4. **TITLE AND SUBTITLE**

The Charging Effect in High-\(T_c\) Superconducting Thin Films

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13. **ABSTRACT** (Maximum 200 words)

Experimental research has been conducted to elucidate the basic physics and possible applications of the charging effect in partially oxygen-depleted YBa\(_2\)Cu\(_3\)O\(_{6-x}\) (YBCO) thin films. A novel laser-writing technique, suitable for patterning and fabrication of monolithic YBCO electronic devices has been developed. The technique allows to define superconducting and insulating regions in the same sample and is based on local laser beam heating of the epitaxial YBCO film in either the presence or the absence of an oxygen atmosphere. Several test structures for our charging-effect experiments have been fabricated using laser writing. The structures are fully monolithic with a partially oxygen-depleted channel and oxygen-rich source and drain electrodes. The devices were tested and showed a substantial charging effect, which we associate with the charge-transfer effects related to electric-field-enhanced changes of the crystalline order in oxygen-deficient YBCO. We have also fabricated and successfully tested laser-written YBCO microwave transmission structures and resonators. The developed devices represent a new approach for the high-temperature superconducting electronics, which consists of exploiting contrasting properties of the oxygen-poor and oxygen-rich YBCO phases to design novel devices.
I. Summary

Experimental research has been conducted to elucidate the basic physics and possible applications of the charging effect in partially oxygen-depleted YBa$_2$Cu$_3$O$_{6+x}$ (YBCO) thin films. A novel laser-writing technique, suitable for patterning and fabrication of monolithic YBCO electronic devices has been developed. The technique allows to define superconducting and insulating regions in the same sample and is based on local laser beam heating of the epitaxial YBCO film in either the presence or the absence of an oxygen atmosphere. Several test structures for our charging-effect experiments have been fabricated using laser writing. The structures are fully monolithic with a partially oxygen-depleted channel and oxygen-rich source and drain electrodes. The devices were tested and showed a substantial charging effect, which we associate with the charge-transfer effects related to electric-field-enhanced changes of the crystalline order in oxygen-deficient YBCO. We have also fabricated and successfully tested laser-written YBCO microwave transmission structures and resonators. The developed devices represent a new approach for the high-temperature superconducting electronics, which consists of exploiting contrasting properties of the oxygen-poor and oxygen-rich YBCO phases to design novel devices.
II. Research Objectives

The main objective of this grant was to conduct a careful and exhaustive experimental examination of the charging effect in HTS thin films and of its possible applications in novel three-terminal superconducting devices. This was planned to achieve through realization of the following research objectives, set forth in the proposal:

1. The first objective of this research was to develop a laser-writing technique, suitable for patterning and fabrication of monolithic YBCO devices.
2. The second objective of this research was to fabricate superconducting, MOSFET-like, structures (SuperFETs) with the thick, partially oxygen-depleted YBCO channel and fully superconducting source and drain electrodes.
3. The third objective of this research was to observe the free-carrier density modulation in SuperFET test devices, including a possible “surface inversion” of oxygen depleted channel.
4. The fourth objective of this research was to conduct a careful analysis of electrical properties of SuperFETs with different dielectric gates.
5. The fifth objective of this research was to extend our results and investigate “transient” superconductivity in HTS materials, when carriers are created by the charging effect (or, e.g., optically induced), rather then by oxygen chemical doping.

III. Research Accomplishments

We have accomplished most of the research objectives set in the grant proposal.

A. Laser-writing technique

We have developed a laser-writing technique, suitable for patterning and fabrication of monolithic YBCO devices. The method is based on the observation that YBCO electrical and optical properties are very sensitive to the material’s oxygen content. Oxygen can be diffused in or out of the YBCO film, by heating the sample in either the presence or the absence of an oxygen atmosphere. The heating can be done locally with a focused laser beam. Thus, an intentionally oxygen depleted (semiconducting) HTS film can be patterned by imbedded oxygen-rich (superconducting) lines, or vice versa.

We have now in our laboratory a fully operational laser-patterning system. The system consists of an Ar-ion cw laser ($\lambda = 0.514 \, \mu m$), shutter, focusing microscope, and computer-controlled X-Y translational stage with a gas chamber and sample holder. This arrangement allows us to reproducibly write two-dimensional patterns with the line dimensions as small as $<5 \, \mu m$. Laser power intensity applied to the film is kept between 0.2 and 5 mW/μm$^2$ and a typical speed is in the range 0.5–5 μm/s. The sample ambient atmosphere is either pure nitrogen or oxygen. The laser-written patterns exhibit superconducting properties ($T_C$, $J_C$, $\Delta T_C$) as good as the untreated films. The R(T) measurements repeated on the same samples, but 8 months after the fabrication showed absolutely no signs of degradation of their superconducting properties. We also did not observe any changes in physical appearances of our aged samples. We want to stress that laser writing is fully reversible and the patterns can be either erased by furnace annealing, or rewritten by subsequent laser writing. The technique is
noninvasive, does not require a patterning mask, and results in completely planar structures, free of surface contamination.

We have published a number of papers (see Sec. IV) devoted to different aspects of our laser-patterning technique. We also submitted an invention disclosure to the University of Rochester Office of Research and Project Administration.

B. Test structures fabricated by laser writing

A number of the charging-effect test structures (SuperFETs) have been fabricated. The structures are fully monolithic and consist of a thick, partially oxygen depleted channel and oxygen-rich, fully superconducting \(T_c = 90\) K source and drain electrodes. The fabrication process is based on the laser-writing technique, described in detail in the previous Section. We start with a partially oxygen-depleted YBCO film \(T_c = 10\text{+60} \) K, depending on the design) and form source and drain regions by laser-controlled diffusion of oxygen. Next, the sample's ambient atmosphere is changed from \(O_2\) to \(N_2\), and oxygen-poor areas are laser patterned on both sides of the drain-source structure. The oxygen-poor regions act as the borders by completely insulating at low temperature the transistor's structure from the rest of the film. As a result, we obtain between the drain and source a narrow, partially deoxygenated transistor's channel. The whole, 0.5-mm-thick SrTiO3 substrate is used as a gate insulator, or the gate dielectric is formed by depositing a thin, amorphous YBCO film on top of the channel. Source, drain, and gate contact pads are formed by thermal evaporation of Ag through appropriate metallic masks.

In addition to SuperFETs, a number of other test devices (e.g., oxygen-poor and oxygen-rich microbridges, interconnects, etc.) have been fabricated using our laser-writing technique. Among them the most interesting are microwave coplanar transmission lines and resonators and optically-controlled, oxygen-poor YBCO switches. We believe that these elements, whose operation is based on properties intrinsic to YBCO materials, can be regarded as a new class of superconducting solid state devices.

C. Experimental system

We have assembled a complete characterization system (so-called "Superconductor Characterization Unit") for our charging effect experiments. The system is controlled by a Macintosh computer, running a LabView data acquisition program. Our measurements are performed in a four-probe geometry on devices operated in a common-source mode. The devices are mounted inside a continuous-flow helium cryostat and temperature stabilized with the accuracy of 0.01 K. The gate-to-channel leakage current is controlled to remain negligible as compared to the measurement current. The drain voltage versus channel current, \(V_{D-ICH}\), characteristics are recorded in a dc current mode for several different values of the sample gate voltage, \(V_g\). For the \(J_c\) definition, we used an arbitrary criterion of 1 \(\mu V/cm\).

The same system also allows us to automatically register resistivity and critical current density versus temperature curves for different, laser-patterned test structures. The dewar has large windows for optical measurements.
D. Results of SuperFET tests

Contrary to most of the people, who look for the field effect in ultrathin YBCO films, our design-concept is based on the field-induced superconductivity in only few surface layers of the oxygen depleted YBCO channel. Thus, our transistor is intended to work in the carrier enhancement mode. In the case of a perfect interface between the YBCO and the gate insulator, we should be able to observe the field-induced modulation of $T_c$ in the top, penetrated by the electric field, monolayers of the channel. However, in the real case, structural imperfections and enhanced charge trapping in YBCO close to the gate insulator cause the surface critical temperature $T_{cs}$ to be lower than that inside the volume of the film, $T_{c0}$. Therefore, in that case one should not expect to observe the field-induced change of the channel $T_c$, since the measured $T_c$ is determined by the $T_{c0}$, which remains unaffected by the electric field. In this latter situation, however, we may expect field-induced changes of the channel $J_c$. The structural imperfections in the YBCO surface layer act below $T_c$ as pinning centers and give a substantial contribution to the volume pinning force in the film. Field-induced changes of their pinning energy may, thus, either decrease or increase the total channel $J_c$, depending on the gate-voltage polarity.

Our best results were obtained on structures with the entire SrTiO$_3$ substrate was used as the gate dielectric. Our main problem with the use of an amorphous YBCO as the gate insulation layer was that amorphous YBCO possessed relatively poor dielectric properties (e.g., large leakage current, even at low temperatures), which lead to a poor device performance. On the contrary, in devices with the SrTiO$_3$ gate, the gate-to-channel leakage current was always below 0.1 nA and was negligible as compared to the measurement current. Application of SrTiO$_3$ as the gate insulator allowed us to achieve significant charging of the superconductor using reasonably low gate voltages, since its dielectric constant can reach $10^3$ at low temperatures. Unfortunately, quasi-ferroelectric properties of SrTiO$_3$ increased the device's time constant to several seconds, what practically prevented us from performing any time dependent charging-effect measurements.

We observed that negative $V_g$ significantly enhanced the channel $J_c$, which in one of the samples increased by 43% for $V_g = -400$ V. Simultaneously, the positive $V_g$ lead to suppression of $J_c$, although its magnitude was not as high as the enhancement observed for negative $V_g$'s. However, the $J_c$ changes were to some extent irreversible, i.e., after removing of the gate voltage the channel $J_c$ did not return completely to its initial value. Subsequently, the field-induced $J_c$ changes registered 40 hours after the first measurement were much less pronounced, although, we still observed both the enhancement and suppression of $J_c$. During the next few days, the sensitivity of channel $J_c$ to $V_g$ continuously decreased and, finally, about one week after the structure fabrication, we did not detect any field-induced response of the sample. In addition to $J_c$ modulation, we found that after the each measurement session $T_{c0}$ of the channel increased by about 0.5-1.5 K and, several days after the structure's preparation and the first measurement, $T_{c0}$ saturated at a value of about 8 K higher than that in the as-fabricated sample. The saturation of $T_{c0}$ coincided with the disappearance of the charging effect in the sample.

Our experimental results lead us to a conclusion that the charging effect observed in our samples is most likely related to the field-enhanced modification of the channel's crystalline structure, rather than to the simple electrostatic response of mobile holes. In fact, the observed behavior can only be plausibly explained using the previously mentioned model, proposed by Chandrasekhar et al. In particular, as an argument for this "chemical" nature of our response, we note the correlation between the sensitivity of our samples to electric field and the slow, but persistent, increase of the channel's $T_c$. A long-term $T_c$ increase in oxygen-deficient
YBCO has been reported by several groups and it is commonly related to the slow ordering of oxygen vacancies in the Cu-O chains. It seems then reasonable to associate the large charging effect in our as-fabricated structures with their enhanced sensitivity to the electric field due to the oxygen system being far from equilibrium. As the oxygen pattern equilibrate, both reversible and irreversible field-induced oxygen-ion rearrangements become, apparently, less plausible and sample sensitivity to the electric field decreases. Also the fact, that the observed changes of $J_c$ and $T_c$ are lower in the samples with higher initial $T_{co}$'s, seems to confirm the above hypothesis. Both the chain-oxygen sensitivity to the electric field in Chandrasekhar's model and the long-term self-ordering of oxygen vacancies are much weaker in YBCO with higher oxygen contents.

Our studies of the charging effect in partially oxygen-depleted YBCO are subject of a number of publications (see Sec. IV).

E. Laser-written microwave structures

We have also demonstrated that the laser-writing patterning technique is a practical method for fabricating microwave YBCO thin-film devices and circuits. We studied the propagation characteristics of YBa$_2$Cu$_3$O$_7$-on-LaAlO$_3$ superconducting coplanar strip transmission lines and resonators. The measurements were performed in the 0.1—15 GHz frequency range at temperatures between 300 K and 24 K. We showed that at temperatures below $T_c$, the $S_{21}$ parameter of our transmission lines was close to 0 dB at all the frequencies, while the Q-factor of the resonator structure was as high as 5000 at 6.5 GHz and 24 K. The transmission line propagation velocity was about $10^8$ cm/s. Our results indicated that the laser-writing patterning technique could be effectively used to fabricate high-quality superconducting microwave elements and circuits. The laser-written oxygen-poor phase was found at low temperatures not to impair performance of tested microwave structures.

Our studies of laser patterned microwave coplanar structures are subject of a number of publications (see Sec. IV).

IV. Future research

The research conducted so far resulted in very interesting findings from the physical point of view; however, they are not sufficient to design a charging-effect transistor applicable for electronic circuits. New transistor designs and substantial improvements in technology are necessary to develop a practical, three-terminal HTS device, based on the charging effect. In future, we will conduct a careful and exhaustive experimental examination of the charge-induced effects in partially oxygen-depleted films with $T_c$'s at about 60 K, as well as in films mildly hydrogenated and/or non-chemically doped by light illumination at low temperatures. We will attempt to arrive at a qualitative and quantitative understanding of the observed phenomena, which should allow us to develop a practical charging effect YBCO transistor. We will also thoroughly study the transistor performance to find its optimal operating conditions and possible applications in electronic circuits.

In the area of technology, we definitely need to improve the quality of the interface layer between YBCO and gate dielectric, and we intend to do it by in-situ growth of a dielectric layer (SrTiO$_3$) on the top of an epitaxial YBCO film. This operation will improve our YBCO-substrate interface, leading to a higher hole mobility in the channel. It will also result in a thin
gate layer, which is necessary for reduction of the magnitude of the gate voltage, and should produce fast response time of our transistor.

The above directions constitute the main goals of our new proposal submitted to AFOSR and already accepted for funding.

V. Publications

The following publications with the grant acknowledgment appeared in print:


The following publications with the grant acknowledgment were accepted for publication and will be published in 1994:


VI. Awards

Roman Sobolewski, Witold Kula, and Wei Xiong received for their presentation "The Meritorious Paper Award," at The 1993 International Cryogenic Materials Conference in Albuquerque, NM.

Wei Xiong received the Travel Assistance Fellowship from the organizers of the 1993 International Cryogenic Materials Conference.

VII. Professional Personnel under Research Grant

Roman Sobolewski, Senior Scientist and Adjunct Associate Professor
Witold Kula, Visiting Research Associate
Wei Xiong, graduate student (supported by the Frank Horton Laboratory for Laser Energetics Fellowship).
Wu, Di, undergraduate student (worked during summer as a part of the University of Rochester Advantage Scholars Internship Program).
Frantzy Duverne and Carlo Williams, undergraduate students (worked during summer as a part of the Ronald E. McNair Post-Baccalaureate Achievement Program).

All participants were affiliated with the Department of Electrical Engineering and the Laboratory for Laser Energetics of the University of Rochester during the period covered by this report. Undergraduate students are EE Majors at the Department of Electrical Engineering.

VIII. Interactions

A. Collaboration with Air Force Wright Laboratory

Our recently initiated collaboration with Dr. R. R. Biggers from the Wright Laboratory Materials Directorate is very promising. Dr. Biggers promised to provide us with ultrathin (~20 nm thick) YBCO films, as well as with a-axis oriented films. He also agreed to act as a Air Force Mentor for prospective graduate student, Carlo Williams, providing that Carlo will be awarded USAF Laboratory Graduate Fellowship.

B. Collaboration with Westinghouse Science & Technology Center

Our collaboration, initiated during the AFOSR STAG Meeting at San Diego, with Dr. J. Gavaler from Westinghouse Science and Technology Center has been very successful. Dr. Gavaler provided us with a number of the highest quality YBCO thin films, tailored to our needs and requirements. By performing laser writing on the best samples available, we were able to prove that this method produces very fine, high quality patterns. The collaboration resulted in several joint publications (see Sec. IV). Dr. Sobolewski visited the Cryogenics Electronics Group at Westinghouse and presented there a seminar on the AFOSR-sponsored research. The HTS research project at Westinghouse is also supported by AFOSR.

C. Collaboration with Southern Methodist University

Our collaboration with Dr. D. P. Butler from the Electrical Engineering Department of SMU has been very successful. Dr. Butler and his student (Mr. W. N. Maung) performed microwave tests on fabricated by us laser-written YBCO microwave coplanar transmission lines and resonators. The results demonstrated that laser writing is suitable for patterning low-loss microwave circuits. The collaboration resulted in several joint publications (see Sec. IV).

D. Conferences attended

Dr. Roman Sobolewski, Dr. Witold Kula, and Wei Xiong participated in the following conferences (The list includes all conferences relevant to the sponsored research, even if participation in some of them was not charged to the AFOSR grant.):

2. R. S. participated in the AFOSR STAG Review Meeting at the University of California at San Diego, CA, 1992, where he presented the review of his research programs, including a report on the University Research Initiative on Superconducting Digital Electronics, sponsored at the University of Rochester by the Army Research Office.

3. R. S. participated in the AFOSR STAG Review Meeting at the Wright-Patterson Air Force Laboratory, Dayton, OH, 1993, where he presented the review of his research programs, including a report on the University Research Initiative on Superconducting Digital Electronics, sponsored at the University of Rochester by the Army Research Office.

4. R. S. attended the 2nd International Israeli Conference on High-Tc Superconductivity in Eilat, Israel, 1993, where he presented one invited and one contributed presentations.


6. R. S. attended the XX International Conference on Low Temperature Physics (LT-20) in Eugene, OR, 1993, where he presented 4 contributed papers.

7. R. S. attended the 1993 International Superconductive Electronics Conference (ISEC'93) in Boulder, CO, where he presented 2 contributed papers.


12. R. S., W. K., and W. X. attended the 1992 Applied Superconductivity Conference, Chicago, IL, where they presented 2 contributed papers. During the ASC'92, R. Sobolewski served as Co-Chair of the session "Field Effects in HTS Thin Films."


E. Seminars

Dr. Roman Sobolewski presented invited lectures at the following institutions:
1. Institute of Physics, Polish Academy of Sciences, Warszawa, Poland, January 1993.

2. Department of Physics, Ben-Gurion University of the Negev, Beer-Sheva, Israel, January 1993.