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#### 13. ABSTRACT (Maximum 200 Words)

The properties of high temperature superconducting compounds, mostly in the form of thin films and thin film devices have been investigated. The main focus of the research was on the use of ozone-assisted molecular beam epitaxy in a shuttered growth mode to produce such films and structures. In addition to superconducting films, non-superconducting mixed-valence manganite perovskites, which exhibit so-called colossal magnetoresistance were grown. The manganites are unique in that their charge carriers are believed to be almost 100% spin polarized. These materials were combined with the cuprates to produce heterostructures in which the suppression of superconducting properties, such as the critical current and critical temperature, was brought about by the injection of spin polarized carriers from the manganite into the cuprate. This work may make possible new classes of devices based on this nonequilibrium spin injection phenomenon.

The symmetry of the pairing state of high temperature superconductors was also investigated, with the objects of study being high-quality single crystals. The results of this work suggest that the pairing is not pure d-wave, but is a time-reversal violating state which is an admixture of s and d-wave symmetries in the form $s + id$.

**High Temperature Superconducting Compounds, Molecular Beam Epitaxy, Cuprates, Manganites, Spin Injection, Pairing State Symmetry**

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31 January 1999

School of Physics and Astronomy
University of Minnesota
Minneapolis, Minnesota 55455

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1.0 Introduction

This research was directed at the investigation of the properties of high-$T_c$ superconducting compounds in the form of thin films and thin film devices. The objective of the work was the elucidation of the underlying mechanism of superconductivity, through the development of tunneling devices and other structures, which also have technological significance.

The main focus of the research was on the fabrication of films and structures using ozone-assisted molecular beam epitaxy (MBE) in a shuttered growth mode. These were engineered at a molecular level using what is known as the block-by-block growth technique, an approach, which facilitates an enhanced degree of control over both materials and interfaces. This may not be the "fastest" thin film growth technique, but it is one, which because of its enhanced degree of control, is excellent for prototyping device concepts. Technology was developed which could also facilitate the fabrication of planar tunneling junctions with deposited barriers.

In addition to superconducting films, non-superconducting mixed valence manganite perovskites, which exhibit so-called colossal magnetoresistance (CMR), were also grown. The CMR materials by themselves are technologically important in the context of magnetic sensors and magnetic circuit elements. The production of heterostructures consisting of manganite perovskites and superconducting cuprates has provided a unique opportunity for new device configurations based on spin injection in high temperature superconductors, which could fill an important need in the field.

The development of devices constructed from high temperature superconducting films has hitherto followed the path of emulating the behavior of low temperature superconductors. Although there have been many ideas presented over the past decade, and substantial progress in the development, and indeed commercialization, of superconducting devices, further refinements in the processing of films and structures, together with new device concepts are needed to make superconducting technology truly competitive in the realm of large-scale microelectronics. There have been few applications, or devices, which have broken new ground entirely, in the sense that their operating principles depend on physical properties or structural features of the cuprates differing from those of metallic and metallic alloy superconductors other than their elevated transition temperatures. In some very important instances this has led to unanticipated difficulties. Although it is possible to produce very large numbers of superconducting tunneling junctions with narrow ranges of operating parameters using metallic superconductors, a similar capability has never been realized for high-$T_c$ materials. In effect this is an obstacle
to the development of configurations of high-\(T_c\) junctions incorporating large numbers of devices where there is a requirement of tight operating margins.

A new class of devices based on phenomena associated with the juxtaposition of ferromagnetic and superconducting oxides may provide a solution to this problem. Their operation depends upon the very high spin polarization of the carriers in ferromagnetic oxides such as the mixed-valence perovskite manganites, and their fabrication is made possible by the structural compatibility of these materials and the superconducting cuprates, which facilitates the formation of monolithic epitaxial heterostructures. The possibility of reproducibly forming the interfaces at which the physical effects occur may make possible the very tight control over device operating parameters needed to realize complex configurations with very large numbers of devices.

In the last years of the grant, the research effort was redirected to the fabrication and investigation of structures consisting of films of high-\(T_c\) superconducting oxides and magnetic oxides. Juxtaposed superconducting and magnetic oxide layers have been grown by molecular beam epitaxy. They have been found to form monolithic single crystal heterostructures. A suppression of the critical current of a superconductor in response to the injection of spin polarized charge carriers derived from one of these oxide ferromagnets has been observed. Our research program, in addition to exploring device configurations, has contributed to the science base needed both to evaluate and optimize the performance of such devices, and to facilitate their fabrication.

The nature of the pairing state of high temperature superconductors has also been studied with support from this grant. Although in the last years of the grant this work did not receive financial support, it was initiated with grant funds, and the results, which are significant will be reported here.

2.0. Accomplishments
2.1 Block-by Block Deposition of High-\(T_c\) Cuprates and Other Oxide Materials

Central to our work is the need to produce films and structures of the highest quality in a highly controlled fashion. The growth of these materials is extremely complex as it usually involves the combination and reaction of four or more elements. In the case of 123 cuprates, such as DyBa\(_2\)Cu\(_3\)O\(_{7-x}\), which we have studied most extensively, this leads to the possibility of a multitude of unwanted phases such as BaCu\(_2\)O\(_2\), Dy\(_2\)O\(_3\), DyCuO\(_2\) and Cu\(_2\)O forming and remaining stable. Hence, it is crucial to control or tailor the growth to avoid the formation of undesired precipitates to obtain the highest quality films in terms of surface morphology, structural and chemical order and the absence of defects.
It is fair to say that we have an established process for growing various cuprates, superconducting and insulating as well as manganite perovskite oxides which exhibit ferromagnetism. Our approach is based on the recent work by the group at IBM Zurich, (Locquet et al. (1994)) which they termed "block-by-block" (BBD) deposition. Using this technique we achieve on a regular basis surface roughnesses of the order of ±1 unit cell, and transition temperatures above 90K. In effect we have a controlled process!

The method involves growing films along a thermodynamically optimum path rather than layer-by-layer. The idea is that during the deposition of any block only one reaction takes place. A block grows two dimensionally and covers the full surface. Block sequences leading to stable phases are avoided so that the reaction path has only one final product. In the BBD technique the different complexes or species which constitute the compound are deposited in succession, but not at the same time. This may have advantages over the other sequential technique that has been used, atomic layer-by-layer molecular beam epitaxy (ALLMBE) (Eckstein, et al, 1994). In the latter, the deposition of atoms is sequenced in a manner as to control kinetically the evolution of the chemical reaction coordinate for each molecular layer. It is believed that only the top molecular layer is involved in the growth so that precise sequences of layers can be assembled with minimal intermixing.

We have successfully used the BBD technique to produce very high quality films of the 123 compounds, the 214 compounds, and the manganite perovskite compounds. Several accounts of aspects of our recent work on the manganites have been published in Applied Physics Letters (Vas'ko et al., 1996).

The perovskite orthomanganite oxides such as the La_{1-x}M_xMnO_3 compounds, where M=Ba, Sr, Ca, and Pb have an intrinsic spin structure similar to that of the metallic multilayers that exhibit GMR. The conductivity of electrons involves a two-step process in which electrons hop from the 3+ to the 4+ Mn site via the intervening oxygen anion. This hopping process is spin-polarized as a consequence of the double exchange mechanism (Zener, 1950 and de Gennes, 1960)). An electron that hops away from the Mn^{3+} remembers the spin state it had on the ion, and the electron hopping onto the Mn^{4+} site must have the same spin. The resistance of the material is then a function of its intrinsic magnetic order. The important feature of these materials is that the carriers of current are highly spin polarized.

In addition to the production of thin films of the cuprates and perovskite manganites, we have succeeded in fabricating heterostructures that are various combinations of these materials. Our work on heterostructures was reported at the 1996 Fall MRS meeting, and the APS March Meeting in 1997.
We have also used the BBD technique to synthesize films with properties not known in advance from their behavior in bulk. As an example, films of the compound Dy$_{0.67}$Ca$_{0.33}$MnO$_{3+δ}$ were prepared. An account of the properties of this material was published in Physical Review B. (Nordman et al., 1996).

2.2 Spin Injection in High Temperature Superconductors

We have succeeded in producing spin injection devices consisting of bilayers of high temperature superconducting cuprates and the mixed valence manganite perovskites. Some devices have included a buffer layer of an insulating cuprate. The work followed directly from the demonstrated compatibility of the processing of cuprates and manganites using block-by-block, ozone-assisted molecular beam epitaxy. The major accomplishment has been the observation of the suppression of critical current in a cuprate by the injection of spin-polarized carriers from a manganite. An account of this research was published this year in Physical Review Letters (Vas'ko, 1997).

The operating principle of bilayer devices is the suppression of the superconducting critical current and transition temperature by injection of spin-polarized carriers from the magnetic layer. Devices based on the trilayer configuration might exploit an additional phenomenon, the possible suppression of the Andreev scattering channel for spin-polarized quasiparticles injected with energies less than the superconducting gap. The evidence for this was recently published in Applied Physics Letters (Vas'ko, 1998). The physics behind the above observation, which is in very preliminary form here, may be the very high degree of spin polarization of the manganites, which does not allow the propagation of the retro-reflected hole with flipped spin, as would occur in ordinary, unpolarized Andreev (1964) reflection. This appears to result in a reduction of the conductance at voltages across the interface with values below the superconducting gap. (A voltage of 0.020V is not too far from the expected gap of a 90K superconductor.) In an idealized situation it may turn out that an interface without any barrier behaves like a tunneling junction with very low conductance at voltages below the gap, with the conductance increasing sharply up to the normal conductance at the gap energy. This is opposite to the situation encountered in conventional Andreev scattering when carriers are injected across a boundary where there is no barrier. In that instance the subgap conductance is twice the conductance above the gap.

2.3 Tunneling Studies

Superconducting tunneling junctions, especially Josephson junctions, are the key to small-scale applications of superconductivity in the areas of sensing and electronics. Since the discovery of high temperature superconductivity there has been a world-wide effort to
produce junctions which are reliable and manufacturable, and possibly compatible with other types of microelectronic processing, and since they would employ high-T_c materials, would operate at liquid nitrogen temperatures (77K) or higher. Although tunneling junctions of several types have been realized, and are even commercially available, there is no junction fabrication technology which is completely controlled and reliable, and achieves levels of performance comparable to those easily achieved with low temperature superconductors requiring hydrogen or helium-based refrigeration.

We had proposed the development of in-line junctions in which the barrier was produced by a surface properties modification technique. The approach involved writing with a scanning tunneling microscope tip. In-line junctions with YBa_2Cu_3O_{7-δ} electrodes have been produced by direct electron beam writing (Tolpygo et al., 1993), by scanning tunneling microscope (STM) etching (Heyvaert et al., 1992), a technique some combining field-induced evaporation, mechanical milling and STM-induced thermal diffusion, and by ion beam etching (Dynes, 1994). Our proposed approach was to produce an oxygen deficiency track by writing across an ultrathin film with an STM in the tunneling mode. Although we succeeded in doing this, the resultant structures were not stable against thermal cycling. As a consequence these efforts have been abandoned. We instead have concentrated on developing a technology that will ultimately permit the fabrication of structures with vertical current transport. These will be useful for spin injection experiments, and for possible planar tunneling configurations. This effort is described in the next section.

2.4 Selective Epitaxy for Vertical Transport Studies.

To achieve the goal of making vertical transport measurements in oxide epitaxial heterostructures, a selective epitaxy scheme has been developed. The purpose of this effort is to realize clean interfaces between the materials of interest while minimizing the amount of post-growth processing needed.

The selective epitaxy process developed here takes advantage of the fact that DyBa_2Cu_3O_7 (DBCO) does not form the superconducting phase except under precise conditions, one of which is good epitaxial match to the substrate. By using physical masks to selectively cover areas of the substrate with amorphous Dy_2O_3, we have been able to define superconducting features as small as 125 microns.

A key issue in any selective epitaxy scheme is the amount of diffusion from the covering material into the epitaxial film. Because the material used here is α-Dy_2O_3, which is stable at the growth temperatures of DBCO, one may expect little Dy diffusion into the growing DBCO film. Figure 1. below shows the SEM beam induced characteristic x-ray
response of a scan across a 250 micron DBCO wire. The changes in the Dy intensity shows a linewidth of roughly 20 microns, which is no larger than the linewidths observed due to the physical mask used. We plan to define smaller features using photolithography to determine the intrinsic linewidth of a-Dy$_2$O$_3$ selective epitaxy.

This procedure allows us to define small areas of epitaxial and superconducting DBCO surrounded by polycrystalline -- and non-superconducting -- DBCO. As can be seen in the left figure, the DBCO grown on a-Dy$_2$O$_3$ is insulating; on the other half of the SrTiO$_3$ substrate, which was not covered with a-Dy$_2$O$_3$, we observe the expected superconducting transition.

This work was published in the Journal of Materials Science and Engineering (Kraus, 1998)

![Graphs](image)

Fig. 1. (Left Panel) Resistance vs. temperature characteristics of DBCO films grown in SrTiO$_3$ and a-Dy$_2$O$_3$ coated SrTiO$_3$. (right panel) Scanning electron microscope induced characteristic X-ray pattern of a 250 micron wide wire, showing an absence of diffusion of Dy$_2$O$_3$ in the region of the wire.

This scheme is used for in-situ construction of isolated epitaxial structures for vertical transport measurements. We begin with the growth of one or two epitaxial oxide layers in the usual way. The substrate is then cooled to room temperature and masked without breaking vacuum. a-DyO is deposited through the mask that consists of a wire array, leaving the epitaxial surface of the film untouched in the shadow of the mask. This first mask is removed and a second wire array mask, with wires turned 90° relative to the first, is inserted, and a-DyO is again deposited. In the intersection of the two masks will be isolated epitaxial surfaces. The substrate is heated to growth temperature for deposition of the top layer, which will be epitaxial and superconducting only in the defined areas. In this
way up to eight isolated heterostructure devices of varying sizes can be made on a single substrate. One *ex-situ* sputtering step is needed as an etch to contact the bottom layer. Because the process is entirely *in-situ* where the interfaces are involved, it meets our goals of clean interfaces and minimal post-growth processing.

2.5 *Studies of the Pairing State of High-T<sub>c</sub> Superconductors*

This work is no longer supported under this program. These results are included for completeness, because of the past history of support of this effort. In subsequent published papers support will be acknowledged.

The nature of the pairing state in high temperature superconductors has emerged as an important delimiter of the mechanism for superconductivity in these materials. The reason for this is that if the pairing state is *d*-wave, then conventional pictures of the mechanism based on phonon exchange cannot be correct, whereas if the pairing is *s*-wave, then models involving spin fluctuation exchange could be ruled out(Scalapino, 1995). The issue can be important technologically because if high temperature superconductors are described by a *d*-wave pairing state then there are always quasiparticles at low temperatures, which would affect microwave properties(Beasley, 1995a). Also a *d*-wave order parameter would have consequences for the behavior of Josephson device configurations which could impact applications(Beasley, 1995b). There has been substantial activity involving the study of the pairing state, and space does not permit a serious review of all of the experiments that have a bearing on the issue. Scalapino (1995) has written such a review. Our work on this subject has involved the investigation of the angular dependence of the transverse magnetization of single crystals. A four-fold symmetric signal of appropriate amplitude would support either *d*-wave or anisotropic *s*-wave pairing symmetry. From the temperature and magnetic field dependence of the signal one could distinguish between these alternatives.

We have been studying the angular dependence of the transverse magnetization (Yip and Sauls, 1992) of the high-*T<sub>c</sub>* superconductor LuBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-d</sub> in the nonlinear regime. The observed amplitude of the signal with angular period π/2 has been found to be smaller than the theoretical prediction for such pairing, and the temperature and field-dependence of the signal was also not consistent with predictions for *d*-wave symmetry. Although the results are consistent with isotropic pairing, they do not rule out nodeless anisotropic pairing. This work has been published in Physical Review Letters (Buan et al., 1994), and was reported on briefly at the Magnetism Conference in Minneapolis, at the Aspen Winter Condensed Matter Physics Conference in 1994, at the APS March Meeting in 1994.
the Grenoble Meeting on superconductivity. It was the subject of an invited talk at the 10th Anniversary Meeting on High Temperature Superconductivity in Houston in 1996.

Because our work is in essence a null result for d-wave pairing, it has been necessary to refine and enhance the experiment to convince the most serious skeptics, who would be partisans for d-wave pairing. For such individuals, "the absence of evidence would not be considered to be evidence of absence." In short, a very high standard of scientific evidence must be applied to a null result. These refinements include the development of techniques for the production of disk-shape single crystal using an ultraviolet excimer laser which produces round crystals with fewer defects than those which are hand ground into a cylindrical shape. An account of this technique has been published in Applied Physics Letters (Bhattacharya et al., 1996). Other refinements include improved analysis, direct readout of the angular position of the sample, and self calibration. For the latter we have positioned a test coil which can produce a known magnetic moment to calibrate the detection system. The result still appears to be a null experiment for d-wave pairing, but a much more credible one than our earlier effort. Accounts of this work are about to appear in Physical Review Letters (Bhattacharya, 1999).

Samples have been obtained from Argonne National Laboratory and from the Universities of Paris and British Columbia. The student was supported by a University Fellowship, and the materials needed for the research are provided by the University.

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### 4.0 Personnel

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5.0 Publications Supported or Partially Supported by the Grant


