HTSC Polaroinc Quasiparticle Injection Devices With an Organic Copper (II) Phthalocyanine Injector

Sunmi Kim, Kiejin Lee, Takayuki Ishibashi, Katsuaki Sato, and Barry Friedman

***Abstract*—We report the nonequilibrium effect of polaronic quasiparticle (QP) injection using an organic injector in a high T_c three terminal device. The organic, copper (II) phthalocyanine (Cu-Pc), used as the injector, is a photoconductor and a p-type semiconductor. The transport properties of Au/Cu-Pc/$Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) tunnel junctions were investigated in the dark and under the He-Ne laser ($\lambda = 632.8$ nm) radiation. We observed that the injection of polaronic QP from the organic Cu-Pc film into the BSCCO film generated a substantially larger nonequilibrium effect as compared to the normal QP injection current. We could increase the current gain by He-Ne laser excitation of the organic photoconductor injector. The tunneling spectroscopy of a Cu-Pc/BSCCO junction exhibited an enhancement of the zero bias conductance peak under the He-Ne laser excitation. The above phenomena are of importance in developing optically controlled three terminal superconducting devices.**

***Index Terms*—Nonequilibrium state, organic copper (II) phthalocyanine, polaronic quasiparticle injection, three terminal superconducting devices.**

I. INTRODUCTION

INVESTIGATION of high-T_c superconductivity (HTSC) three terminal devices has been extensively studied by injecting quasiparticles (QP) [1]–[3] or spin-polarized QP [4]–[6] into tunnel junctions. The QP injection into a superconductor creates a nonequilibrium state which suppresses the superconducting order parameter and depresses the critical current density [7]. The generation of a strong nonequilibrium state in the HTSC is related to the high current gain of the device. In order to get higher current gain in HTSC, many authors have reported that the spin-polarized QP injection from a ferromagnet injector into a HTSC has caused a strong nonequilibrium effect [4]–[6].

In this context, using an organic photoconductor, we investigated injection of polaronic QP from an organic material to get an effective nonequilibrium state. Note that polaronic quasiparticle injection from an organic photoconductor, unlike spin injection from a ferromagnet can open the possibility of optical control of superconductivity as well as high current gain. Therefore it is necessary and important to understand the tunneling phenomena taking place at the interface between a HTSC and an organic photoconductor.

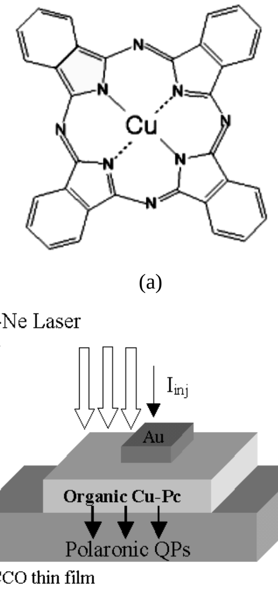

Fig. 1. (a) Molecular structure of copper (II) phthalocyanine and (b) the schematic structure of an Au/Cu-Pc/BSCCO tunnel junction.

For organic injector, we selected copper (II) phthalocyanine (Cu-Pc). Fig. 1(a) shows molecular structure of Cu-Pc. It is known to be a p-type semiconductor and photoconductor. Its molecular formula is $C_{32}H_{16}CuN_8$. As shown in Fig. 1(a), Cu-Pc has fourfold symmetry and a copper lies at the center of the phthalocyanine ring. This ring structure has hydrocarbon chains which play an important role in the formation of polarons [8].

The polaronic QP injection from Cu-Pc into the HTSC is expected to form a strong nonequilibrium state due to the interaction between polaronic QP's and Cooper pairs. In this paper we will discuss the transport properties of Au/Cu-Pc/$Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) tunnel junctions due to nonequilibrium effects in the dark and under the He-Ne laser radiation as well as tunneling spectroscopy.

II. EXPERIMENTAL

Fig. 1(b) shows the device geometry of the Au/Cu-Pc/BSCCO tunnel junction as an organic conductor/superconductor (Or/S) junction structure. The BSCCO thin films were prepared by molecular beam epitaxy on MgO substrates [9].

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The fabricated BSCCO thin film includes the ab plane as well as surface oriented along the c direction. The BSCCO film of thickness 150 nm has an average roughness of about 5 nm. The organic Cu-Pc thin film interlayer between the Au and BSCCO thin films was deposited by thermal evaporation at 380°C in the rate of 0.05 nm/sec onto substrate maintained at room temperatures and the thickness was 100 nm.

For an electrical configuration of three terminal devices two currents were fed into the superconductor film: one is the injection current $(I_{\rm inj})$ and the other is the transport current (I_T). The collected current $(I_T + I_{\rm inj})$ flows out through the third terminal of superconductor. The $I_{\rm inj}$ goes from the organic Cu-Pc thin film to the BSCCO thin film. The response of the critical current (I_c) of a film to injected current is exhibited as the current gain [14]:

$$G \equiv -\frac{dI_c}{dI_{\rm inj}} \tag{1}$$

The I_c can be obtained from the expression $I_c = (I_c^+ - I_c^-)/2$, where I_c^+ and I_c^- are the maximum and minimum zero-voltage current, respectively. The minus sign is included to make the gain positive since the critical current is expected to decrease with injection.

He-Ne laser with $\lambda = 632.8$ nm in which Cu-Pc has a high intensity of absorption was used as an excitation light source for the photoconduction measurements. The current-voltage (I-V) characteristics were measured using a dc four-probe method. The conductance spectra were measured using a lock-in amplifier.

III. RESULT AND DISCUSSION

A. *The Optical Properties of Cu-Pc Thin Films*

The structure of Cu-Pc has three dominant different crystal phases: α-, β-, and x-phases with a different angle between the stacking axis and the normal to the molecular plane [10]. Fig. 2 shows the optical absorption spectra of Cu-Pc. The α-phase of Cu-Pc thin films shows two absorption maxima located at wavelengths of 625 nm and 694 nm [11], [12]. As shown in Fig. 2, the intensity of the lower energy maximum peak is larger than that of the second peak. This behavior represents the typical features of the α-phase of Cu-Pc. Considering these results we choose He-Ne laser with wavelength in the vicinity of absorption maximum in order to get effective optical response.

At low temperature it was found that an exciton peak that is formed by an electron and hole pair bound together with molecular vibrations within a single molecule as shown in Fig. 2. This is the evidence that the carriers in Cu-Pc are dressed by lattice vibrations, forming polarons as in an ionic crystal [13].

B. *The Polaronic Quasiparticle Injection Properties in Au/Cu-Pc/BSCCO Tunnel Junctions*

For normal QP injection, the order parameter of the superconductor is perturbed from its equilibrium state near the injector.

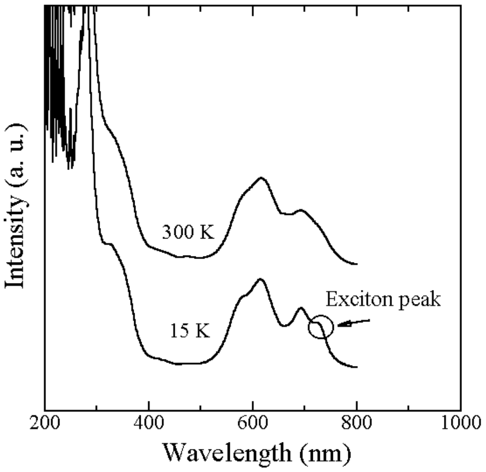


Fig. 2. Absorption spectra of Cu-Pc film at 15 K and 300 K.

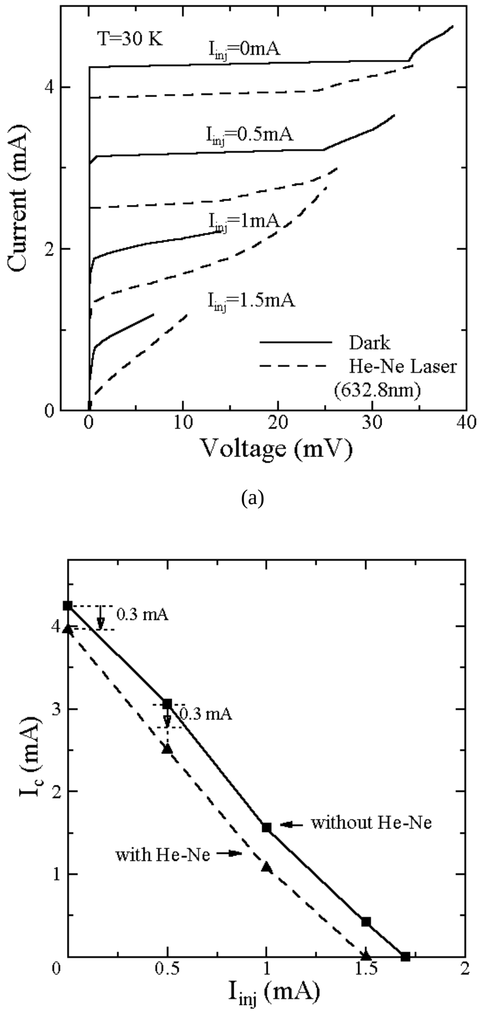
The superconducting energy gap (Δ) in a thin film decreases with increasing injection current as [14]:

$$\frac{d\Delta}{dJ_{\rm inj}} \cong -\frac{\tau_{\rm eff}}{2eN(0)d} \tag{2}$$

Where $N(0)$ is the single-spin density of states in the superconductor, $J_{\rm inj}$ is the injected current density ($J_{\rm inj} = I_{\rm inj}/A$, where A is the contact area), $\tau_{\rm eff}$ is the effective quasiparticle recombination time including phonon trapping effects and d is the thickness of the perturbed region. This means that both the nonequilibrium quasiparticle density and the suppression of the gap increase linearly with increasing $\tau_{\rm eff}$.

In the case of polaronic quasiparticle tunneling since the net relaxation time $\tau_{\rm eff}$ is increased due inelastic tunneling (described below), it generates an effective nonequilibrium state in the HTSC by (2). For the Or/S tunnel junction, the charge transport in organic Cu-Pc layer involves polarons consisting of electrons dressed with phonons [15]. These injected polarons involve a phonon component with the recombination time τ_p of $\sim 10^{-15}$–10^{-14} sec, which is faster than that of QP ($\sim 10^{-12}$ sec) relaxation time τ_R in HTSCs [16], [17]. Since the phonon recombination time of Cu-Pc is shorter than that of the QP $(\tau_p < \tau_R)$, it is expected that the polarons in Cu-Pc split into electrons and phonons at the interface and only the electrons tunnel into BSCCO thin film leaving phonons at the interface due to inelastic tunneling processes. Therefore the $\tau_{\rm eff}$ is increased due to the phonon contribution at the interface. Thus, electrical impedance is created by phonons at the boundary between the Cu-Pc and the HTSC BSCCO film which generates a nonequilibrium state in the HTSC.

The experimental transport properties of a Au/Cu-Pc/BSCCO junction at 30 K are showed in Fig. 3(a). The solid line corresponds to a modulation of I_c controlled by $I_{\rm inj}$ without irradiation, while the dashed line corresponds to that under the irradiation of He-Ne laser. To make clear for the transport properties Fig. 3(b) shows the I_c suppression versus $I_{\rm inj}$ for Or/S junction. The calculated current gain of this device using (1) was 2.49 without and 2.83 with He-Ne laser irradiation, respectively. Note that, in the absence of a nonequilibrium effect, a current gain of unity arises solely from current pair breaking.



(a)

(b)

Fig. 3. (a) I-V characteristics due to injection current with and without He-Ne laser irradiation at 30 K. (b) BSCCO film critical current I_c as a function of injection current I_{inj} for Au/Cu-Pc/BSCCO junction.

For normal metal/superconductor (N/S) junction, the current gain always was about unity [1], it was explain by the current pair-breaking model when only the distributed current summation effect is considered. Our result is clearly deviated from it, indicating that a nonequilibrium effect takes place due to the polaronic QP injection into the BSCCO film. Here we consider the simple heating effect, assuming that the injection current only has the effect of raising the film temperature. However it is hard to say that the higher current gain for Or/S junction is only from the simple heating effect, because the simple heating model may not be explained by the improved current gain due to He-Ne laser excitation.

As can see in Fig. 3(b), without current injection the I_c suppressed from 4.25 mA to 3.95 mA by the irradiation of laser. The I_c suppression of 0.3 mA is due to the pumped QP's under irradiation, the perturbation results in the suppression of superconductivity. When the I_{inj} 0.5 mA is applied, the I_c of 4.25 mA decreased to 3.06 mA by current injection without irradiation, expected by polaronic QP injection effect. Under the irradiation, the I_c suppression was expected to 2.76 mA, however, it was observed 2.51 mA under the He-Ne laser irradiation. These facts indicate that the additional suppression of I_c led to the improved current gain and it may be attributed to an additional nonequilibrium effect by the polaronic QP injection due to the photo-generated current in Cu-Pc.

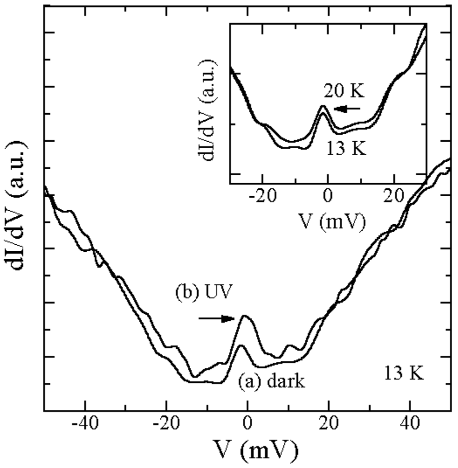


Fig. 4. Differential conductance for Au/Cu-Pc/BSCCO tunnel junction (a) in dark and (b) with He-Ne laser at 13 K. The inset shows the ZBCP at 13 K and 20 K.

For the investigation of tunneling properties at the boundary, we studied the tunnel conductance of a Cu-Pc/BSCCO tunnel junction. Fig. 4 shows the differential conductance spectra of a Cu-Pc/BSCCO junction with and without He-Ne laser.

The typical conductance spectra for a normal metal/d-wave superconductor tunnel junction including the (110) interface show the zero bias conductance peak (ZBCP) [18]–[21] and have been observed in QP tunneling experiment performed by many groups [22]–[24]. At the Or/S interface, the differential conductance characteristics are affected by the same interfacial boundary condition with the N/S junction and a ZBCP is also expected for a non-c-axis oriented interface. Thus, the observed ZBCP may be interpreted as the Andreev bound state of a polaronic QP from the Cu-Pc film into a BSCCO d-wave superconductor.

For a Cu-Pc/BSCCO junction, it was observed that the ZBCP as compared to Au/BSCCO junction was slightly broadened and observed up to 70 K [25]. These behaviors may be due to an injection of polaronic QP carriers from the Cu-Pc into a superconductor. The most striking difference of the Or/S junction from a normal metal/superconductor (N/S) junction was observed under the He-Ne laser illumination. Note that, in the large absorption wavelength region from 260 to 800 nm, the Cu-Pc film has a high photogenerated carrier density. When the He-Ne laser radiates to the sample, the magnitude of the ZBCP was enhanced as shown in Fig. 4(b). 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 [26] have indicated that features at low energy in N/S 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 BSCCO and the mismatch suppresses the ZBCP. By generating charge carriers one decreases the wave vector difference and the height of the ZBCP increases.

IV. CONCLUSION

We have reported the nonequilibrium transport properties of Cu-Pc/BSCCO tunnel junctions as a novel HTSC three terminal device. The organic Cu-Pc layer as a polaronic QP injector played an important role in the generation of a substantially larger nonequilibrium effect as compared to the normal QP injection current. The tunneling spectroscopy of a Cu-Pc/BSCCO junction exhibited the enhancement of ZBCP under the He-Ne laser excitation; this effect is caused by Andreev reflection of photogenerated charge carriers. The above phenomena are of importance in developing optically controlled three-terminal superconducting devices.

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