Persistent photoconductivity in overdoped high-T_c thin films

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Overdoped $Tl_2Ba_2CuO_{6+\delta}$ exhibits persistent photoconductivity at low temperatures. This effect has been observed before only in underdoped $RBa_2Cu_3O_{7-\delta}$ (R=rare earth or yttrium). Contrary to $RBa_2Cu_3O_{7-\delta}$, $Tl_2Ba_2CuO_{6+\delta}$ shows either a persistent increase or decrease of the carrier density with illumination, depending on doping and wavelength of the incident light. Thus it is possible to increase or decrease the superconducting transition temperature in $Tl_2Ba_2CuO_{6+\delta}$ reversibly. These photoinduced changes can be explained by the existence of localized states in the charge reservoir layer. [S0163-1829(97)06046-3]

An interesting feature of the high-T_c superconductors is that it is possible to change their superconducting and normal state properties by ''doping,'' e.g., by chemically changing their stoichiometry. Moreover $RBa_2Cu_3O_{7-\delta}$ (R123, R=rare earth or yttrium) thin films show persistent photoconductivity[1] (PPC) and persistent photoinduced superconductivity[2] (PPS). After illumination with visible light of an oxygen deficient R123 thin film, its normal state resistance decreases and its superconducting transition temperature T_c increases substantially. This effect is persistent at temperatures below 100 K and relaxes typically within a day at room temperature. Hall effect[3] and structural[4] measurements show a remarkable similarity between this ''photodoping'' and oxygen doping in R123.[5]

Here, we report PPC in $Tl_2Ba_2CuO_{6+\delta}$ (Tl2201), which is to our knowledge the first high-T_c material to show this effect besides R123. In contrast to R123,[6] Tl2201 has a rather simple structure with only one CuO_2 plane per unit cell sandwiched between TlO layers, and *no* CuO chains.[7] This shows clearly that PPC in high-T_c materials does not require CuO chains. By increasing in Tl2201 the oxygen concentration, it is possible to decrease the T_c from 85 to 0 K.[8] Thus the Tl2201 films used in this study are in the *overdoped* regime, meaning a decreasing T_c with increasing carrier density n ($\partial T_c/\partial n < 0$), while the R123 films used in earlier measurements[1-3] are in the *underdoped* regime ($\partial T_c/\partial n > 0$). With appropriate illumination we can change n reversibly, which allows us to verify the overdoped nature of our Tl2201 samples directly and unambiguously.

The Tl2201 films were grown by rf sputtering on $SrTiO_3$ substrates by a method described in detail in Ref. 9. The thicknesses of the films were 500–800 Å, which is below the optical penetration depth of ≈ 1000 Å. Therefore the films were transparent and completely penetrated by the light used in the experiments. After growth, the T_c of the films was adjusted between 10 and 80 K by annealing in argon or air. For the transport measurements, the films were photolithographically patterned into a standard four-point and Hall bar geometry. To reduce contact resistance, the contacts were made to small silver pads, which were sputtered through a contact mask onto the film surface.

The four-point resistance and the Hall coefficient were measured in a He-flow cryostat equipped with optical quartz windows. Since the photoinduced changes are small ($\Delta\rho/\rho \lesssim 1\%$), it was necessary to keep the temperature during the measurement stable within a few mK. For the optical excitation either a 1000-W Hg-Xe arc lamp or a halogen lamp was used. While using the Hg-Xe arc lamp far-infrared wavelengths were eliminated by using a liquid water filter, in order to protect other optical elements and the sample from excessive heat. For the excitation, a specific wavelength in the range 250–1000 nm (4.8–1.1 eV) was selected using interference bandpass filters with a bandwidth of 10 nm. The light intensity at the sample was carefully measured for each wavelength and was adjusted to typically 0.1 mW/cm^2 in order to avoid any significant heating of the sample. After the excitation the sample was relaxed to its initial state by warming it up for several minutes to above 100 K.

Figure 1 shows the basic effect of illumination on the resistivity of Tl2201. Depending on the doping level and the wavelength the normal state resistivity ρ and the T_c can either increase or decrease. The Tl2201 thin film with an initial T_c of 60 K [see Fig. 1(a)] shows an increase in both T_c and ρ during illumination with 1000 nm light, while both T_c and ρ decrease during illumination with 400 nm light. In contrast, a higher-doped Tl2201 film, with a T_c of 13 K, shows only a decrease of T_c and ρ, which is shown in Fig. 1(b) for 440 nm light. Notice that since these Tl2201 films are overdoped, the change of T_c and ρ have the same sign, unlike in R123, where T_c increases and ρ decreases.[2] This is an unequivocal signature for overdoping. The photoinduced changes of T_c and ρ in Tl2201 are comparable to the changes observed in almost optimally doped R123, but considerably smaller than in underdoped R123.[10] The measurements of the temperature dependence of the resistance were done during illumination to measure the saturation changes. With the light off, the PPC would, even at low temperatures, slowly relax. However, any significant thermal heating due to the illumination can be ruled out, because of the very low power densities (≈ 0.1 mW/cm^2).

Figure 2 shows for both Tl2201 films the time dependence of the resistivity ρ and Hall coefficient R_H in the nor-
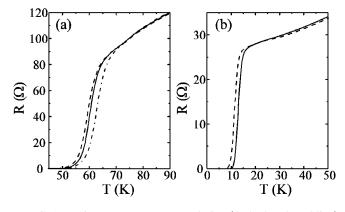
FIG. 1. Resistance vs temperature during (dashed or dotted line) and without (solid line) illumination for Tl2201 thin films with different doping. (a) Initial $R(T)$ (solid line) with $T_c = 60$ K and $R(T)$ during illumination with 1000 nm (dash-dotted line) and 400 nm (dashed line) light. (b) Initial $R(T)$ with $T_c = 13$ K (solid line) and $R(T)$ during illumination with 440 nm (dashed line) light.

mal state during illumination. Except for the sign in Fig. 2(a), this photoinduced change in ρ and R_H has the same functional dependence as in $R123$ and can be fitted to a stretched exponential.[11] The excitation time constants in Tl2201 are a few minutes, much faster, than the few hours in $R123$. This is remarkable since the light intensities used here were two order of magnitudes lower than used on $R123$.[12]

The changes of R_H have the same sign as ρ (see Fig. 2). In a simple one-band model ($R_H \propto 1/n$, n being the carrier density) this indicates that the carrier density can either decrease [Fig. 2(a)] or increase [Figs. 2(b) and 2(c)] with illumination. It is interesting to notice that the Hall mobility $\mu = c|R_H|/\rho$ has the opposite trend.

The spectral dependences of the photoinduced changes of ρ are shown in Fig. 3, where the resistivity change at satu-
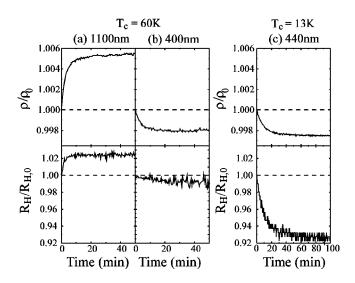

FIG. 2. Time dependence of the photoinduced changes of the resistivity ρ and the Hall coefficient R_H. The Tl2201 thin film with $T_c = 60$ K was measured at $T = 80$ K, $H = 7$ T with illumination of 1100 nm (a) and 400 nm (b) light, while the Tl2201 thin film with $T_c = 13$ K was measured at $T = 20$ K, $H = 7$ T with illumination of 440 nm (c) light. ρ_0 and $R_{H,0}$ are resistivity and Hall coefficient of the samples in the initial fully relaxed state, which are also indicated by dashed lines.
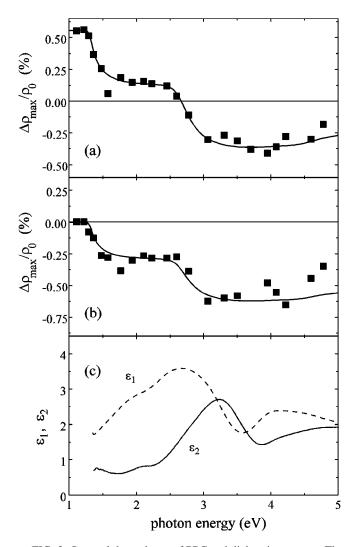

FIG. 3. Spectral dependence of PPC and dielectric constant. The saturation resistivity change $\Delta\rho_{max}$ normalized to the initial resistivity ρ_0 vs the incident photon energy for the $T_c = 60$ K (a) and the $T_c = 13$ K (b) sample (measured at 85 K and 30 K, respectively). The solid lines are guides to the eye. (c) The real part ϵ_1 (dashed line) and imaginary part ϵ_2 (solid line) of the dielectric function of optimally doped ($T_c = 85$ K) Tl2201 measured at 300 K taken from Ref. 13.

ration $\Delta\rho_{max}$ is plotted against the incident photon energy. Independent of doping there are three distinct energy regions, below 1.3 eV, 1.3–2.8 eV, and above 2.8 eV. In each of these energy regions $\Delta\rho_{max}$ is almost constant. For the lower-doped Tl2201 sample ($T_c = 60$ K), the energy region with a photoinduced increase of ρ changes continuously into the region with a photoinduced decrease of ρ. On the other hand, the spectral efficiency $\eta(\hbar\omega) = [d\ln R(n)/dn]_{n=0}$ ($\hbar\omega$ being the incident photon energy and n being the photon dose) is featureless from 1 to 4.8 eV. This is in contrast to $R123$, where a large enhancement of η is observed for 4.1 eV.[12]

In Fig. 3 the spectral dependence of PPC is also compared to the dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ of optimally doped Tl2201 ($T_c = 85$ K).[13] The imaginary part ϵ_2 shows a peak right where the second plateau in the spectral dependence of the PPC starts. This peak at 3.3 eV is attributed to transitions
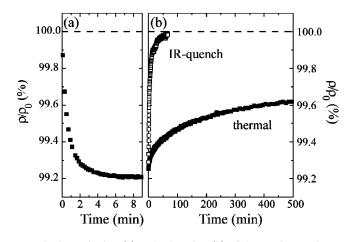
FIG. 4. Excitation (a) and relaxation (b) of the persistent photoconductivity in Tl2201 with $T_c = 13$ K measured at $T = 30$ K. (a) Excitation with 400 nm light. (b) Relaxation thermally (solid symbols) and with infrared quenching at 1100 nm (open symbols). ρ_0 is the initial resistivity of the fully relaxed sample, which is also indicated by dashed lines.

FIG. 5. Photoinduced resistivity change at $T = 30$ K in Tl2201 ($T_c = 13$ K) using 630 nm light. The sample was either initially fully relaxed (solid symbols) or excited up to saturation with 440 nm light (open symbols) prior to the measurement. ρ_0 is the resistivity of the fully relaxed sample.

from the Fermi level to the upper Hubbard band in Tl2201 and shifts to slightly higher energies with increased doping.[14]

As mentioned before, the time constant for excitation is much faster in Tl2201 than in R123. Also the time constant for relaxation is much shorter as is shown in Fig. 4. In R123 there is no relaxation measurable below approximately 100 K and there is only very slow relaxation of order of hours at room temperature.[11] In comparison, in Tl2201 even at low temperatures there is a thermal relaxation of the photoinduced effects. In Fig. 4(b) this is shown for the higher-doped sample ($T_c = 13$ K) at $T = 30$ K after excitation with 400 nm light. After stopping the illumination the resistivity relaxes very slowly (typically a day or longer) back to its initial ρ. This relaxation is much faster at higher temperatures and takes only a few minutes above 100 K. In addition it is possible to quench the resistivity in the higher-doped sample back to its original value by illuminating the sample with 1100 nm infrared light. The original ρ is this way recovered within an hour. This observation is remarkably different from R123, where only a partial infrared quenching is observed for wavelengths from 980 to 1480 nm (1.3–0.8 eV).[15] However, it might be possible that a complete infrared quenching for R123 exists for energies below 0.8 eV, although this would be below the energy barrier for thermal relaxation of 0.9 eV.[1]

Also note that the resistivity after illumination is independent of the initial resistivity, which is shown in Fig. 5. In Fig. 5 the sample is initially either fully relaxed or excited up to saturation with 440 nm light. After illumination with 630 nm, the final resistivity is independent of the initial one and the time constant for the photoinduced resistivity change is in both cases similar. This shows that the photoinduced changes in Tl2201 are completely reversible.

There are essentially two models to explain the PPC in R123. One is based on ordering of the oxygen in the CuO chains,[16] while the other, a purely electronic mechanism, is based on photogeneration of electron-hole pairs, together with trapping of electrons at oxygen vacancies in the CuO chains.[1,10]

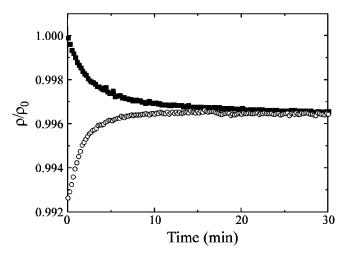It has been suggested that pressure-induced T_c changes in

Tl2201 are due to interstitial oxygen ordering in the TlO layers.[17] In fact, the pressure-induced changes show two metastable states with different energy barriers for relaxation, reminiscent of the two distinct photoinduced excited states (Fig. 3). However, independent of doping, applying pressure leads *only* to a T_c decrease, in contrast to the photoinduced changes. Therefore it is doubtful that pressure and photoinduced changes are due to the same mechanism. Moreover, a structural ordering mechanism for PPC is ruled out in Tl2201, since oxygen ordering always leads to a decrease in resistivity[17] and thus is clearly irreversible unless thermally relaxed. On the other hand, the sign of the photoinduced resistivity changes depends on doping (Figs. 1 and 2) and is reversible (Fig. 5), which would imply the unlikely case that illumination with a single wavelength either *orders* or *disorders* oxygen, depending on doping or initial resistivity.

On the other hand, a purely electronic mechanism, similar to the ones proposed for R123,[1,10] can account for most of the observed photoinduced effects. In this model illumination creates an electron-hole pair, and the electron is trapped at a localized state outside the CuO_2 planes, while the remaining hole enhances the conductivity. The spatial separation of the trapped electrons in the charge reservoir layers and the holes in the CuO_2 planes causes a long relaxation time.

For R123 it is proposed that oxygen vacancies in the CuO chains trap the photogenerated electrons.[1,10] In Tl2201 there are two types of structural defects[18]—Cu for Tl substitution in the TlO layers and interstitial oxygen between the TlO layers—which might trap the photogenerated electrons. The presence of these two types of defects can also explain the observed spectral dependence with two excitation levels (Fig. 3). For higher doping ($T_c = 13$ K) the two types of defects could act as traps for photogenerated electrons, which are accessible above different thresholds for the incident photon energies (≥ 1.3 and ≥ 2.8 eV, respectively). On the other hand, for the lower doping ($T_c = 60$ K), the localized electron states belonging to one of the two types of

defects could have moved below the Fermi energy, so that these states are occupied in the fully relaxed state. Then it is possible that infrared light (<1.3 eV) excites the electrons out of these localized states and thus reduces the hole density in the CuO_2 planes, which in turn would decrease the conductivity.

If this model is correct, PPC should be present in most high-T_c materials, since all it requires are localized electron states spatially separated from extended hole states in the conduction layers (CuO_2 planes). So far the search for PPC in other high-T_c materials has been unsuccessful.[16] $Bi_2Sr_2CaCu_2O_{8+\delta}$ shows upon illumination only an irreversible increase of resistivity, which can be explained by loss of oxygen.[19] On the other hand, preliminary results on $La_{2-x}Sr_xCuO_4$ indicate that there may be PPC in this material.[20] Furthermore, $Tl_2Ba_2CaCu_2O_8$ exhibits metastable photoinduced changes of its magnetic properties,[21] which may be related to PPC. Thus PPC might exist in most high-T_c materials.

This result has important consequences for measurements using optical probes, e.g., Raman scattering or photoemission spectroscopy. The increased doping level during illumination, which leads to a reduced T_c, might be responsible for the very low values of the energy gap $2\Delta/k_B T_c$ in strongly overdoped Tl2201 observed with Raman scattering.[22] Furthermore, the wavelength dependence of the 2Δ peak observed in Raman scattering for Tl2201 shows a strong enhancement at the same energies (≈ 3.0 eV) where the spectral dependence of the PPC indicates an increase in carrier density (Fig. 3).[14]

While the PPC might need to be considered for measurements with optical probes, it also can be used as a tool for investigating doping effects. The reversible photodoping allows one to measure in *one* sample the dependence of other physical properties (e.g., the energy gap) on the carrier concentration in the high-T_c materials.

In summary, we have shown that $Tl_2Ba_2CuO_{6+\delta}$ shows persistent photoconductivity. This is to our knowledge the first time that this effect is observed in another high-T_c material besides $RBa_2Cu_3O_{7-\delta}$ and shows that persistent photoconductivity is not unique to high-T_c materials with CuO chains. Depending on doping level and illumination wavelength the normal state resistivity and T_c can either increase or decrease, consistent with overdoping ($\partial T_c/\partial n < 0$). This together with the fact that the saturation resistivity after illumination is independent of the initial state shows that the mechanism for the persistent photoconductivity in this material is purely electronic. The spectral dependence shows two distinct excitation levels, which might be related to the two different defects in $Tl_2Ba_2CuO_{6+\delta}$. The observed reversible photodoping might be important for measurements using optical probes and can be used to study the doping dependence of other physical properties.

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