Scanning Tunneling Spectroscopy Study of Proximity Effect in Bilayer Manganese/Cuprate Thin Films

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Recent experimental studies have indicated novel superconducting proximity effects in thin-film heterostructures comprising ferromagnetic manganites and superconducting cuprates. To look for such effects microscopically, we performed scanning tunneling spectroscopy on La2/3Ca1/3MnO3/YBa2Cu3O7−δ (LCMO/YBCO) bilayer thin films. c-axis oriented films of varying thickness were grown on SrTiO3 substrates using pulsed laser-ablated deposition. Heteropitaxiality of the films was confirmed by cross-sectional transmission electron microscopy. Tunneling spectra were measured at 4.2 K, and analyzed for signatures of a pairing gap on the LCMO layer. For bilayer samples with LCMO thickness down to 5nm, asymmetric conductance spectra characteristic of single-layer LCMO films were observed, showing no clear gap structures. These observations are consistent with a very short-range proximity effect involving spin-singlet pairs, and difficult to reconcile with longer-range proximity scenarios involving spin-triplet pairs.

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I. INTRODUCTION

It is well known that ferromagnetism competes with spin-singlet superconductivity by favoring parallel alignment of electron spins. In ferromagnet/superconductor (F/S) heterostructures, this competition gives rise to a variety of phenomena, such as a strong suppression of the superconducting proximity effect (PE) and the so-called π-state, where the superconducting order parameter penetrates into the ferromagnet with a spatially-modulated phase.¹,² There has also been experimental evidence for spin-triplet superconductivity occurring in thin-film heterostructures made of a half-metallic ferromagnet and an s-wave superconductor.³ Recent advances in thin-film growth of complex oxides have allowed such phenomena to be studied using the nearly half-metallic La2/3Ca1/3MnO3 (LCMO) and the d-wave superconductor YBa2Cu3O7−δ (YBCO). Epitaxial thin-film heterostructures of these lattice-compatible perovskites have shown several novel effects. Of particular interest is the dependence of the superconducting critical temperature Tc on the LCMO layer thickness in LCMO/YBCO superlattices, showing rapid enhancement of Tc below ~40nm thickness which is substantially longer than the estimated PE depth.⁴⁻⁶ Similarly long length scales were also seen for the proximity-induced metal-to-insulator transition in LCMO/YBCO superlattices.⁷ One proposed explanation for these effects is an anomalously long-ranged PE associated with spin-triplet pair formation in LCMO.⁸⁻¹² Unlike spin-singlet pairs, spin-triplet pairs are not easily broken by an exchange field, and can thus penetrate deep into the ferromagnet.¹ Other experiments have indicated significant orbital reconstruction at LCMO/YBCO interfaces¹³ and nontrivial magnetic modulations in LCMO/YBCO superlattices¹⁴, mechanisms which could also facilitate long-range superconducting PE in LCMO.

The superconducting PE in bilayer thin films can be directly probed with scanning tunneling spectroscopy (STS), by measuring the tunneling density of states (DOS) at known distances from the bilayer interface. A proximity-induced gap in the DOS spectrum would be a signature of Cooper-pair formation and provide a measure of the pairing amplitude.¹⁵ Previous studies have used STS to probe the PE of either a conventional or cuprate superconductor on a normal metal.¹⁶,¹⁷ For F/S bilayers, STS has also been used to observe proximity-induced gap spectra on the surface of CuNi/Nb [check] and SrRuO3/YBCO thin films.¹⁸⁻²⁰ Since it is a local probe, STS is more immune to large-scale sample inhomogeneities which can affect bulk resistivity measurements, while being more sensitive to spatial variations in the quasiparticle DOS.

In this work, we present STS measurements at 4.2 K on epitaxially-grown LCMO/YBCO bilayer thin films as a function of the LCMO layer thickness. Tunneling conductance spectra taken on LCMO/YBCO films with the LCMO layer thicker than 10 nm are similar to spectra taken on single-layer LCMO films, showing a V-shaped profile with no clear gap structure. Bilayer films with the LCMO layer ~5 nm thick show similar spectra with some variation versus tip position, but also no signature of a proximity-induced gap. Our results indicate that the superconducting order parameter in the LCMO layer is suppressed well within ~5 nm from the LCMO/YBCO interface, implying a very short-range PE consistent with predominantly spin-singlet pairing.

II. EXPERIMENT

The LCMO/YBCO films used in our experiment were grown by pulsed laser-ablated deposition (PLD) on (001)-oriented SrTiO3 (STO) substrates. A layer of YBCO was
FIG. 1: (a) Transmission Electron Microscope cross-sectional image of a c-axis oriented bilayer film with 10 nm of LCMO and 20 nm of YBCO grown on an STO substrate, with interfaces indicated by arrows. LCMO/YBCO interface is smooth over ∼100 nm and heteroepitaxial, as shown in the atomically-resolved image (b).

First deposited on STO at 760°C in 250 mTorr O2, followed by in-situ deposition of LCMO at 760°C in 500 mTorr O2. We use a 248 nm excimer laser, pulsed at 2-5 Hz, producing ∼2 J/cm² laser fluence on the target. The films were annealed in 760 Torr of O2 at 800°C for 2 minutes, then cooled to room temperature at a rate of 10 °C/min. We grew various films ranging in LCMO thickness from 5 to 20 nm and YBCO thickness from 20 to 40 nm. All the films were confirmed to be superconducting by resistivity measurements, showing $T_c \approx 84$ K and 89 K for films with LCMO thickness $\approx 5$ and 10 nm, respectively.

The microstructure of our LCMO/YBCO films was characterized by transmission electron microscopy (TEM). Figure 1 shows the cross-sectional TEM image of a LCMO/YBCO film, clearly indicating heteroepitaxial growth with unit-cell interfacial roughnesses over a range of ∼100 nm. The roughness of the top surface is ∼3 nm. Similar TEM images were seen on other LCMO/YBCO samples, attesting to the overall heteroepitaxiality of our PLD process, and providing strong evidence that our STS spectra were obtained on sufficiently smooth regions with good structural order.

Our STS measurements were made with a home-built scanning tunneling microscope (STM) operating ∼1 mTorr of 4He exchange gas at 4.2 K. The LCMO/YBCO films were loaded into the STM shortly after growth, in order to minimize surface contamination. Pt-Ir tips were used and the typical junction impedance was ∼10 GΩ. STS data were taken by suspending the STM feedback to fix the tip-sample distance and then measuring the tunneling current $I$ vs. the bias voltage $V$ between sample and tip. Fifty $I$-$V$ curves were averaged at each tip location and then numerically differentiated to yield the conductance $dI/dV$ spectra. To ensure reproducibility of data, we obtained spectra at multiple locations over a scan range of 0.5 x 0.5 µm² on each sample, and measured several samples for each layer thickness.

III. RESULTS AND DISCUSSION

First we present STS data measured on LCMO/YBCO films with the thickest LCMO layers. The main plot of Figure 2 shows the $dI/dV$ spectra for two films, one with 10 nm and the other with 20 nm of LCMO deposited over 20 nm of YBCO. These spectra have a characteristic 'V' shape with some asymmetry, but showing no clear gap structures as would be expected for a proximity-induced pair potential. Instead, there is substantial conductance at zero bias, indicating finite DOS at the Fermi level. These bilayer data are also qualitatively similar to data taken on single-layer LCMO films, as shown in the inset for a 60nm LCMO film deposited on STO substrate. Similar V-shaped spectra have been seen in other transition-metal oxides, and appear to be characteristics of strongly-correlated oxide materials. It is worth noting that in the case of the PE between Au and (001) YBCO films studied in Ref. 17, the proximity-induced superconducting gap decreases exponentially as a function of the dis-
warranted, the LCMO thickness in our films at each tip position could not be precisely determined, since their surface roughness was \( \sim 3 \) nm. Nevertheless, the STS characteristics of our LCMO/YBCO bilayer films with 5 nm of LCMO are generically similar to data taken on single-layer LCMO films, consistent with the LCMO layer not being superconducting.

Finally we discuss the implications of our STS data on the superconducting PE in LCMO/YBCO heterostructures. For conventional PE between a normal metal (N) and a spin-singlet superconductor (S), it is generally accepted that the pair potential penetrates into N within an exponential decay length \( \xi_N \), which is typically \( \sim 100 \) nm, while the pair potential is suppressed on the S side within a superconducting coherence length \( \xi_S \). For PE between a ferromagnetic metal (F) and S, it is believed that the pair-potential penetration is greatly diminished by the ferromagnetic exchange field, which also suppresses Andreev reflection across the F/S interface. Thus the pair-potential decay length for a F/S junction should be far shorter than for an N/S junction.

For the F/S case, the proximity-induced pair potential in F is expected to oscillate and decay on a length scale of \( \xi_{F0} = h v_F / 2 E_{ex} \) and \( \xi_F = \sqrt{\hbar D / 2 E_{ex}} \) in the clean and dirty limits, respectively, where \( v_F \) is the Fermi velocity, \( E_{ex} \) is the exchange energy, \( D = v_F l \) is the diffusion coefficient and \( l \) is the mean free path in F. For LCMO we estimate both \( \xi_{F0} \) and \( \xi_F \) to be \( \sim 0.5 \) nm, by using \( v_F = 7.4 \times 10^5 \) cm/s (Ref. 29), \( E_{ex} = 3 \) eV (Ref. 30) and \( l \sim a \) a few unit cells (Ref. 31). These estimates indicate that proximity-induced superconductivity involving only spin-singlet pairs should be heavily suppressed in LCMO, decaying over just a few unit cells. Our STS measurement on LCMO/YBCO bilayer films are consistent with such a short-ranged PE, showing no clear gap structures in the DOS spectra down to LCMO thickness of \( \sim 10 \) unit cells.

IV. CONCLUSION

We have performed scanning tunneling spectroscopy at 4.2 K on LCMO/YBCO bilayer thin films. Samples with LCMO layers 10 nm and thicker showed V-shaped spectra that are characteristic of single-layer LCMO films, without clear gap structures as would be expected for a proximity-induced pair potential. Samples with LCMO layers down to 5 nm thickness showed some spectral variation with tip position but also no signatures of

![FIG. 3](Color online) Spectral variation as a function of tip position measured on a LCMO/YBCO bilayer film an LCMO thickness of 5 nm. (a) \( dI/dV \) spectra measured in steps of 15 nm along a height gradient on the surface, starting at a high position (black) and ending at a low position (red). Spectra are offset vertically for clarity. (b) I-V curves for the characteristic metallic (black) and insulating (red) spectra. (c) Relative height of the surface measured using a topographic scan, with markers indicating the positions of the spectra measured in (a). (d) Topographic image with the measurement path indicated by a red line (150×150 nm² scale, 1 V bias, 100 pA current).
proximity-induced superconductivity. Our results indicate that the proximity-induced pair potential in LCMO is suppressed well within 5 nm from the LCMO/YBCO interface, consistent with a very short-range F/S proximity effect involving spin-singlet pairs, and difficult to reconcile with longer-range proximity scenarios involving spin-triplet pairing.

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