Polaronic quasiparticle injection in organic copper (II) phthalocyanine/$Bi_2Sr_2CaCu_2O_{8+\delta}$ tunnel junctions

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We report the current transport properties of an organic conductor/superconductor tunnel junction as a high-T_c superconducting three terminal device. The organic copper (II) phthalocyanine (Cu–Pc) layer was used for a polaronic quasiparticle (QP) injector. The junction was investigated in the dark and under ultraviolet radiation. The injection of polaronic QP from the Cu–Pc interlayer into a superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) thin film generated a substantially larger nonequilibrium effect as compared to the normal QP injection current. The tunneling spectroscopy of a Cu–Pc/BSCCO junction exhibited a zero bias conductance peak, which may be interpreted as Andreev reflection at a Cu–Pc/*d*-wave superconductor junction. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1467703]

The investigation of nonequilibrium superconductivity incorporating organic photoconductors is an attractive subject because of the application to possible optoelectronic devices and may lead to a new class of superconducting devices.[1] Organic photoconductors are a practical photoreceptor for electrophotographic systems and many applications using photoconduction mechanisms have been reported. A nonequilibrium state in a superconductor can be induced by injecting photons or phonons with energy greater than the superconducting energy gap, so that the number of quasiparticles (QP) becomes greater than that in thermal equilibrium. Effective ways to induce a strongly perturbed nonequilibrium state have been investigated by injecting QP into the tunnel junction with a high-T_c superconductor (HTSC).[2–5] Compared with quasiparticle injection into a low-T_c superconductor, the carrier density of a HTSC is smaller than a low-T_c superconductor, thus, higher gain was expected.[2–5] Recently, in order to get higher current gain in HTSCs, many authors have reported that the spin-polarized QP injection from a ferromagnetic injector into a HTSC has caused a strong nonequilibrium effect.[6–9] In this context, using an organic photoconductor, the investigation of nonequilibrium superconductivity due to the injection of polaronic QP from organic material is an intriguing subject and can open the possibility of optical control of superconducting devices. To achieve these goals it is important to have a physical understanding of the phenomena taking place at the interface between a HTSC and an organic photoconductor.

In this letter, we report the Cooper pair breaking in a HTSC due to the injection of polaronic QP from the organic photoconductor copper (II) phthalocyanine (Cu–Pc) into a $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) thin film. When the organic material is interlaid between normal metal and HTSC, the perturbed QP in the organic conductor, where the charge transport occurs by polaron hopping,[10] will act as a polaronic QP injector at the interface between the organic conductor and the HTSC. The polaronic QP injection from Cu–Pc into a HTSC is expected to form a strong nonequilibrium state due to the interaction between polaronic QPs and Cooper pairs. Thus, we observed that the current gain of Cu–Pc/BSCCO tunnel junctions was higher than that of Au/BSCCO junctions. This behavior is interpreted as the nonequilibrium effect due to the organic interlayer. The dependences of the differential conductance of Cu–Pc/BSCCO tunnel junctions have been studied with and without ultraviolet (UV) excitation. We observed a zero bias conductance peak (ZBCP) which may be interpreted as a scattering process at an organic Cu–Pc/*d*-wave superconductor junction.

The BSCCO thin films were prepared by molecular beam epitaxy with a sequential deposition technique on MgO (110) substrates.[11] The growth temperature and the growth rate of BSCCO thin film were 740 °C and 29 nm/h, respectively. The fabricated BSCCO thin films have a cleaved surface which includes the *ab* plane as well as surfaces oriented along the *c* direction. A BSCCO film of thickness 150 nm has an average roughness of about 5 nm. The surface of our BSCCO thin films is not flat but is subjected to many steps. In the case of the BSCCO thin films grown on a MgO substrate, several kinds of *c*-axis-oriented grains with different in-plane orientations are grown due to the large mismatch between the lattice constants of BSCCO and MgO. For a Au/Cu–Pc/BSCCO junction, the organic Cu–Pc thin film interlayer between the normal metal Au and the BSCCO thin film was deposited by thermal evaporation. The interlayer thickness of the Cu–Pc thin film was 100 nm. The organic

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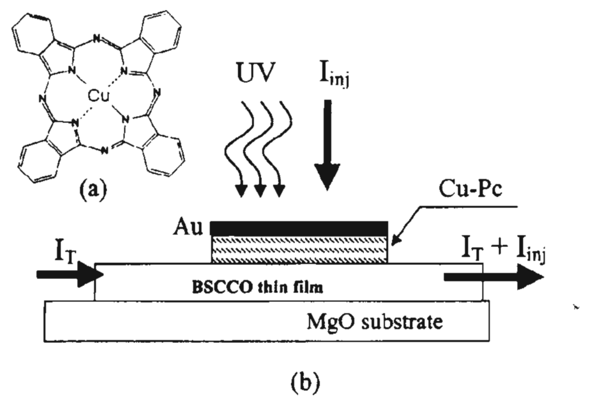

FIG. 1. (a) Molecular structure of copper (II) phthalocyanine and (b) the schematic structure of an Au/Cu–Pc/BSCCO tunnel junction.

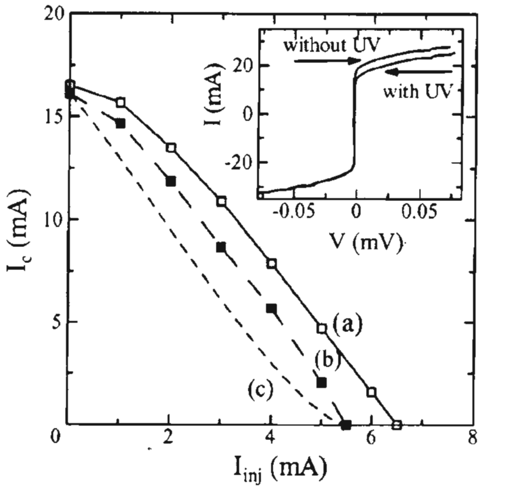

FIG. 2. BSCCO film critical current as a function of injection current for a Au/Cu–Pc/BSCCO junction (a) without and (b) with UV. (c) The dashed line corresponds to the calculated curve for a simple heating model. The inset shows the $I-V$ characteristics with and without UV at $I_{inj} = 1$ mA.

material Cu–Pc is known to be a p-type semiconductor and the molecular formula is $C_{32}H_{16}CuN_8$.[10] As shown in Fig. 1(a), it has fourfold symmetry and copper lies at the center of the phthalocyanine ring. This ring structure has long hydrocarbon chains which play an important role in the formation of polarons.[12] The normal metal Au was deposited as an electrode on a Cu–Pc film. The junction area is 100 $\times 100\ \mu m^2$. The device geometry is depicted in Fig. 1(b). Two currents were fed into the superconductor film: one is the injection current (I_{inj}) and the other is the transport current (I_T) through a superconductor thin film. The I_{inj} goes from the organic Cu–Pc thin film to the BSCCO thin film. A xenon discharge lamp (300 W) was used as the exciting UV light source for the photoconduction measurements. The current–voltage ($I-V$) characteristics of the junctions were measured using a dc four-probe method and the conductance spectra were measured using a lock-in amplifier.

The measured critical temperature of the BSCCO thin film was about 72 K. The resistive transition of BSCCO film for a Au/Cu–Pc/BSCCO tunnel junction with a Cu–Pc ($d_{Cu-Pc} = 100$ nm) interlayer also showed a distinct resistive transition at 72 K, independent of Cu–Pc. This fact means that there is no degradation of superconductivity by the deposition of the Cu–Pc layer.

The nonequilibrium effect in a Au/Cu–Pc/BSCCO tunnel junction can arise by polaronic QP injection from the organic Cu–Pc layer. This is quite different from the QP injection effect in normal metal/superconductor tunnel junctions. The charge transport in the Cu–Pc layer involves polarons consisting of electrons dressed with phonons.[13] These injected polarons involve a phonon component with the recombination time of $\sim 10^{-15} - 10^{-14}$ s, which is faster than that of QP ($\sim 10^{-12}$ s) relaxation time in HTSCs.[14,15] Since the phonon recombination time of Cu–Pc is shorter than that of the QP, it is expected that the polarons in Cu–Pc split into electrons and phonons at the interface and only the electrons tunnel into the BSCCO thin film. The phonons are left at the interface due to inelastic tunneling process. Thus, electrical impedance is created by phonons at the boundary between the Cu–Pc and the HTSC BSCCO film and generates a nonequilibrium state in the HTSC.

Figure 2 shows the critical current suppression due to the injection current for an Au/Cu–Pc/BSCCO junction with and without UV excitation. Note that the typical photoconduction rise and decay time of Cu–Pc is about 350–400 ns in the visible region.[16] The inset shows the $I-V$ characteristics with and without UV at $I_{inj} = 1$ mA. The dotted line corresponds to the expected simple heating curve, assuming that the injection current only has the effect of raising the film temperature. The qualitative discrepancy is evident, indicating a nonequilibrium state different from simple heating.[3,6] For Au/BSCCO junctions, the current gain was always equal or less than unity. These facts indicate that, in the absence of a nonequilibrium state, a current gain of unity arises solely from current pair breaking.[6] In addition, the current gain strongly depended on the junction geometry. To increase the current gain, an improved geometry is needed instead of the simple cross-type tunnel junction structure used in this experiment. Note that T_c was changed with changing injection current and decreased approximately linearly with increasing injection current. It can be also explained by the suppression of order parameter of a superconductor under the influence of external dynamic pair breaking by polaronic QP injection.[1,17] Without UV excitation, the measured current gain was over 2.5, which may be attributed to a nonequilibrium effect due to suppression of superconductivity by the polaronic QP injection. With UV radiation, the measured current gain was increased to 2.8 which may be attributed to an additional nonequilibrium effect by the polaronic QP injection due to the photogenerated current in the Cu–Pc. We observed that the current gain was increased as the thickness of Cu–Pc interlayer decreased. These facts indicate that the steady-state nonequilibrium effects, depending on the thickness of the Cu–Pc, build up at the effective area of the Cu–Pc.

In order to investigate the tunneling properties at the boundary, we studied the tunnel conductance of Au/BSCCO and Cu–Pc/BSCCO tunnel junctions. Figure 3 shows the temperature dependence of the differential conductance spectra for a Cu–Pc/BSCCO junction with $d_{Cu-Pc} = 100$ nm. The inset shows the typical conductance results for a metal/d-wave superconductor tunnel junction including the (110) interface. For the Cu–Pc/BSCCO junction, it can be observed

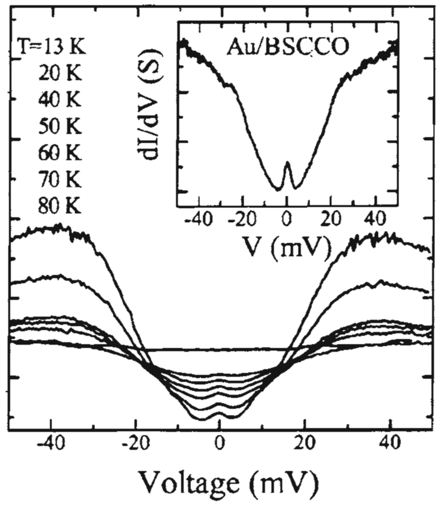

FIG. 3. Temperature dependence of the differential conductance for a Au/Cu–Pc/BSCCO tunnel junction. The inset shows the differential conductance for a Au/BSCCO tunnel junction.

that the ZBCP, as compared to Au/BSCCO junction, was slightly broadened and observed up to 70 K. These behaviors may be a result of the injection of the polaronic QP carriers from Cu–Pc into the superconductor. Note that, according to theory,[18–21] a ZBCP is expected when the tunnel boundary is formed at the (110) surface of a *d*-wave superconductor. These effects have been observed in QP tunneling experiments performed by many groups.[22–25] At an organic conductor/HTSC interface, the differential conductance characteristics are affected by the same interfacial boundary condition and a ZBCP is also expected for a non-*c*-axis oriented interface. Thus, the observed ZBCP may be interpreted as the Andreev boundary state of a polaronic QP from the Cu–Pc film into a BSCCO *d*-wave superconductor. The change of ZBCP heights as a function of temperature increased nonlinearly as bath temperature was reduced. Alff *et al.* reported a $1/T$ dependence of the ZBCP using a bicrystal junction and our results had a similar dependence on temperature.[26]

Note that, in the large absorption wavelength region from 260 to 800 nm, the Cu–Pc film has a high photogenerated carrier density. As the UV intensity increased, the photocurrent increased proportionally. We observed that ohmic contact was formed at the interface between the electrode and the Cu–Pc. When the UV radiation illuminated the sample, the magnitude of the ZBCP was enhanced. These facts indicate that when the junction is illuminated the number of charge carriers becomes larger in Cu–Pc and the height of the ZBCP increases. Previous calculations in Ref. 27 have indicated that features at low energy in metal/superconductor junctions are very sensitive to having different Fermi energies (Fermi wave vector mismatch) on the two sides of the junction. That is, before illumination, the Fermi wave vector in Cu–Pc is much smaller than the Fermi wave vector in BSCO and the mismatch suppresses the ZBCP. By generating charge carriers one decreases the wave vector difference and the height of the ZBCP increases. The detailed understanding of how this enhancement depends on the intensity of the UV radiation will be described elsewhere.

In summary, we have reported the current transport properties of Cu–Pc/BSCCO tunnel junctions as a novel HTSC three terminal device. The Cu–Pc layer was used for a polaronic QP injector. The injection of polaronic QP from the Cu–Pc interlayer into a superconductor BSCCO thin film generated a substantially larger nonequilibrium effect as compared to the normal QP injection current. The tunneling spectroscopy of a Cu–Pc/BSCCO junction exhibited a ZBCP. The above phenomena are of importance in developing optically controlled three terminal superconducting devices.

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