probe data at various temperatures. Using the relation \( \rho_{dc} = \frac{\rho}{\beta} \), the value of resistivity originated from electron-impurity scattering was determined by a non-geometry-sensitive optical method to be \( \rho_{\epsilon-i} = 74.8 \mu \Omega \cdot \text{cm} \), nearly the same as the geometry-sensitive DC contact measurement value of 74.7 \( \mu \Omega \cdot \text{cm} \). Meanwhile, the deviation of the temperature-dependence slope \( \beta \) of the electron-phonon term obtained by the two methods agrees well (<10%) considering the four-point probe method is dependent on a geometry factor with limited accuracy. The results seem to suggest that our method is applicable to electrical transport measurement of both metals and semiconductors with conduction electrons through impurity and optical doping at various temperatures, providing a potentially fast, non-destructive and micro-area detection method for semiconductor industrial applications.

Thus, we have demonstrated that the large discrepancies in the electrical transport properties...
between the Drude–Sommerfeld model and DC contact measurements in metallic elements can be resolved by DLF-BE analysis. The bound electron contributions result in an extra damping effect of conduction electrons at plasma resonance and a shift of plasma resonance frequency. From a physics point of view, the optical radiation should also interact with the background lattice, where the atoms are surrounded (or screened) by bound electrons to cause polarization (bound electron cloud deformation), which in turn affects the conduction electrons. The elastic deformation screens conduction electron charge, leading to a change in effective carrier density and a shift of the plasma resonance. The inelastic deformation causes additional scattering/loss in conduction electron movement and reduces quantum relaxation time.

CONCLUSION
In this study, by adopting DLF analysis into the physics of plasma resonance, the reciprocal quantum relaxation time in DC field $1/\tau_D$ and at non-zero frequency $1/\tau_{AC}$ is directly measured for the first time through a damping effect of plasma resonance. The DLF-BE analysis results are consistent with various experimental results and theoretical calculations. The results show that bound electron inelastic scattering to conduction electrons is the dominating damping effect of quantum relaxation time at optical frequencies. Although bound electron contributions to dielectric functions have been known for a long time, the contribution to quantum relaxation time of conduction electrons has never been realized until now.

METHODS

Calculations of $\varepsilon^B(\omega)$ and $\omega_p$ using DFT
The DFT calculations were carried out with the Perdew–Burke–Ernzerhof exchange-correlation function using the Vienna Ab initio Simulation Package (VASP) [31–33]. The plane-wave energy cutoff was set to 300–428 eV depending on the systems, and projector augmented-wave pseudopotentials were used. For the transition metals Ni, Ag and Au, the Hubbard U method was utilized with effective U–J values of 3.5, 2.8 and 3.2 eV, respectively. Monkhorst-Pack $k$-point grids were used for sampling the Brillouin zone, with spacing of $\sim 0.03 \text{ Å}^{-1}$. The imaginary dielectric function of bound electrons was calculated following Fermi’s golden rule under the dipole approximation [34], as shown in Equation (15).

$$
\varepsilon^B(\omega) = \left( \frac{1}{4\pi\varepsilon_0} \right)^2 \left( \frac{2\pi e}{m\omega} \right)^2 \sum_{k,e,v} \left| \Psi_k^e \right|^2 \delta \left( E_k^e - E_k^v - \hbar\omega \right),
$$

where $e$ is the polarization vector of the incident electric field, $p$ is the momentum operator, and $e$ and $v$ represent the conduction and valence bands, respectively. The real dielectric function of bound electrons $\varepsilon^R(\omega)$ was then obtained from $\varepsilon^B(\omega)$ through the Kramers–Kronig relation. $\omega_p$ was obtained through direct-current electrical conductivity calculation using the Boltzmann transport equation (Equation (16)), as implemented in the BoltzTraP2 program [35]

$$
\omega_p^2 = 4\pi \sigma_{dc} / \tau_{dc} = \frac{e^2}{2\pi^2} \int \sum_n \frac{\partial E_{n,k}}{\partial k} \left( -\frac{\partial f(E,T)}{\partial E} \right) \delta \left( E - E_{n,k} \right) \times dk dE,
$$

where $E_{n,k}$ is the orbital energy calculated using VASP and $f$ the Fermi-Dirac distribution. Then $\omega_{p,DFT}$ can be estimated by $\omega_i = \omega_p / \sqrt{1 + \varepsilon^R(\omega_i)}$.

ITO measurements
ITO films of nominal thickness of 180 nm were purchased from Hefei Kejing Material Technology Co., Ltd., prepared by magnetron sputtering. Spectra of

| Parameters | 303 K | 318 K | 333 K | 348 K | 363 K | 378 K |
|------------|-------|-------|-------|-------|-------|-------|
| $\frac{1}{2\pi\tau_D}$ (cm$^{-1}$) | 422   | 434   | 430   | 444   | 449   | 447   |
| $\frac{1}{2\pi\tau_{AC}}$ (cm$^{-1}$) | 233   | 235   | 237   | 239   | 241   | 243   |
| $\omega_p^2$ (cm$^{-1}$) | 15 782.4 | 15 766.6 | 15 773.6 | 15 760.7 | 15 752.6 | 15 741.7 |
| $\omega_p^2$ (cm$^{-1}$) | 7980.6 | 7971.9 | 7975.7 | 7968.4 | 7964.0 | 7958.6 |
| $\varepsilon_0(\omega)$ | 3.9   | 3.9   | 3.9   | 3.9   | 3.9   | 3.9   |
| $\varepsilon^B(\omega)$ | 0.114 | 0.115 | 0.116 | 0.117 | 0.118 | 0.119 |
| $\rho_D \cdot (\mu\Omega \cdot \text{cm})$ | 101.9 | 105.0 | 103.9 | 107.5 | 108.8 | 108.5 |
the ellipsometric angles $\psi$ (amplitude ratio) and $\Delta$ (phase shift difference) were acquired at various temperatures with a commercial spectroscopic ellipsometer (RC2, J. A. Woollam) operating in reflection mode in the 210–2500 nm wavelength range. Focusing probes were used to reduce the beam diameter to 500 $\mu$m at the sample surface. All the measurements were performed at incidence angle of 70°. The complex dielectric function calculated from $\psi$ and $\Delta$ was achieved using CompleteEASE software, with surface roughness considered. The refractive index $n$ and the extinction coefficient $k$ of ITO parameterized @632.8 nm at room temperature are 1.740 and 0.033, respectively. A standard heat stage (HTC-100) was used to control temperature. Rate of temperature change was slow enough (0.5 K/minute) to ensure the cooling of the sample. The measurements were performed at incidence angle 50°. The temperature were 1.740 and 0.033, respectively. A standard heat stage (HTC-100) was used to control temperature. Rate of temperature change was slow enough (0.5 K/minute) to ensure the cooling and heating data were consistent for more accurate temperature measurement.

**SUPPLEMENTARY DATA**

Supplementary data are available at NSR online.

**ACKNOWLEDGEMENTS**

All the first-principles calculations were carried out in the Center for Computational Science and Engineering of Southern University of Science and Technology.

**FUNDING**

This work was supported by the National Key Project of Research and Development Plan (2018YFB0703600) and High-level Special Funds (G022S6301, G022S6401). G.-F.L. was supported by the fund of the Guangdong Provincial Key Laboratory of Computational Science and Material Design (2019B030301001) and the Introduced Innovative R&D Team of Guangdong (2017ZT07C062).

**AUTHOR CONTRIBUTIONS**

X.-D.X. and H.W. proposed and supervised the project. P.Z. and X.-D.X. developed and established the DLF method. P.Z. and Y.-L.L. designed the experiments. P.Z., H.-Q.T. and C.-C.G. carried out the optical characterizations. P.Z. performed the data analysis with input from all authors; G.-F.L. carried out DFT calculations. P.Z., C.-C.G., H.W. and X.-D.X. co-wrote the manuscript. All authors commented on the manuscript.

**Conflict of interest statement.** None declared.

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