Optical study of plasmons in $Tl_2Ba_2Ca_2Cu_3O_{10}$

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The spectral functions of $Tl_2Ba_2Ca_2Cu_3O_{10}$ thin films have been determined accurately from combined reflectance and spectroellipsometric measurements. The plasmon spectrum of $Tl_2Ba_2Ca_2Cu_3O_{10}$ consists of an optic plasmon at about 1.2 eV and a broad band of acoustic plasmons. The latter is revealed by the characteristic quadratic frequency dependence of the loss function, $\mathrm{Im}(-1/\epsilon)=\beta\omega^2$, for $\hbar\omega \leq 1$ eV.

To elucidate the mechanism of high-temperature superconductivity in the cuprates, it is desirable to have a detailed knowledge of the relevant, low-energy electronic states and collective excitations in these materials. Optical spectroscopy is a useful source of such information, and hence the spectra of La-Sr-Cu-O, Y-Ba-Cu-O, and Bi-Sr-Ca-Cu-O have been studied extensively.[1] The most common technique[2] is that of measuring the normal-incidence reflectance spectrum, and utilizing the Kramers-Kronig transformation to determine the complex dielectric function $\epsilon=\epsilon_1+i\epsilon_2$ as well as other spectral functions. This method, however, requires extrapolations which can generate substantial errors[3,4] in the energy range where the free-carrier plasmons occur, which is of primary interest here. It has been recently demonstrated[4] that this uncertainty can be eliminated by performing additional spectroellipsometric measurements in the visible to ultraviolet region. With this technique, the spectral functions were determined[4] with substantially improved accuracy for $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$. The principal finding of Ref. 4 was that

$$\mathrm{Im}(-1/\epsilon)=\beta\omega^2 \tag{1}$$

for $\hbar\omega \leq 1$ eV, in both compounds, and this unusual dependence was tentatively associated with possible layered-electron-gas[5] (LEG) behavior. This interpretation has been supported by subsequent detailed calculation[6] of the LEG energy-loss function, which indeed behaves according to Eq. (1) for the relevant geometry (i.e., for nearly normal incidence, which implies very small in-plane momentum transfer). An important inference is that in these materials, there exists a broad band of acoustic plasmons or "electronic sound" excitations, which could play a role[7] in the high-T_c superconductivity phenomenon.

With this motivation, we have performed normal-incidence reflectance and spectroellipsometric measurements on high-quality oriented thin films[8] of $Tl_2Ba_2Ca_2Cu_3O_{10}$. Utilizing the algorithm proposed in Ref. 4, we have determined the key spectral functions of $Tl_2Ba_2Ca_2Cu_3O_{10}$ in a broad (far infrared through ultraviolet) spectral range. This in turn enables us to examine the nature of the plasmon spectrum, and in particular the existence of acoustic plasmons, in this important member of the superconducting cuprate family—currently the highest-T_c material known.

Superconducting $Tl_2Ba_2Ca_2Cu_3O_{10}$ films were sputter deposited at ambient temperature in a symmetrical rf diode sputtering system from two identical $\frac{1}{2}$-in. targets.[9] The sputtering targets have a nominal composition of $Tl_2Ba_2Ca_2Cu_3O_{10}$; they were prepared using procedures similar to those used for the preparation of the superconducting pellets.[10] These two targets were configured in opposition to each other with a separation of one inch; the substrates were placed outside of the discharge region and parallel to the center line of the targets to minimize the resputtering effect encountered previously when sputtering a Y-Ba-Cu-O target. Results of optical emission studies suggest that the films thus deposited are not subject to energetic particle bombardments during deposition, resulting in a film composition practically identical to that of the targets.[9] The sputtering was done in mixture of Ar and (0–50%) O_2 having a total pressure of 40–60 mTorr, resulting in a typical deposition rate of 25–80 Å/min with a total rf input power of 30 W. The films used in this work were deposited on randomly cut yttrium-stabilized ZrO_2 substrates, and they were about 1 μm thick.

These films were amorphous as-deposited and a post-annealing step at 810–900 °C for ≥ 15 min was required to make them superconducting. Substantial loss of Tl was observed during post-annealing in an open vessel at about 800 °C. To minimize the loss of Tl, the samples were wrapped in gold foils with $Tl_2Ba_2Ca_2Cu_3O_{10}$ pellets for post-annealing, which was typically done in a sealed quartz tube.[9] In order to obtain the films with a zero resistance $T_c \geq 120$ K, the films typically needed to be deposited at ambient temperature, wrapped with freshly prepared $Tl_2Ba_2Ca_2Cu_3O_{10}$ pellets, and annealed at 880–900 °C for about 2 h.

The temperature dependence of the film resistivity was measured by the low-frequency (85 Hz) ac four-point-probe technique. X-ray diffraction and electron microprobe analysis indicated that the films with a zero resistance $T_c \approx 120$ K were highly textured, with the c axis perpendicular to the substrate surface, and they were comprised mostly of the $Tl_2Ba_2Ca_2Cu_3O_{10}$ phase.

Our near-normal incidence reflectance measurements were made with a Bio-Rad FTS-40V Fourier-transform infrared (FTIR) spectrometer (far infrared), a Bio-Rad FTS-40 FTIR spectrometer (mid-infrared), and a Perkin-Elmer Lambda 9 double-beam, double monochromator spectrophotometer (near infrared through near ultraviolet). For measurements in the mid-infrared range, a Spectra-Tech IR-PLAN Microscope was coupled to the Bio-Rad FTS-40 FTIR spectrometer. The microscope was equipped with a Hg-Cd-Te detector (cooled with liquid nitrogen) and provided spatial resolution better than 100 μm. No significant changes were observed in the reflectance when the spot was moved across the film surface. The agreement between the spectra taken on different spectrometers was good in the spectral regions where they overlap. For measurements in the visible range, a Perkin-Elmer 60 mm Integrating Sphere was coupled to the Perkin-Elmer Lambda 9 spectrophotometer in order to record the diffuse reflectance spectra. Ellipsometric measurements were performed on a SOPRA ESG4 Multilayer Optical Scanning Spectrometer, and repeated for comparison on a Model 445A15 Rudolph Instruments Automatic Spectro-Ellipsometer; the results were quite similar.

Since our spectra of as-grown and annealed films showed low specular and large diffusive reflectance in the short-wavelength region, indicating substantial surface roughness on the μm length scale, we attempted to improve the surface quality by low-energy, low-incidence-angle ion milling. That approach is quite effective in improving the optical quality of post-annealed Y-Ba-Cu-O films.[11] We milled the films in Ar^+-ion beam for 15 min, followed by $O_2{}^+$-ion beam milling for another 10 min; the beam voltage was 500 V and the incident angle was about 20° for both species. The thickness of the layer removed by this procedure was about 2000 Å. As in the case of Y-Ba-Cu-O, we observed substantial improvement of the surface quality and an increase of the specular reflectance. The effectiveness of this ion milling treatment in reducing the surface roughness was also directly confirmed by Atomic Force Microscopy with an atomic resolution; the details of that study are given elsewhere.[11]

In Fig. 1, we present the specular reflectance spectrum (solid line), taken at nearly normal incidence, of our best, ion-milled $Tl_2Ba_2Ca_2Cu_3O_{10}$ film. For comparison, we have also plotted the reflectance calculated from the pseudodielectric functions determined from ellipsometric spectra; the agreement is satisfactory.

To determine the complex index of refraction, $n+ik$, we utilize the algorithm introduced in Ref. 4: (i) assuming that R_H=const for $\hbar\omega \geq \hbar\omega_H = 4.5$ eV, we used the Kramers-Kronig transformation to determine the phase $\theta_{\text{uncorr}}(\omega)$; (ii) from the ellipsometric pseudodielectric function, we calculated $\theta_{\text{ellips}}(\omega)$, for 1.5 eV $\leq \hbar\omega \leq 4.5$ eV; (iii) we calculated the difference $\Delta\theta(\omega) = \theta_{\text{ellips}}(\omega) - \theta_{\text{uncorr}}(\omega)$, and fit this difference by a polynomial $p(\omega) = a_1\omega + a_3\omega^3 + \cdots + a_{2r+1}\omega^{2r+1}$; and (iv) utilizing the corrected phase $\theta_{\text{corr}}(\omega) = \theta_{\text{uncorr}}(\omega) + p(\omega)$, we calculated $n = (1-R)/(1+R-2\sqrt{R}\cos\theta)$ and $k = 2\sqrt{R}\sin\theta/(1+R-2\sqrt{R}\cos\theta)$. From these values, we calculate $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$, and the dielectric energy-loss function $\text{Im}(-1/\epsilon) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2)$, which are shown in Figs. 2 and 3, respectively.

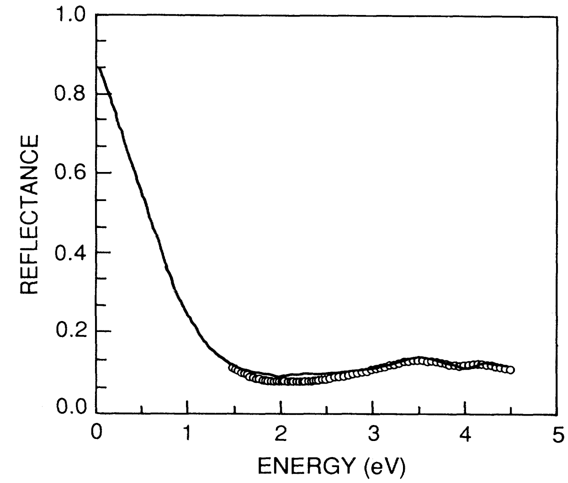

FIG. 1. Broad range specular reflectance from a c-axis oriented $Tl_2Ba_2Ca_2Cu_3O_{10}$ thin film measured directly (solid line), and calculated from ellipsometric spectra (open circles).

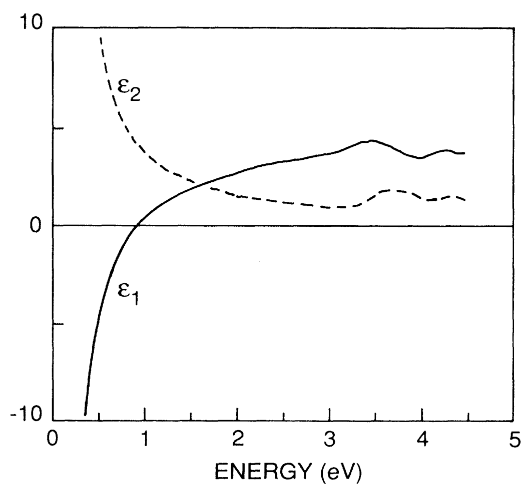

FIG. 2. The calculated real and the imaginary part of the complex dielectric function $\epsilon_1 + i\epsilon_2$ of $Tl_2Ba_2Ca_2Cu_3O_{10}$.

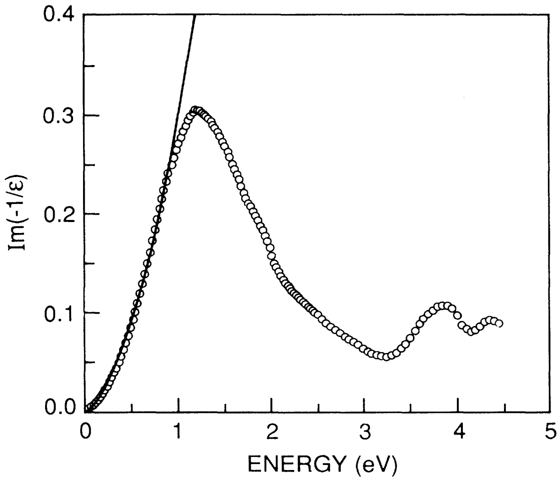

FIG. 3. The calculated loss function of $Tl_2Ba_2Ca_2Cu_3O_{10}$ (open circles). The solid line is a fit to Eq. (1), $\mathrm{Im}(-1/\epsilon)=\beta\omega^2$, for $\hbar\omega \leq 1$ eV.

The first impression one gets from Figs. 1–3 is a strong overall similarity to the corresponding spectral functions of $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$. This is not surprising, since in cuprate superconductors the low-energy optical response is dominated by the infrared absorption of charge carriers (holes), which are more or less confined to the Cu-O layers, and the corresponding electronic states do not differ much from one cuprate to another.

Second (and consistent with the above statement), in $Tl_2Ba_2Ca_2Cu_3O_{10}$ we observe one optic plasmon, at about 1.2 eV. Namely, at that energy one can see in Fig. 3 a pronounced peak of the dielectric loss function, while Fig. 2 shows that $\epsilon_1(\omega)$ has a zero near 1 eV, which is reasonably close. Similar features also appear[4] in $YBa_2Cu_3O_7$ (at 1.4 eV) and $Bi_2Sr_2CaCu_2O_8$ (at 1.1 eV), and their plasmon origin has been confirmed by electron-energy-loss spectroscopy.[12]

Since we know the high-frequency dielectric constant, we can estimate (with about ±20% accuracy) the *bare* plasma frequency, defined by $\omega_p^2=4\pi Ne^2/m^*$, where N is the carrier concentration and m^* is the optical effective mass. For $Tl_2Ba_2Ca_2Cu_3O_{10}$, we get $\hbar\omega_p=2.6 \pm 0.5$ eV, which places it between[4] $Bi_2Sr_2CaCu_2O_8$ where $\hbar\omega_p=2.4\pm0.3$ eV and $YBa_2Cu_3O_7$ where $\hbar\omega_p=3.2\pm0.3$ eV. (For the latter two compounds, the error margin is smaller because the charge-transfer gap is known from other independent spectroscopic experiments.)

Next, as shown in Fig. 3, the loss function of $Tl_2Ba_2Ca_2Cu_3O_{10}$ is quite accurately quadratic in energy up to $\hbar\omega \leq 1$ eV. Following Refs. 4 and 6, we interpret this finding as an indication of LEG behavior. Notice that the applicability of the LEG model implies that charge carriers are more or less free to move within individual metallic slabs, while their motion in the direction perpendicular to the slabs is suppressed substantially. It also suggests that the "electronic sound" excitations indeed exist in Tl-Ba-Ca-Cu-O, as well as in Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O. Given that this was not the case with the superconductors known so far, it would be of interest to study whether and how these peculiar excitations affect the superconducting state in the cuprates. Indeed, it was already proposed[7] that such plasmons may contribute significantly to the pairing interaction, thereby increasing the value of T_c.

Finally, let us point out some limitations of the present work, thus suggesting the opportunities for improvements. Our films required post-annealing (so far, no *in situ* growth of Tl-Ba-Ca-Cu-O has been reported), which caused recrystallization and substantial surface roughness. Some improvement was achieved by ion milling, as described earlier, but we were still unable to reach the optical quality of, say, cleaved $Bi_2Sr_2CaCu_2O_8$ single crystals. Indeed, our ellipsometric data indicate the existence of a partially void top layer, and hence there was some (even if minor) discrepancy between the ellipsometric and the reflectance results. Further, there is some uncertainty related to stoichiometry. Existence of other phases (at the level of a few percent), the observed sample-to-sample variations in T_c $(R=0)$ from 116 to 123 K, and the possibility that some disorder may be quenched in by relatively fast cooling, all leave room for further study and improvement. However, in spite of these limitations, we believe that the spectral functions presented in this work are essentially characteristic of $Tl_2Ba_2Ca_2Cu_3O_{10}$; the aggregate error should not exceed ±(5–10)%, and these small differences will not affect our principal conclusions.

To summarize, we have recorded reflectance and ellipsometric spectra of $Tl_2Ba_2Ca_2Cu_3O_{10}$, and determined its complex dielectric function as well as other spectral functions, from the far infrared through the ultraviolet region. We have observed one optic plasmon at 1.2 eV. The corresponding bare plasma frequency is $\hbar\omega_p=2.6 \pm 0.5$ eV. The dielectric loss function is quadratic in energy up to about 1 eV. We ascribe this dependence to LEG behavior and to the existence of a broad band of acoustic plasmons. Similar findings have already been reported[4] for $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$, and it is possible that this peculiar behavior is generic—and perhaps even essential—for all high-T_c cuprate superconductors.

Note added: After this work was completed, we received copy of a report by C. M. Foster, K. F. Voss, T. W. Hagler, D. Mihailovic, A. J. Heeger, M. M. Eddy, W. L. Olson, and E. J. Smith (unpublished), in which the infrared reflectance spectrum (0.05 eV $\leq \hbar\omega \leq$ 0.3 eV) of a $Tl_2Ba_2CaCu_2O_8$ film is reported, which is similar to the corresponding portion of the spectrum of our films prior to ion milling. The same is true for the ellipsometric spectrum of $Tl_2Ba_2CaCu_2O_8$ [M. K. Kelly, P. Barboux, J. M. Tarascon, and D. E. Aspnes, Phys. Rev. B **40**, 6797 (1989)].

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