13:13:34 OCA PAD INITIATION - PROJECT HEADER INFORMATION 04/24/89

Active

Project #: E-21-T20 Cost share #: E-21-328 Rev #: 0
Center # : R6583-T20 Center shr #: F6583-T20 OCA file #: 128
Work type : RES
Contract#: F30602-88-D-0025-0020 Mod #: Document : CONT
Prime #: Contract entity: GTRC

Subprojects ? : N
Main project #:

Project unit: EE Unit code: 02.010.118
Project director(s):
PARIS D T EE (404)894-2902

Sponsor/division names: AIR FORCE / GRIFFISS AFB, NY
Sponsor/division codes: 104 / 023

Award period: 890331 to 890831 (performance) 890930 (reports)

Sponsor amount	New this change	Total to date
Contract value	20,000.00	20,000.00
Funded	20,000.00	20,000.00
Cost sharing amount		2,222.00

Does subcontracting plan apply ?: N

Title: HI-CRITICAL TEMPERATURE SUPERCONDUCTIVITY

PROJECT ADMINISTRATION DATA

OCA contact: Brian J. Lindberg 894-4820

Sponsor technical contact

CAPTAIN S. BACHOWSKI

DEPARTMENT OF THE AIR FORC
ROME AIR DEVELOPMENT CENTER/ESME
GRIFFISS AFB, NY 13441-5700

Sponsor issuing office

GERARD J. BROWN/PKRM
(315)330-7060
ROME AIR DEVELOPME T CENTER
DIRECTORATE OF CONTRACTING (PKRM)
GRIFFISS AFB, NY 13441-5700

Security class (U,C,S,TS) : U
Defense priority rating : DO-A7
Equipment title vests with: Sponsor GIT
NONE PROPOSED OR ANTICIPATED.

ONR resident rep. is ACO (Y/N): Y
GOVT supplemental sheet

Administrative comments -
DELIVERY ORDER FULLY FUNDS TASK S-9-7552 (ALFRED UNIVERSITY).

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 02/11/91

Project No. E-21-T20 Center No. R6583-T20

Project Director JOY E B School/Lab ELEC ENGR

Sponsor AIR FORCE/GRIFFISS AFB, NY

Contract/Grant No. F30602-88-D-0025-0020 Contract Entity GTRC

Prime Contract No.

Title HI-CRITICAL TEMPERATURE SUPERCONDUCTIVITY

Effective Completion Date 900228 (Performance) 900330 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	
Final Report of Inventions and/or Subcontracts	Y	
Government Property Inventory & Related Certificate	Y	
Classified Material Certificate	Y	
Release and Assignment	Y	
Other	N	

Comments

Subproject Under Main Project No.

Continues Project No.

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	Y
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other	N
	N

NOTE: Final Patent Questionnaire sent to PDPI.

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: MAY-JUN '88

	CURRENT QUARTER FUNDING		$0.00
	CURRENT QUARTER EXPENDITURES		$0.00
	CONTRACT CEILING		$4,200,000.00
	FUNDING TO DATE	-	$0.00
*	PENDING COMMITMENTS	-	$766,000.00
	AVAILABLE FUNDING		$3,434,000.00
	FUNDING TO DATE		$0.00
	YTD EXPENDITURES	-	$0.00
	OUTSTANDING EXPENDITURES		$0.00

*	C-8-2120 WESTINGHOUSE/BEAUDET	$56,000.00
	C-8-2129 RENSSELAER/DAS	$100,000.00
	E-8-7066 UNIV OF PENN/STEINBERG	$100,000.00
	E-8-7124 BOSTON COLLEGE/McFADDEN	$35,000.00
	E-8-7125 BRANDEIS UNIV/HENCHMAN	$23,000.00
	E-8-7126 PENN STATE/CASTLEMAN	$22,000.00
	A-8-1631 UNIV OF PENN/STEINBERG	$100,000.00
	B-8-3617 GA WASHINGTON UNIV/MELTZER	$100,000.00
	B-8-3618 GA WASHINGTON UNIV/BERKOVICH	$100,000.00
	C-8-2492 GA TECH/SMITH	$50,000.00
	A-8-1203 GA TECH/HUGHES	$80,000.00
	TOTAL PENDING	$766,000.00

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: JUL-SEPT '88

CURRENT QUARTER FUNDING			$698,034.00
DO #	0001	$56,000	
	0002	$95,141	
	0003	$78,854	
	0004	$230,000	
	0005	$45,561	
	0006	$25,000	
	0007	$20,000	
	0008	$98,374	
	0009	$29,403	
	0010	$19,701	
		$698,034	

	CURRENT QUARTER EXPENDITURES		$0.00
	CONTRACT CEILING		$4,200,000.00
	FUNDING TO DATE	-	$698,034.00
*	PENDING COMMITMENTS	-	$426,563.00
	AVAILABLE FUNDING		$3,075,403.00
	FUNDING TO DATE		$698,034.00
	YTD EXPENDITURES	-	$0.00
	OUTSTANDING EXPENDITURES		$698,034.00

*	DO # 0001	INCREMENTAL FUNDING	$90,729.00
	0002	INCREMENTAL FUNDING	$66,680.00
	0003	INCREMENTAL FUNDING	$54,154.00
	0004	INCREMENTAL FUNDING	$20,000.00
	C-8-2400	STATE UNIV OF NY/FAM	$95,000.00
	C-8-2402	RENSSELAER/SAULNER	$100,000.00
	TOTAL PENDING		$426,563.00

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: OCT-DEC '88

CURRENT QUARTER FUNDING			$120,834.00
DO # 0004	$66,680		
0006	$54,154		
	$120,834		
CURRENT QUARTER EXPENDITURES			$28,740.82
CONTRACT CEILING			$4,200,000.00
FUNDING TO DATE		-	$818,868.00
* PENDING COMMITMENTS		-	$784,729.00
AVAILABLE FUNDING			$2,596,403.00
FUNDING TO DATE			$818,868.00
YTD EXPENDITURES		-	$28,740.82
OUTSTANDING EXPENDITURES			$790,127.18

* DO # 0001	INCREMENTAL FUNDING		$90,729.00
0007	INCREMENTAL FUNDING		$20,000.00
C-8-2400	STATE UNIV OF NY/FAM		$95,000.00
C-8-2402	RENSSELAER/SAULNER		$100,000.00
B-9-3592	UNIV OF CA/DAVIS/LEVITT		$60,000.00
N-9-5514	SOHAR INC./HECHT		$50,000.00
C-9-2015	NCS/O'NEAL		$100,000.00
A-9-1120	HITEC, INC./KAZAKOS		$75,000.00
E-9-7057	UNIV OF TX/ARLINGTON/FUNG		$40,000.00
E-9-7093	MONTANA STATE/JOHNSON		$34,000.00
S-9-7552	ALFRED UNIV/SYNDER		$20,000.00
C-9-2404	STANFORD UNIV/WIDROW		$100,000.00
	TOTAL PENDING		$784,729.00

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: JAN-MAR '89

CURRENT QUARTER FUNDING			$574,457.00
DO #	0001	$90,729	
	0011	$75,000	
	0012	$75,000	
	0013	$59,989	
	0014	$49,989	
	0015	$70,000	
	0016	$43,750	
	0017	$30,000	
	0018	$22,000	
	0019	$38,000	
	0020	$20,000	
		$574,457	

CURRENT QUARTER EXPENDITURES		$86,324.15
CONTRACT CEILING		$4,200,000.00
FUNDING TO DATE	-	$1,393,325.00
* PENDING COMMITMENTS	-	$594,651.00
AVAILABLE FUNDING		$2,212,024.00
FUNDING TO DATE		$1,393,325.00
YTD EXPENDITURES	-	$115,064.97
OUTSTANDING EXPENDITURES		$1,278,260.03

*	DO # 0007	INCREMENTAL FUNDING	$20,000.00
	0011	INCREMENTAL FUNDING	$19,568.00
	0012	INCREMENTAL FUNDING	$24,700.00
	0015	INCREMENTAL FUNDING	$29,783.00
	0016	INCREMENTAL FUNDING	$31,250.00
	0017	INCREMENTAL FUNDING	$10,000.00
	0018	INCREMENTAL FUNDING	$12,000.00
	0019	INCREMENTAL FUNDING	$12,000.00
	C-8-2404	STANFORD UNIV/WIDROW	$100,000.00
	N-9-5732	GRIFFIN	$25,000.00
	A-9-1476	BOWDOIN COLLEGE/CHONACKY	$20,350.00
	E-9-7110	UNIV OF LOWELL/SALES	$50,000.00
	S-9-7559	UNIV OF MICHIGAN/ROBINSON	$20,000.00
	B-9-3621	SRI/LUNT	$20,000.00
	N-9-5308	KAMAN SCIENCES	$100,000.00
	E-9-7119	DARTMOUTH COLLEGE/CRANE	$100,000.00
		TOTAL PENDING	$594,651.00

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: APR-JUN '89

	CURRENT QUARTER FUNDING		$160,350.00
	DO # 0021	$25,000	
	0022	$45,000	
	0023	$20,350	
	0024	$50,000	
	0025	$20,000	
		$160,350	
	CURRENT QUARTER EXPENDITURES		$318,963.82
	CONTRACT CEILING		$4,200,000.00
	FUNDING TO DATE	-	$1,553,675.00
*	PENDING COMMITMENTS	-	$718,994.00
	AVAILABLE FUNDING		$1,927,331.00
	FUNDING TO DATE		$1,553,675.00
	YTD EXPENDITURES	-	$434,028.79
	OUTSTANDING EXPENDITURES		$1,119,646.21

*	DO # 0007	INCREMENTAL FUNDING	$20,000.00
	0011	INCREMENTAL FUNDING	$19,568.00
	0012	INCREMENTAL FUNDING	$24,700.00
	0015	INCREMENTAL FUNDING	$29,783.00
	0016	INCREMENTAL FUNDING	$31,250.00
	0017	INCREMENTAL FUNDING	$10,000.00
	0018	INCREMENTAL FUNDING	$12,000.00
	0019	INCREMENTAL FUNDING	$12,000.00
	0022	INCREMENTAL FUNDING	$54,693.00
	B-9-3621	SRI/LUNT	$20,000.00
	N-9-5308	KAMAN SCIENCES	$100,000.00
	E-9-7119	DARTMOUTH COLLEGE/CRANE	$100,000.00
	N-9-5740	CHRISTIANSON	$15,000.00
	N-9-5317	UNIV OF CO/NORGARD	$50,000.00
	S-9-7625	UNIV OF CA/DAVIS/KOWELL	$20,000.00
	N-9-5314	KAMAN SCIENCES	$100,000.00
	N-9-5315	KAMAN SCIENCES	$100,000.00
		TOTAL PENDING	$718,994.00

E-21-128

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: JUL-SEP '89

CURRENT QUARTER FUNDING			$476,000.00
DO #	0017	$10,000	
	0026	$15,000	
	0027	$20,000	
	0028	$50,000	
	0029	$40,000	
	0030	$30,000	
	0031	$20,000	
	0032	$66,000	
	0033	$70,000	
	0034	$85,000	
	0035	$70,000	
		$476,000	
CURRENT QUARTER EXPENDITURES			$415,422.69
CONTRACT CEILING			$4,200,000.00
FUNDING TO DATE		-	$2,029,675.00
* PENDING COMMITMENTS		-	$253,994.00
AVAILABLE FUNDING			$1,916,331.00
FUNDING TO DATE			$2,029,675.00
YTD EXPENDITURES		-	$849,451.48
OUTSTANDING EXPENDITURES			$1,180,223.52

* DO #	0007	INCREMENTAL FUNDING	$20,000.00
	0011	INCREMENTAL FUNDING	$19,568.00
	0012	INCREMENTAL FUNDING	$24,700.00
	0015	INCREMENTAL FUNDING	$29,783.00
	0016	INCREMENTAL FUNDING	$31,250.00
	0018	INCREMENTAL FUNDING	$12,000.00
	0019	INCREMENTAL FUNDING	$12,000.00
	0022	INCREMENTAL FUNDING	$54,693.00
	N-0-5703	UNIV OF SOUTHERN FLA/WILSON	$50,000.00
		TOTAL PENDING	$253,994.00

E-21-T20

CONTRACT FUNDS STATUS REPORT (DD FORM 1586)
CONTRACT NUMBER F30602-88-D-0025
QUARTER: OCT-DEC '89

CURRENT QUARTER FUNDING				$292,994.00
DO #	0001	$9,000	C-8-2129	
	0011	$19,568	C-8-2400	
	0012	$24,700	C-8-2402	
	0015	$29,783	C-9-2015	
	0016	$31,250	A-9-1120	
	0018	$12,000	E-9-7093	
	0019	$62,000	C-9-2109	
	0022	$54,693	C-9-2404	
	0028	$50,000	N-9-5308	
		$292,994		

CURRENT QUARTER EXPENDITURES		$286,691.16
CONTRACT CEILING		$4,200,000.00
FUNDING TO DATE	-	$2,322,669.00
* PENDING COMMITMENTS	-	$595,000.00
AVAILABLE FUNDING		$1,282,331.00
FUNDING TO DATE		$2,322,669.00
YTD EXPENDITURES	-	$1,136,142.64
OUTSTANDING EXPENDITURES		$1,186,526.36

*	DO # 0007	S-8-7592	INCREMENTAL FUNDING	$20,000.00
	0029	E-9-7119	INCREMENTAL FUNDING	$60,000.00
	0030	N-9-5317	INCREMENTAL FUNDING	$20,000.00
	0034	N-9-5314	INCREMENTAL FUNDING	$15,000.00
	0016	N-9-5315	INCREMENTAL FUNDING	$30,000.00
	N-0-5703	UNIV OF SOUTHERN FLA/WILSON		$50,000.00
	A-0-1102	UNIV OF CA/SMOOT, BARBER, GT		$100,000.00
	P-0-6011	NCSU/VANDERLUGT		$100,000.00
	C-0-2456	NEW JERSEY INST/BAR-NESS		$100,000.00
	P-0-6014	STEVENS INST/ZMUDA		$100,000.00
	TOTAL PENDING			$595,000.00

WAITING FOR PROPOSALS:
P-0-6018 UAH/CAULFIELD
P-0-6021 GT/SUMNERS
P-0-6022 CORNELL UNIV/TANG
B-0-3353 ROCHESTER INST/LASKY

E-21-T20

ROME AIR DEVELOPMENT CENTER
EXPERT SCIENCE AND ENGINEERING PROGRAM
CONTRACT NO. F30602-88-D-0025

R & D STATUS REPORT

PERIOD COVERED: 3/31/89 to 6/30/89

TASK NUMBER: S-9-7552

TITLE: Fabrication of High Temperature Ceramic Superconducting Thin Films

PRINCIPAL INVESTIGATOR: Robert L. Snyder

INSTITUTION: New York State College of Ceramics, Institute for Ceramic Superconductivity

OTHER PARTICIPANTS AND TITLES:
One (1) Postdoc - John Simmins

A. TECHNICAL PROGRESS ACHIEVED ON EFFORT:

It has been established that use of nickel substrates is detrimental to the development of superconductivity in both Ba- and Bi-based films. Bi-based films have been deposited on magnesia and 15 mole% yttria stablized zirconia. We have shown that the film thickness definitely affects the time required for complete reaction of the film with the substrate. Sufficiently thick films were required to prevent substantial film-substrate reaction and to provide long heat treatment period, which is probably a mandate for developing the superconducting phases. X-ray diffraction indicated the presence of the superconducting 2212 and the semiconducting 2111 phases in most of the films. The amount of these phases varied according to the post-deposition annealing conditions. However, resistivity measurement showed no evidence for a superconducting behavior implying a non-continuous dispersion of the superconducting phases. Most of the films showed a semiconducting behavior indicating a continuous pathway of the semiconducting 2111 phase.

The main drawback with using Ba-based compositions has been the low degree of vaporization. An aerosol spray technique is being implemented as a possible solution to achieve complete vaporization of the feed.

Continued next sheet

atomization unit has just been purchased which will enable the use of metal ion solutions instead of powders, as input to the plasma flame.

Deposition, using powders as feed material to the plasma, on an unheated substrate has produced amorphous films of the correct stoichiometry. Various heat treatment temperature-time schedules were tried in an attempt to crystallize the superconducting phases after film deposition. The temperatures ranged from 790 to 900°C for times ranging from 2 to 30 minutes. Sometimes two annealing schedules were used. However, heat treatment to develop the superconducting properties in the deposited films has not yet proved fruitful. This problem has been solved by most other workers by heating the substrate during deposition. We had hoped to avoid this step in order to make the process more amenable to a mass production environment, however, it appears that substrate heating will be required. At the moment we will use resistive heating, however in the future we plan to used high intensity radiant heating to allow for film deposition onto a continuously moving substrate.

B. TRAVEL:

Two (2) trips to Buffalo @ $54/day to use testing equipment.

C. PRESENTATIONS AND PUBLICATIONS:

1. T. K. Vethanayagam, W. A. Schulze, J. A. T. Taylor, and R. L. Snyder, "Inductance Technique for Measuring Transition Temperatures of Superconducting Powders", International Journal of Modern Physics B, 3(5), 1989, pp763-772.
2. T. K. Vethanayagam, R. L. Snyder, and J. A. T. Taylor, "Atmospheric Plasma Vapor Deposition of Ba-Y-Cu-Oxide and Bi-Sr-Ca-Cu-Oxide Thin Films", Thermal Spray Technology - New Ideas and Processes, ed. David L. Houck, ASM International, Ohio, 1989, pp233-238.
3. J. L. Porter, T. K. Vethanayagam, R. L. Snyder, and J. A. T. Taylor, "Reactivity of Ceramic Superconductors with Palladium Alloys" - submitted for publication.

D. LEVEL OF EFFORT BY EACH CONTRIBUTOR (IN MAN-MONTHS OR MAN-HOURS)

Robert L. Snyder - 84 hours

Postdoc - (John Simmins) 320 hours

E-21-T20

Institute for Ceramic Superconductivity

New York State College of Ceramics
Alfred University
Alfred, New York 14802

Dr. Robert L. Snyder

(607) 871-2438

November 7, 1990

contract E-21-T20 0020
E-21-T25 0025

Georgia Institute of Technology
ATTN: Brian J. Lindberg
Office of Contract Administration
Centennial Research Building
Atlanta, GA 30332-0420

RE: Subcontract # E-21-T20-S1

Dear Mr.Lindberg:

Enclosed please find the final report for our work on the atmospheric pressure plasma vapor deposition technique for making superconducting thin films. I have also enclosed our latest paper on the subject in Appl. Phys. Lett. This paper was featured in last week's edition of the Nikkei Superconductors newsletter. The Japanese clearly appreciate the importance of this technique which has now produced a large number of superconducting films. Our first experiment on making a Thallium film in collaboration with Allen Hermann (their discoverer) was successful in producing a superconducting film with a Tc of about 90K.

Sincerely,

Robert L. Snyder

RLS/rs

Final Report to U. S. Air Force RADC

RF Plasma Aerosol Deposition of Superconductive YBaCuO Films at Atmospheric Pressure

Prepared by R.L. Snyder and X.W. Wang
Institute for Ceramic Superconductivity, NYSCC
Alfred University, Alfred, NY 14802.

September 1990

Part A. Outline

This project was supported by the U.S. Air Force Rome Air Defense Center. Additional fundings were provided by the New York State Institute on Superconductivity, and the Center for Advanced Ceramic Technology at Alfred University.

Superconductive films have been deposited by the RF plasma aerosol technique at atmospheric pressure. The zero resistance temperature of an as deposited film in 93K, with critical current of 0.8×10^4 A/cm^2 at 77K. The detailed experimental results are reported in Part B.

There have been two U.S. Patents allowed, three papers to be published, including one paper in Applied Physics Letters.

Part B. Main Body

ABSTRACT

Superconducting $Y_1Ba_2Cu_3O_{7-\delta}$ films were produced by a radio frequency (RF) plasma aerosol evaporation technique at atmospheric pressure without post-annealing. Aqueous solutions containing Y, Ba, and Cu were generated as an aerosol which was then injected into the plasma region. The ionized species were deposited onto substrates outside of both the plasma and flame regions. The substrate temperature was 400-600°C. The deposition rate is 0.01-100 μm/(min cm^2), and the film thickness is 1-200 μm. For an "as deposited" film on a single crystalline MgO substrate (100) with substrate temperature of 600°C, the onset temperature of the superconducting transition is 100K, with a transition width (10% - 90%) of 3K, and zero resistance at 93K. The critical current density of the film is 0.8 x 10^4 A/cm^2 at 77K. An optimum substrate temperature for this technique is discussed. The as-deposited films are compared with other post-annealed films (850°C, 1 hour). Since this technique does not require a vacuum environment it has potential for large scale production of thin films.

I. Introduction

Since the discovery of high T_c superconductivity[1], dozens of techniques have been developed to make films either inside of a vacuum chamber[2,3,4,5] or under normal atmosphere[6,7]. To-date, the best superconducting films are thin films with a thickness less than 10 μm, obtained by evaporation or sputtering methods in vacuum.[2,3] However, all of the vacuum technologies are limited in that they can produce only small film sizes and vacuum is ill suited for mass production procedures. Large scale production of films may rely on the development of non-vacuum techniques, such as tape casting[8], plasma spraying[6,7], or plasma vapor deposition. During the plasma vapor deposition of films[4,5], powder (or solution aerosol) is injected into the plasma (or flame) region, and the vapor is deposited onto a substrate to form a film thicker than 10 μm. Plasma spraying on the other hand, deposits the liquid or partially melted solid onto the substrate.

Our previous work[9] injected a fine powder into the plasma and, depending on conditions, sometimes produced plasma vapor deposited films but more often produced plasma sprayed films due to partial vaporization. We have modified this plasma technique, and obtained superconductive films with a solution mist injection method.[10]

II. Experiments

The starting powders were $Y(NO_3)_3$, $Ba(NO_3)_2$ and $Cu(NO_3)_2$ with purity

of 99.9% or higher. These powders were mixed according to the stoichiometric ratio of Y:Ba:Cu in 1:2:3, and then dissolved in distilled (or deionized) water with a concentration of 150 g/l or less. The aqueous solution was then stirred thoroughly and poured into a plastic bowl, see Fig. 1.

A DeVilbiss Ultrasonic Nebulizer Model Ultra-Neb 99, normally used in hospital respiratory therapy, was used as an aerosol generator, to produce a mist in the space above the aqueous solution. Under the pressure of an argon or oxygen carrier gas, the mist is fed into the O_2/Ar plasma region. After travelling through the flame region, the ionized vapor is deposited onto a substrate. The substrate temperature is maintained at a fixed temperature during deposition. Between the plasma and flame regions, additional oxygen can be supplied through two auxiliary gas inlets. At the beginning of an experiment, the plasma oscillation and/or the mist injection may be unstable. A shutter is placed above the flame region to block unwanted vapor from the substrate. Depending on the concentration of the solution, the deposition rate varies from 0.01-100μm/(min cm^2). Depending on the deposition rate and the deposition time, the film thickness varies from 1 to 200μm. Other experimental conditions are summarized in Table 1.

III. Results

Each film was formed on a substrate at a fixed substrate temperature during deposition. The substrate varied from 400°C to 600°C with the temperature accuracy of ±10°C. The "as deposited" films were black, and examined as described next.

1. Substrate temperature of 600°C.

Film resistances were measured by a standard 4-probe method. For an as-deposited film on a single crystalline MgO (100) substrate, the resistivity vs. temperature curve is shown in Fig. 2. The onset temperature is 100K, with a transition width (10%-90%) of 3K, and zero resistance at 93K. (The temperature accuracy is ±0.5K.) The critical current density of the film is 0.8 x 10^4 A/cm^2 at 77K. The thickness of this film is about 15 μm. Figure 3(A) is the x-ray diffraction pattern of an "as-deposited" superconductive film on a single crystalline MgO (100) substrate. As compared with a standard powder diffraction pattern of pure $Y_1Ba_2Cu_3O_{7-\delta}$ in Fig. 3(C), the film shows a pure 123 phase. The scanning electron microscope (SEM) reveals that grains of the "as-deposited" films are uniformly distributed, and grain sizes are smaller than 1 μm^3. Energy dispersive x-ray analysis (EDAX) shows uniform grain compositions containing the three desired metals.

Some other films were deposited at the substrate temperature of 600°C, and then post-annealed at 850 ± 10°C for 1 hour, with a flow of oxygen at a pressure of about 1 bar in the oven. The resistivity vs. temperature curve of a

post-annealed film on MgO (100) substrate is shown in reference 10. The onset temperature is 105K, with a transition width of 6K, and zero resistance at 91K. The thickness of this film is about 20μm. Figure 3(B) is the x-ray diffraction pattern of the post annealed superconductive film, and shows a pronounced (00ℓ) orientation. The SEM reveals that grains of the post-annealed films are uniformly distributed, and grain sizes are 1 x 1 x 10 μm^3. The surface morphology of the film is very similar to that of other post annealed films.[11] EDAX also shows uniform grain compositions containing the three desired metals.

2. Substrate temperatures of 500°C and 400°C

A film was formed at 500°C on a MgO (100) substrate. The X-ray diffraction pattern of the as-deposited film is plotted in Fig. 4(B). As compared with the standard 123 pattern shown in Fig. 4(C), the film shows a pure 123 phase. The film was then post-annealed at 850°C for 1 hour. The diffraction pattern of the post-annealed film is plotted in Fig. 4(A) and shows a pure 123 phase as compared with the standard 123 pattern of Fig. 4(C).

Another film was formed at 400°C on MgO (100). The diffraction pattern of the as-deposited film is plotted in Fig. 5(B). The major phase in the film is 123, as compared with the standard 123 pattern in Fig. 5(C). Another minor phase is barium copper oxide. A strong diffraction peak around 43 degrees is due to the substrate MgO. The film was post-annealed at 850°C for 1 hour. The pattern of the annealed film is plotted in Fig. 5(A). The dominant phase in the film is 123, and a minor phase is barium copper oxide.

3. Substrate temperature of 450°C

Films were formed at 450°C on MgO (100), or yttrium stabilized zirconia (YSZ) single crystal, i.e. ZrO_2 (100). These films were post-annealed at 850°C for 1 hour. The x-ray diffraction patterns of post-annealed films on MgO (100) and ZrO_2 (100) are shown in Fig. 6(A) and 6(B) respectively. The dominant phase in each film is 123 as compared with the standard pattern in Fig. 6(C). Another minor phase is barium copper oxide.

A graph of resistivity vs. temperature is shown in Fig. 7 for a film formed on a MgO (100) substrate. The onset temperature of superconductive transition is 102K, zero resistance temperature is 92K, and transition width is 3K. The critical current density is 1.3 x 10^3 A/cm^2 at 77K. The film thickness is about 15μm.

IV. Conclusions

It has been shown that the aerosol mist injection method can be used to produce oxide-superconductive films in ambient atmosphere by RF plasma evaporation. Besides the experimental set up shown in Fig. 1, we also have tried other configurations, i.e. mist or powder injection in the flame region, and powder injection in the RF plasma region. It is observed that films deposited by

the mist injection methods are more uniform than that of the powder methods which are usually a hybrid plasma spray procedure. It is observed that films deposited by the ionized vapor from the plasma region are more homogeneous than that from the flame region. It is believed that oxygen is ionized into the O_2^+ state in the plasma region. The positive oxygen ion may be helpful in the formation of the superconductive $Y_1Ba_2Cu_3O_{7-\delta}$ structure[3]. It is also observed that when the substrate holder is ground electrically, the as-deposited film is superconductive. The optimum substrate temperature is 600°C for this non-vacuum technique.

References

[1] See, for example, A.W. Sleight, Science 242, 1519 (1988).

[2] B. Oh, M. Naito, S. Arnason, P. Rosenthal, R. Barton, M.R. Beasley, T.H. Geballe, R.H. Hammond, and A. Kapitulnik, Appl. Phys. Lett. 51, 852 (1987). M. Hong, S.H. Liou, J. Kwo, and B.A. Davidson, Appl. Phys. Lett. 51, 694(1987). D. Dijkkamp, T. Venkatesan, X.D. Wu, S.A. Shaheen, N. Jisrawi, Y.H. Min-Lee, W.L. McLean, and M. Croft, Appl. Phys. Lett. 51, 619 (1987).

[3] S. Witanachchi, H.S. Kwok, X.W. Wang, and D.T. Shaw, Appl. Lett. 53, 234 (1988).

[4] K. Terashima, K. Eguchi, T. Yoshida, and K. Akashi, Appl. Phys. Lett. 52, 1274 (1988).

[5] A. Koukitu, Y. Hasegawa, H. Seki, H. Kojima, I. Tanaka, and Y. Kamioka, Jpn. J. Appl. Phys. 28, L1212 (1989).

[6] J.J. Cuomo, C.R. Guarnieri, S.A. Shivashankar, R.A. Roy, D.S. Lee, R. Rosenberg, Adv. Ceramic Mat. 2. 442 (1987).

[7] W.T. Elam, J.P. Kirkland, R.A. Neiser, E.F. Skelton, S. Sampath, and H. Herman, Adv. Ceramic Mat. 2, 411 (1987).

[8] M. Ishii, T. Maeda, M. Matsuda, M. Takata, and T. Yamasunua, Jpn. J. Appl. Phys. 26, L1959 (1987).

[9] T.K. Vethanayagam, J.A.T. Taylor, and R.L. Snyder, Proc. of National Thermal Spray Conference, Oct. 1988, Cincinnati, OH.

[10] Preliminary results were reported, for example, X. Wang, H. H. Zhong, and R. L. Snyder, in Proc. of Conf. on Sci. & Tech. of Thin Film Superconductors, April, 1990, Denver, CO.

[11] H. S. Kwok, P. Mattocks, D. T. Shaw, L. Shi, X. W. Wang, S. Witanachchi, Q. Y. Ying, J. P. Zheng, "Laser deposition of YBaCuO Superconducting Thin Films", in Proc. of World Congress on Superconductivity; ed. C.G. Burnham, et al., (World Scientific, New Jersey, 1988).

Table 1 Deposition Conditions

Unit	Parameters	Value
Ultrasonic nebulizer	Power	70W
	Frequency	1.63MHz
Mist carrier gas, Ar or O_2	Flow rate	100-150 ml/min
Solution	Misting rate	2 ml/min
RF plasma generator	Power	30KW
	Frequency	4MHz
Plasma gas	Ar flow rate O_2 flow rate	15 l/min 40 l/min
Auxiliary gas, O_2	Flow rate	5 l/min
Film formation	Deposition rate thickness	0.01-100 μm/(min cm^2) 1-200 μm
Distance	Between substrate and top of plasma torch	7.5-12.5 cm
Film area		30-40 cm^2

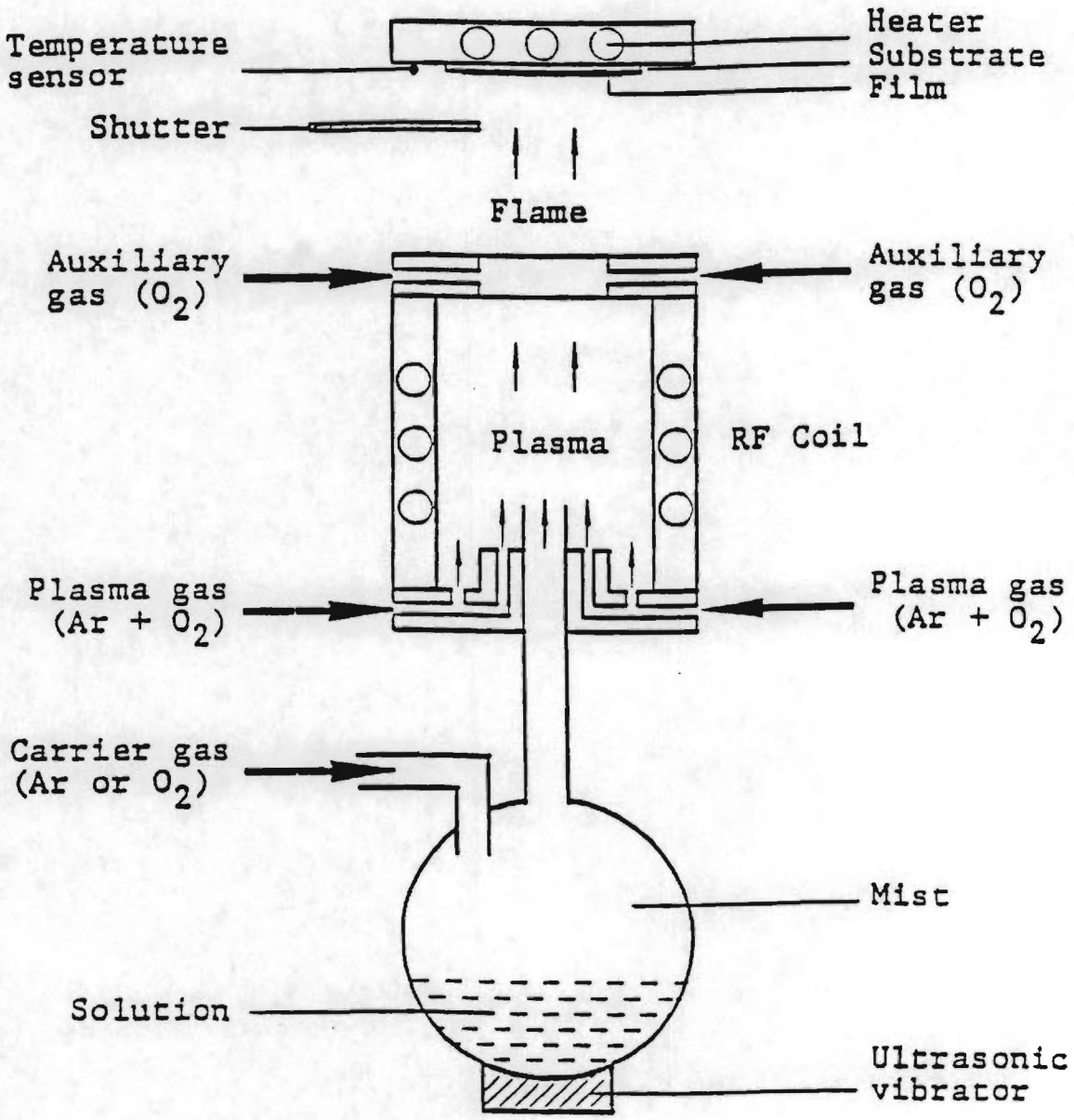


Fig. 1 Experimental set up.

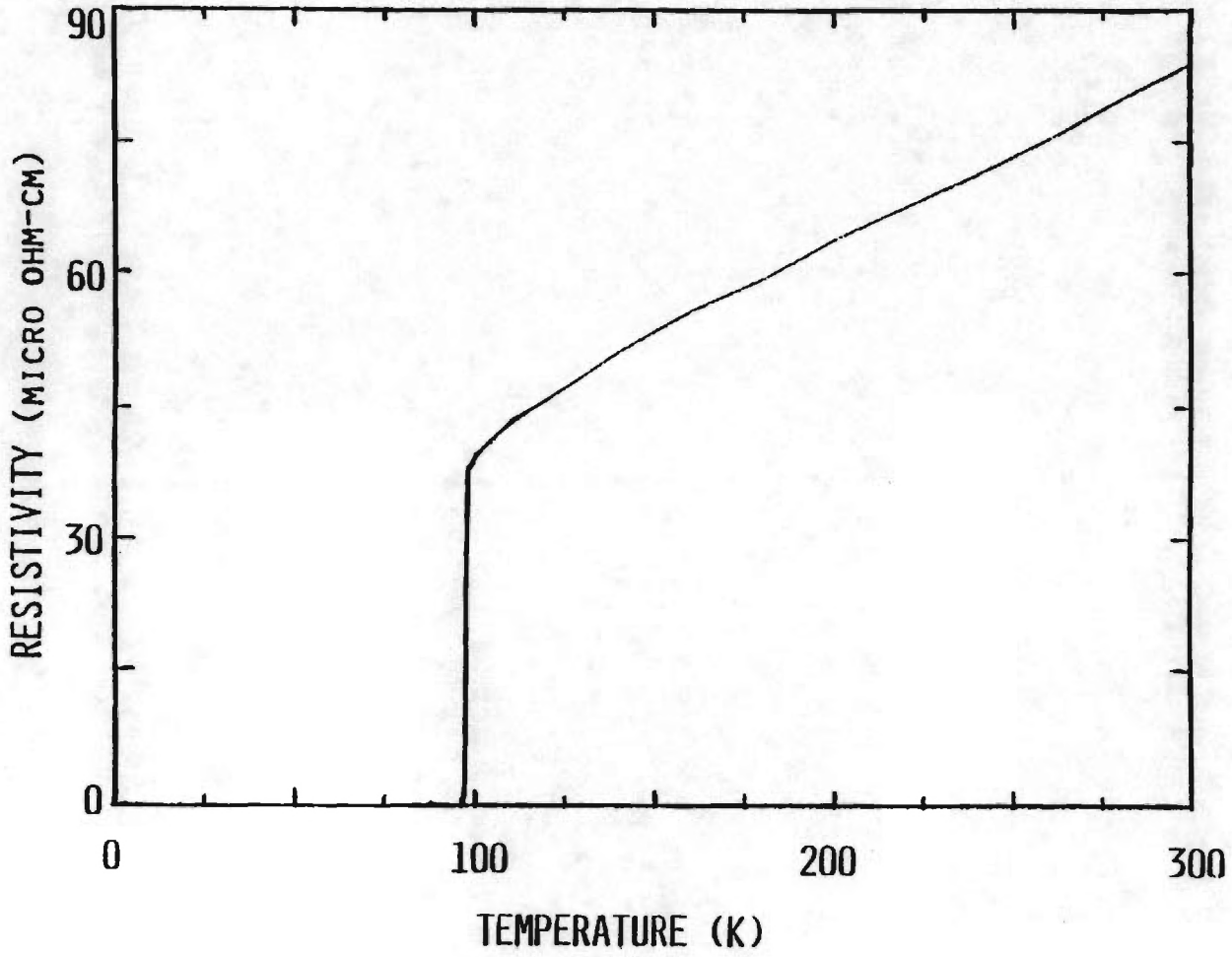


Fig. 2 Resistivity vs. temperature for an as-deposited film on a MgO (100) substrate. The substrate temperature during deposition was 600°C.

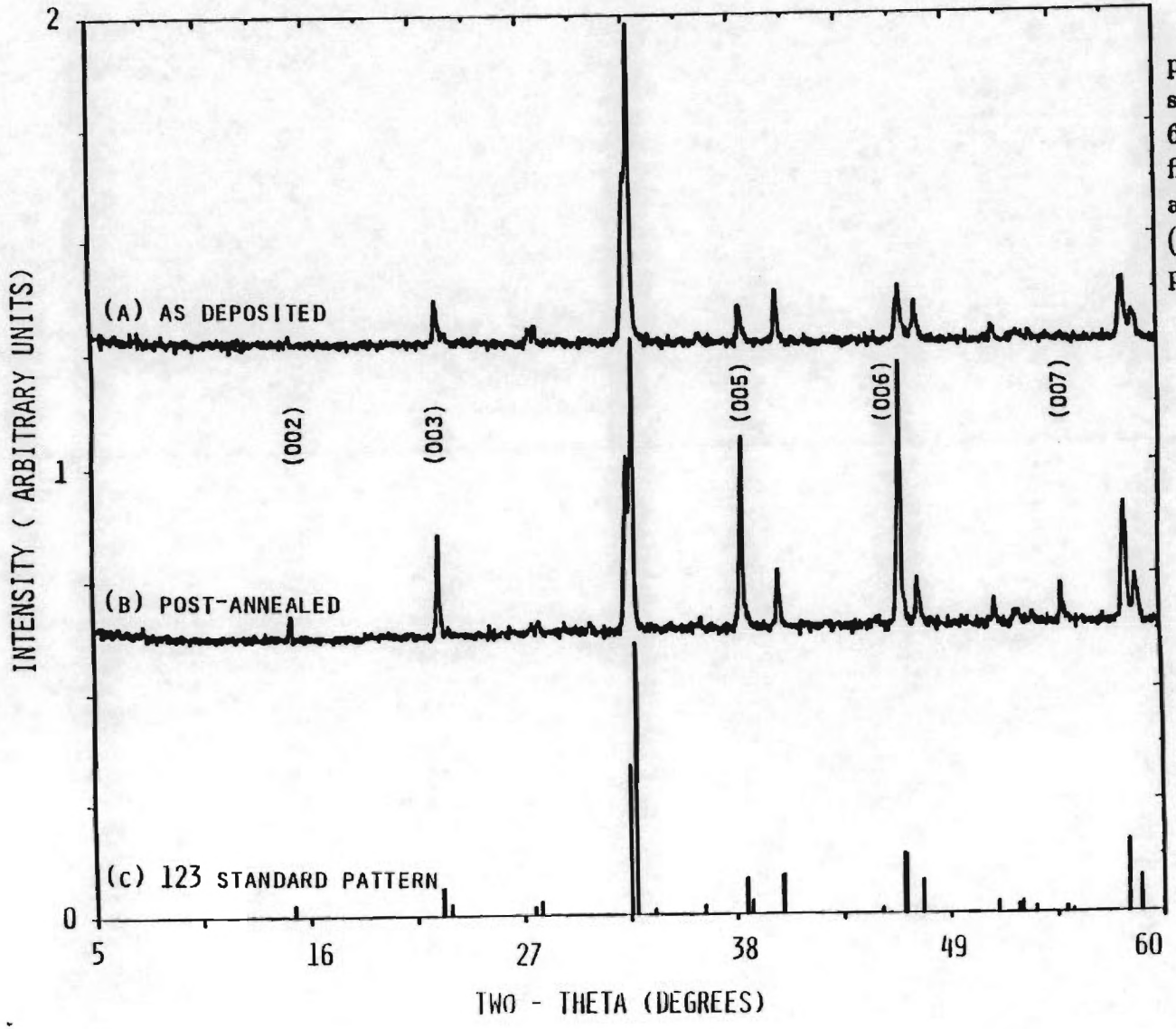


Fig. 3 X-ray diffraction patterns of films with substrate temperature of 600°C, (A) as deposited film on MgO (100), (B) post-annealed film on MgO (100), (C) $Y_1Ba_2Cu_3O_{7-\delta}$ standard powder diffraction pattern.

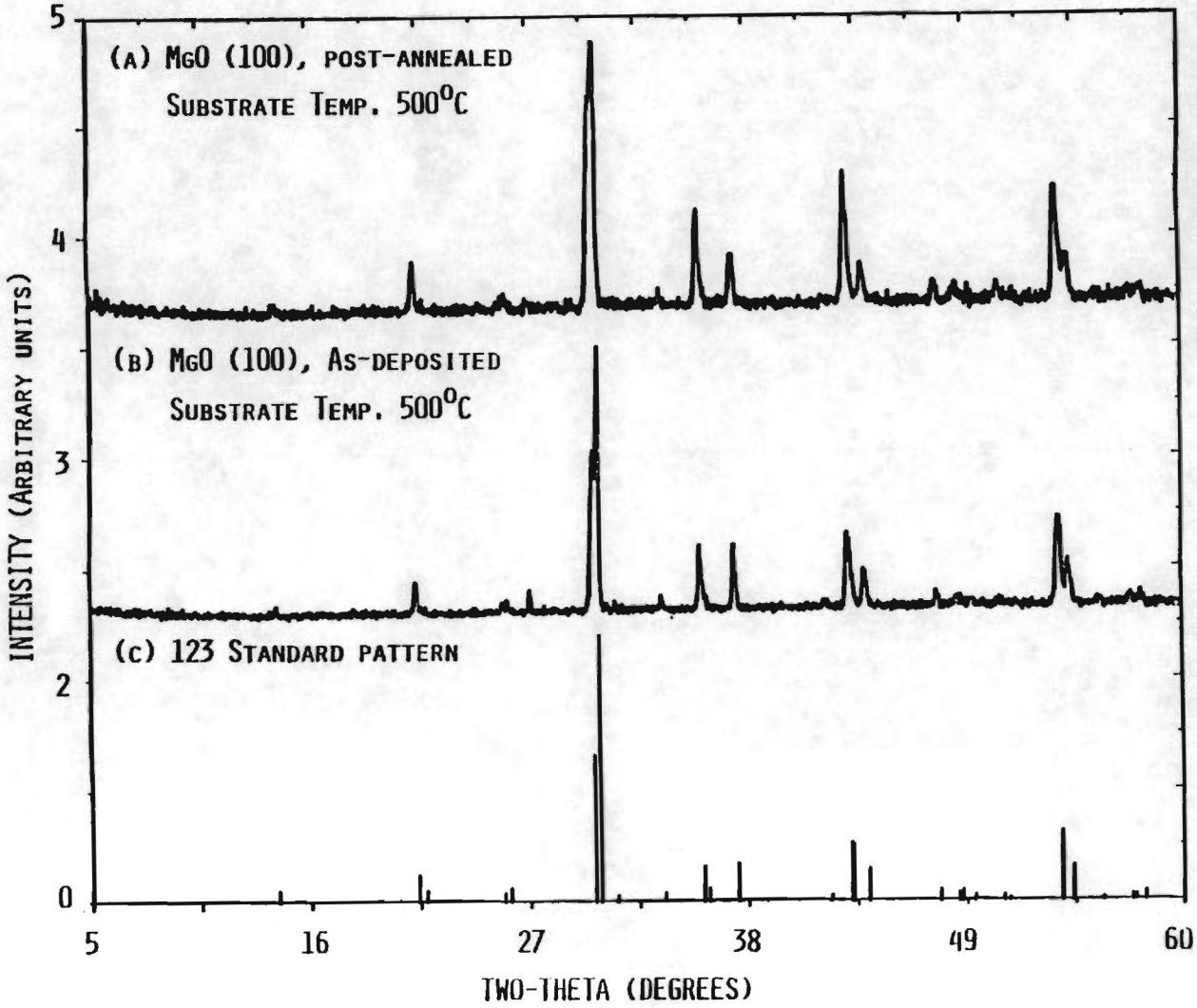


Fig. 4 X-ray diffraction patterns of films with substrate temperature of 500°C, (A) post-annealed film on MgO (100), (B) as-deposited film on MgO (100), (C) $Y_1Ba_2Cu_3O_{7-\delta}$ standard powder diffraction pattern.

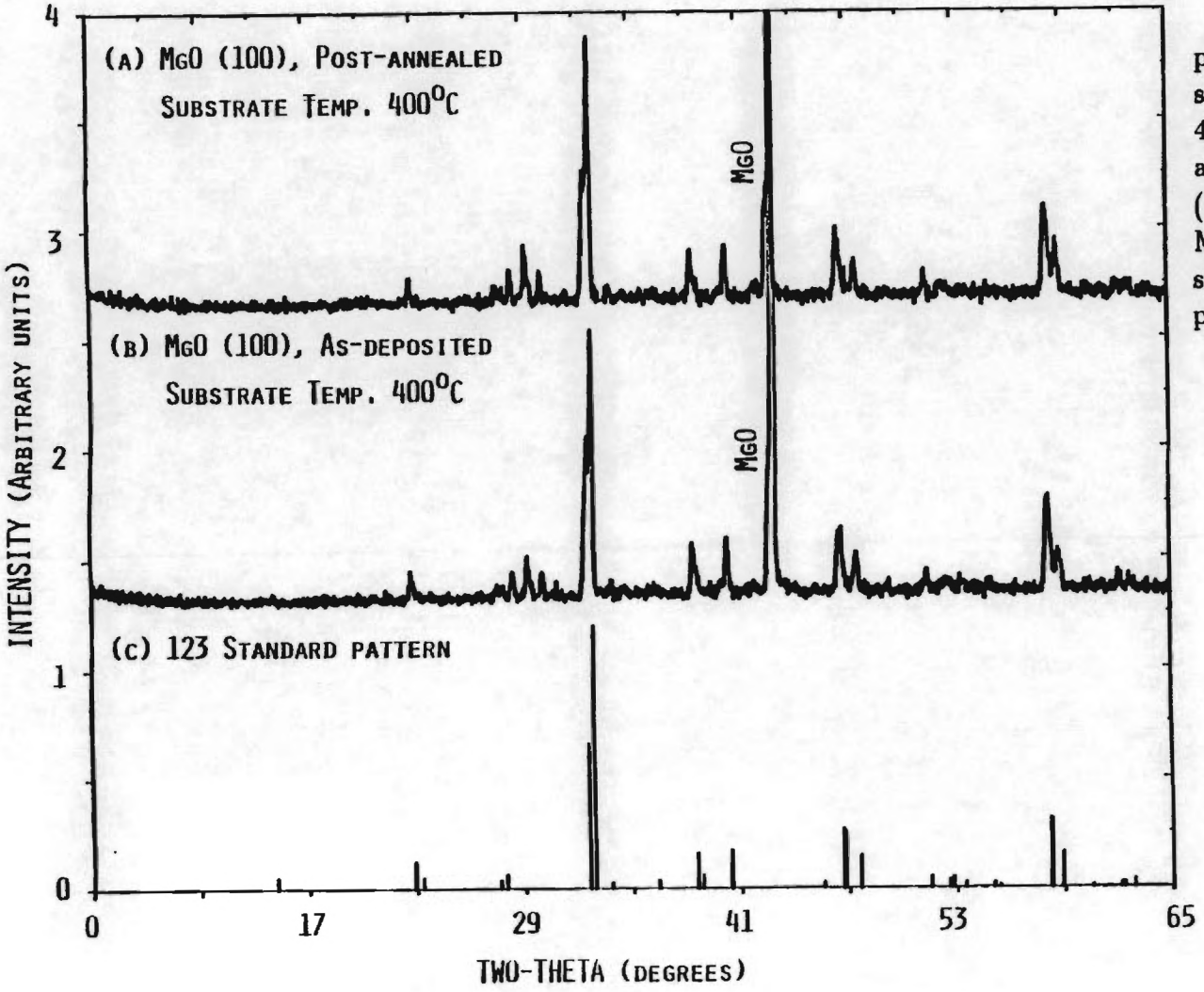


Fig. 5 X-ray diffraction patterns of films with substrate temperature of 400°C, (A) post-annealed film on MgO (100), (B) as-deposited film on MgO (100), (C) $Y_1Ba_2Cu_3O_{7-\delta}$ standard powder diffraction pattern.

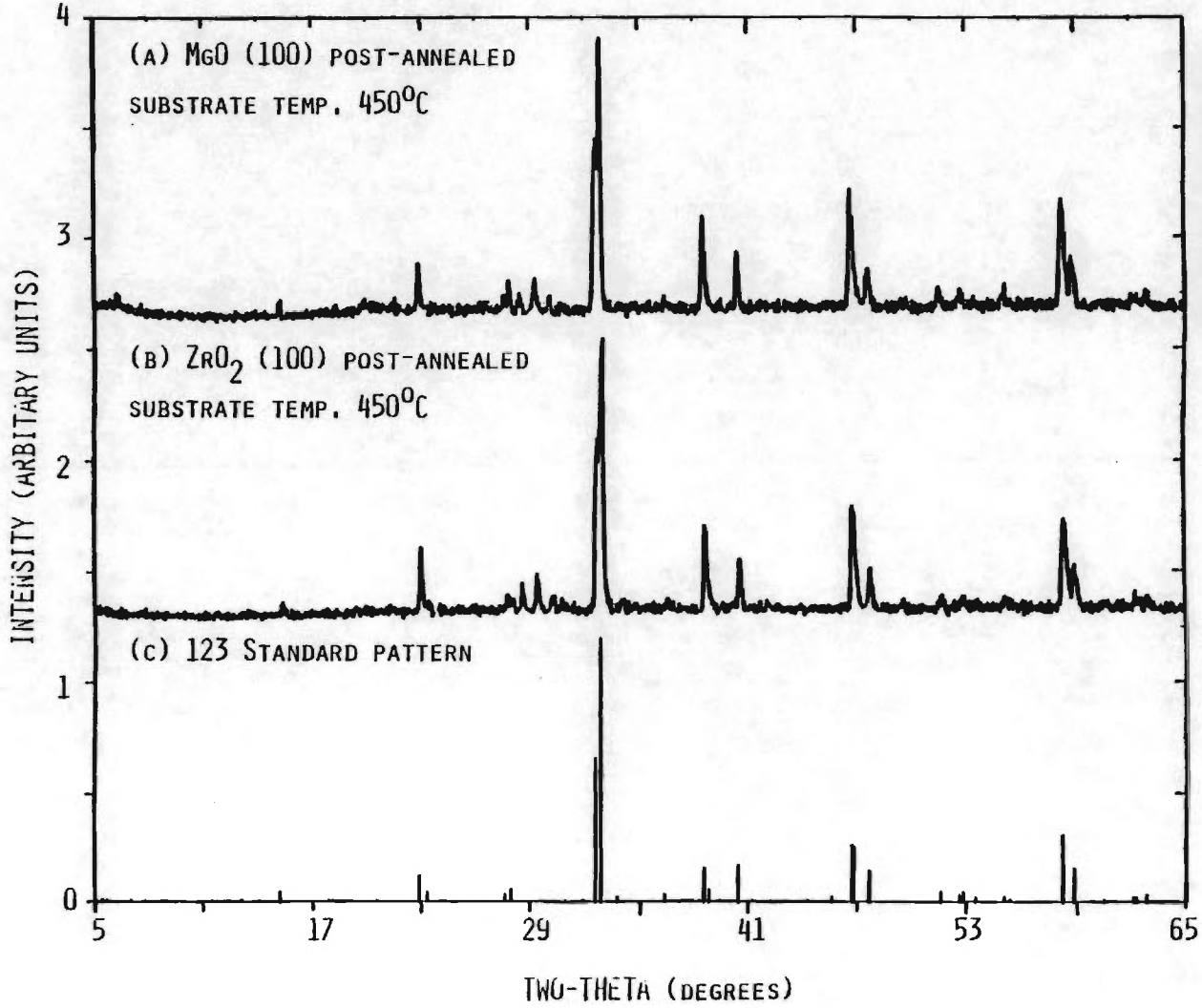


Fig. 6 X-ray diffraction patterns of films with substrate temperature of 450°C, (A) post-annealed film on MgO (100), (B) post-annealed film on ZrO_2 (100), (C) $Y_1Ba_2Cu_3O_{7-\delta}$ standard powder diffraction pattern.

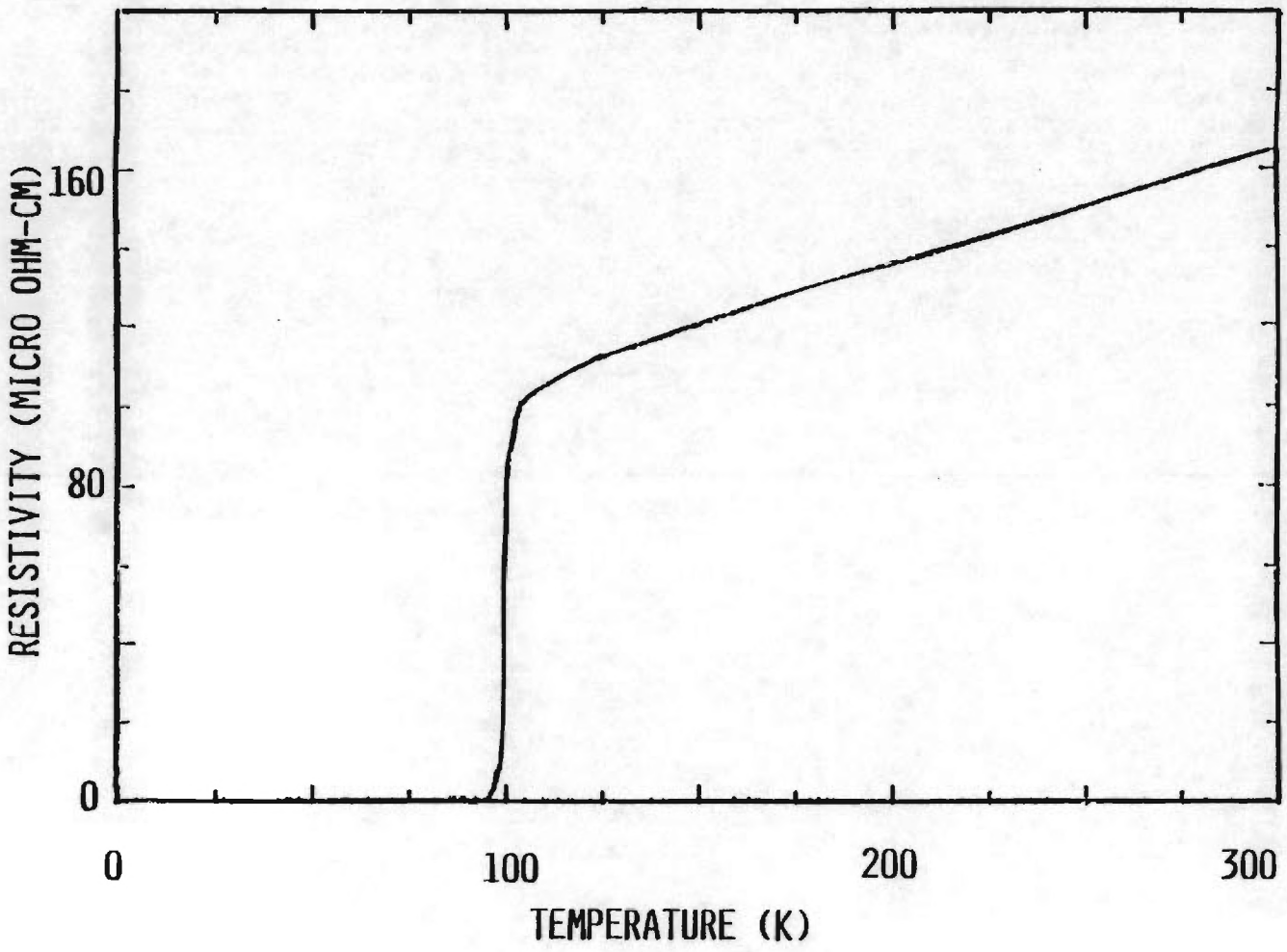


Fig. 7 Resistivity vs. temperature for a post-annealed film on a MgO (100) substrate. The substrate temperature during deposition was 450°C.

1990年10月15日発行（隔週月曜日）第67号　1989年2月22日第3種郵便物認可

日経超電導
NIKKEI SUPERCONDUCTORS 1990 10. 15

FROM THE EDITOR

バナジウム酸化物の追試報告は依然ない。日立製作所からも，新しい実験データの報告はない。しかし，いくつかの研究所で精力的に実験が続けられているので，焦らずに結果に期待したい。なお，10月3日の物理学会シンポジウムでNTTが130Kでマイスナー効果を観測したと発表したが，これは数日後に取り消された（p.1）。Tl系超電導体の基本特許が米国で成立した。臨界温度が77Kを超える実用的な高温超電導材料としては，世界で初めて成立した特許となる（p.1）。応用研究者の注目を集めている磁気浮上力の強いY系バルク試料を，新日本製鉄が希望者に出荷すると述べている。これによって新しい応用分野が開拓されれば楽しみだ（p.4）。

●新物質探索，スーパーHI-T_c

▶▶ NTT，バナジウム酸化物でマイスナー効果観測と発表したが，後に撤回

NTT電子応用研究所は，日立製作所が発表したバナジウム酸化物超電導体（Tl-Sr-V-O）の追試過程で，Bi-Sr-V-Oが130Kでマイスナー効果を示すと10月3日の物理学会シンポジウムで急きょ発表した。しかしその後，観測したデータは超電導以外の原因による可能性が大きいと述べ，事実上，物理学会の報告を撤回した。*nature*誌への論文投稿も取り下げる予定。

物理学会でNTTは，SQUID磁束計で130K以下で負の磁化率（ゼロ磁界冷却）を測定したと発表した。再現性は高く試料の安定性も良いと述べ，参加者に大きなインパクトを与えた。非銅系の高温超電導体の世界が確実に開かれたというニュースが広まり，大学や企業でいっせいに追試が始まった。

しかし物理学会に引き続いて名古屋で開かれた文部省重点領域研究の発表会で，NTTは自ら測定に問題があったことを認め，物理学会の発表内容を撤回した。SQUID磁束計の試料設置部分に残留磁界があったためと，試料が強磁性体であったために，みかけの負の磁化率がデータに現れた可能性があると述べた。これは，Quantum Design社製のSQUID磁束計で強磁性体を測定したときにしばしば現れる「一種の装置のクセのようなもの」（ある大学の研究者）として，一部の研究者には知られていた。また「Bi-Sr-V-O，Tl-Sr-V-Oとも超電導現象に似た挙動を示すが，超電導ではなく強磁性の可能性の方が高い」と，米Houston大学のC.W. Chu教授が9月24日に開かれたASC'90の席上でも指摘していた（本誌1990年10月1日号，p.2）。

●特許，Tl系，米国

▶▶ アーカンソー大のTl系基本特許が米国で成立

米Arkansas大学が1988年に発見したTl系超電導体の基本特許が10月9日に米国で成立した。発明者はAllen M. Hermann氏（現Colorado大学Boulder校教授）とZhengzhi Sheng氏の二人で，出願者はArkansas大である。物質の組成はTlRBaCuO（RはBaを除く2A族元素）とTlSrCuOで，臨界温度は120Kとしてい

わずか1層でもゼロ抵抗になった

同グループは，前述したように，Y系の厚さが1層でも10Kで抵抗がゼロになったことも報告した（オンセット温度は70K）。これまでも1層でゼロ抵抗になったという報告はあったが，たいていの場合，絶縁層と超電導層を繰り返し何層も積み重ねた超格子でT_cを測っていた。この際，絶縁層の一部が切れていて，超電導層がつながり実効的に厚くなっている可能性が捨てきれなかった。今回は，超電導層は全体でも1層だけなので，1層でも超電導になるということがより明確になった。

東京大学工学部の内田慎一助教授は，「純粋な2次元面では，熱力学的に有限温度で超電導にならないとされている。今回の実験で，波動関数が近接効果により，どの程度3次元性を獲得できているかたいへん興味がある。この研究をもとに，近接効果を調べられるだろう」という。

また，トンネル接合などの電子デバイスを作る上で重要になる。トンネル接合を作るときは，絶縁膜を薄くすることが必要で，絶縁層との界面での超電導層のT_c劣化を避けなければならない。1層で超電導になれば，界面直下でも超電導性が保てるといえる。また，将来の精巧な電子デバイス作製にもつながるかもしれない。

Y系薄膜の上にPrBaCuO層を付けないと，Y系は超電導にならなかった。「PrBaCuO層からY系薄膜にキャリヤが注入されているのかもしれない」（寺嶋氏）という。

なお，$SrTiO_3$上にY系薄膜を成膜する前に，PrBaCuOバッファ層を6層積層しているのは，基板の格子定数と結晶系（斜方晶）をY系に合わせるためである。

●米国，厚膜

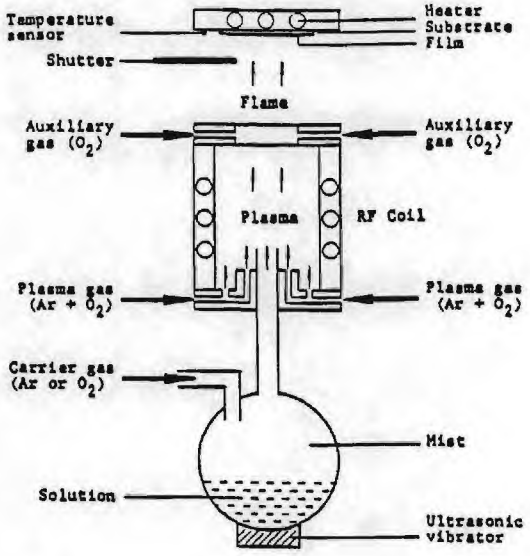
ニューヨーク州の2大学，熱プラズマ法を使い大気中で良質のY系膜を作る

米New York州立大学Buffalo校と米Alfred大学セラミック超電導研究施設はそれぞれ独立に，霧状の超電導原料を高周波コイルの中を通して基板に蒸着させることにより，大気中，アズ・デポで臨界温度(T_c)や臨界電流密度(J_c)が高いY系超電導膜を高速で作ったと発表した（New York州立超電導研究所(NYSIS)主催の第4回国際会議)。この方法は，原料が安く装置に真空系を全く含まないことから，長尺線材や大面積の超電導膜を作る実用的な方法であるとしている。

New York州立大の特長は77K，ゼロ磁界中でのJ_cが40万A/cm^{2}と高いこと。基板にはYSZを使い，基板温度600～700℃，成膜速度は1分あたり約0.01μm，T_cは86Kというものである。これに対し，Alfred大の試料のJ_cは77Kで8000A/cm^{2}とあまり高くないが，成膜速度が最高で1分あたり100μmと速い上に，T_cは93Kと高い。基板にはMgOを使い，基板温度を600℃とした。

日本では東北大学金属材料研究所の香川昌宏助手（庄野研究室）が1987年にこの方法と同じ原理でLa系超電導体の合成を開始した。その後，同研究室博士過程の鈴木光雄氏がY系とBi系で合成研究を行っている。しかし，米国の大学の例はアズ・デポで作ってT_cやJ_cが高いことで日本の複数の研究者も今回の成果を高く評価している。東北大が原料を上から下へ飛ばすのに対し，米国の大学の方法は逆に下から上へ飛ばしている。

Alfred大学の例を図に示した。プラスチック容器の中にY，Ba，Cuそれぞれの硝酸塩を1：2：3の比で配合した水溶液を入れる。病院で呼吸器の治療に用い



ている噴霧器で原料を霧状にして，ArやO_2ガスとともに高速で高周波コイルの中へ入れる。コイル中でイオン化した原料が，600℃に加熱した大気中のMgO基板に堆積するという仕組みである。詳細は*Applied Physics Letters*(*APL*)誌で近々紹介されることになっている。New York州立大の成果は，*APL*誌10月１日号で紹介された。また，東北大はY系の成果を11月に開催されるISS'90で紹介し，Bi系の成果を英国の学会誌に投稿した。

熱プラズマを使う方法は，低価格，高速で大量生産向き

東京大学工学部の寺嶋和夫講師によれば，今回の方法は高圧力のプラズマ（熱プラズマ）を利用する手法の一つで，高周波スパッタリング，プラズマCVDなど，低圧力で高周波を利用する方法と比べて研究例が少ない。しかし，「レーザを使う方法やCVD法などは，電子デバイスなどの小さな試料を作るにはよいが，原料や運転コストを考えると，とても線材の大量生産や大面積のシールド容器を作るには向いていない」という。

寺島氏によれば，熱プラズマ法は①液体原料を高周波コイルに導く方法（ICPスプレー法），②粒径が数10～数100μmの大粒の超電導粉末をコイルの中で溶融して基板に堆積する方法（溶射法），③粒径１μm以下の微粉末をコイルの中で蒸発させて基板に堆積する方法（プラズマ・フラッシュ蒸着法），の三つに大別できる。米国の２大学と東北大の方法は①に属する。東大の吉田豊信教授，寺嶋講師の研究室は③を研究しており，成膜速度を0.1～0.2μm／分にしてJ_cではすでに30万A/cm^2(77K)を得ているという。

●バルク，マグネット，溶融法，Y系

▶▶ 新日鉄，「浮上力が5.6kgのY系バルクを出荷可能」と述べる

新日本製鉄は，永久磁石との反発（浮上）力の大きいY系バルクをサンプル出荷できると述べた。このサンプルは，直径４cm，厚さ１cmの円柱状で，QMG(quench and melt growth) 法で作製したもの。サマリウムーコバルト磁石との反発力は5.6kg。フィッシング効果でぶら下げられる力は２kg。臨界電流密度J_cは77K，１Tで２万A/cm^{2}程度。「有償で提供することも，ユーザーとの共同研究のために無償で提供することもできる」（第一技術研究所未来領域研究セン

rf plasma aerosol deposition of superconductive $Y_1Ba_2Cu_3O_{7-\delta}$ films at atmospheric pressure

X. W. Wang, H. H. Zhong, and R. L. Snyder
Institute for Ceramic Superconductivity, NYSCC, Alfred University, Alfred, New York 14802

(Received 14 May 1990; accepted for publication 7 August 1990)

Superconducting films of $Y_1Ba_2Cu_3O_{7-\delta}$ were produced by a radio frequency (rf) plasma aerosol evaporation technique at atmospheric pressure. Aqueous solutions of the ions were generated as an aerosol and the mist was injected into the plasma region, and then deposited onto substrates outside of both the plasma and flame regions. The substrate temperature was about 600 °C. The deposition rate is 0.01–100 μm/(min cm^2) and the film thickness is 1–200 μm. For an "as-deposited" film on a single-crystalline MgO substrate (100), the onset temperature of the superconducting transition is 100 K, with a transition width (10–90%) of 3 K, and zero resistance at 91 K. For another film post annealed at 850 ± 10 °C for 1 h, the onset temperature is 105 K, with a width of 6 K, and zero resistance at 91 K. Since this technique does not require a vacuum environment, it has potential for large scale production of thin films.

Since the discovery of high T_c superconductivity,[1] dozens of techniques have been developed to make films either inside of a vacuum chamber[2–5] or under normal atmosphere.[6,7] To date, the best superconducting films are thin films with a thickness less than 10 μm, obtained by evaporation or sputtering methods in vacuum.[2,3] However, all of the vacuum technologies are limited in that they can produce only small film sizes and vacuum is ill suited for mass production procedures. Large scale production of films may rely on the development of nonvacuum techniques, such as tape casting,[8] plasma spraying,[6,7] or plasma vapor deposition.[4,5] During the plasma vapor deposition of films, powder (or solution aerosol) is injected into the plasma (or flame) region, and the vapor is deposited onto a substrate to form a film thicker than 10 μm. Plasma spraying, on the other hand, deposits the liquid or partially melted solid onto the substrate.

Our previous work[9] injected a fine powder into the plasma and, depending on conditions, sometimes produced plasma vapor deposited films but more often produced plasma sprayed films due to only partial vaporization. We have modified this plasma technique, and obtained superconductive films with a solution mist injection method.

The starting powders were $Y(NO_3)_3$, $Ba(NO_3)_2$, and $Cu(NO_3)_2$ with purity of 99.9% or higher. These powders were mixed according to the stoichiometric ratio of Y:Ba:Cu in 1:2:3, and then dissolved in distilled (or deionized) water with a concentration of 150 g/ℓ or less. The aqueous solution was then stirred thoroughly and poured into a plastic bowl; see Fig. 1.

A DeVilbiss Ultrasonic Nebulizer Model Ultra-Neb 99, normally used in hospital respiratory therapy, was used as an aerosol generator, to produce an aerosol mist in the space above the aqueous solution. Under the pressure of an argon or oxygen carrier gas, the mist is fed into the O_2/Ar plasma region. After traveling through the flame region, the ionized vapor is deposited onto a substrate. The substrate temperature is maintained at 600 ± 10 °C during deposition. Between the plasma and flame regions, additional oxygen can be supplied through two auxiliary gas inlets. At the beginning of an experiment, the plasma oscillation and/or the aerosold injection may be unstable. A shutter is placed above the flame region to block unwanted vapor from the substrate. Depending on the concentration of the solution, the deposition rate varies from 0.01 to 100 μm/(min cm^2). Depending on the deposition rate and the deposition time, the film thickness varies from 1 to 200 μm. Other experimental conditions are summarized in Table I. Both films "as-deposited" and films "post-annealed" at 850 ± 10 °C for 1 h were examined as described next.

The "as-deposited" films were black, and their film resistances were measured by a standard four-probe method. For a film on a single crystalline MgO (100) substrate, the resistivity versus temperature curve is shown in Fig. 2 (a). The onset temperature is 100 K, with a transi-

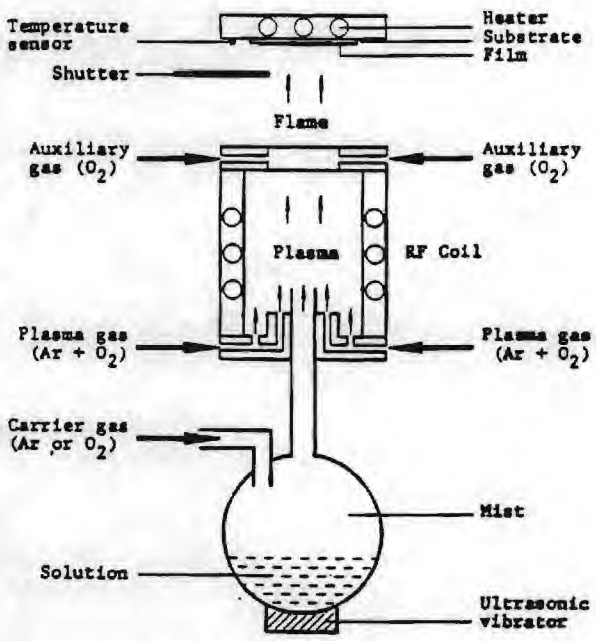


FIG. 1. Experimental setup.

 0003-6951/90/411581-03$02.00

TABLE I. Deposition conditions.

Item	Unit	Parameters	Value
1	Ultrasonic nebulizer	Power	70 W
		Frequency	1.63 MHz
2	Mist carrier gas, Ar or O_2	Flow rate	100–150 mℓ/min
3	Solution	Misting rate	2 mℓ/min
4	rf plasma generator	Power	30 kW
		Frequency	4 MHz
5	Plasma gas	Ar flow rate	15 ℓ/min
		O_2 flow rate	40 ℓ/min
6	Auxiliary gas, O_2	Flow rate	5 ℓ/min
7	Film formation	Deposition rate	0.01–100 μm/(min cm^2)
		thickness	1–200 μm
8	Distance	Between substrate and top of plasma torch	7.5–12.5 cm
9	Film area		30–40 cm^2

tion width (10–90%) of 3 K, and zero resistance at 91 K. (The temperature accuracy is ±0.5 K.) The thickness of this film is about 45 μm. For another film on a MgO (100) substrate post annealed at 850 ± 10 °C for 1 h, the resistivity versus temperature curve is shown in Fig. 2(b). The onset temperature is 105 K, with a transition width of 6 K, and zero resistance at 91 K. The thickness of this film is about 20 μm.

Figure 3(a) is the x-ray diffraction pattern of the "as-deposited" superconductive film (45 μm) on a single-crystalline MgO (100) substrate. As compared with a standard powder diffraction pattern of pure $Y_1Ba_2Cu_3O_{7-\delta}$ in Fig. 3(c), the film shows a pure 123 phase. Figure 3(b) is the pattern of a post-annealed superconductive film (20 μm, 850 °C, 1 h) on a MgO (100) substrate, and shows a pronounced (00l) orientation.

The scanning electron microscope (SEM) reveals that grains of the films are uniformly distributed, and grain sizes are smaller than 1 μm^3; see Fig. 4. Energy dispersive x-ray analysis shows uniform grain compositions containing the three desired metals.

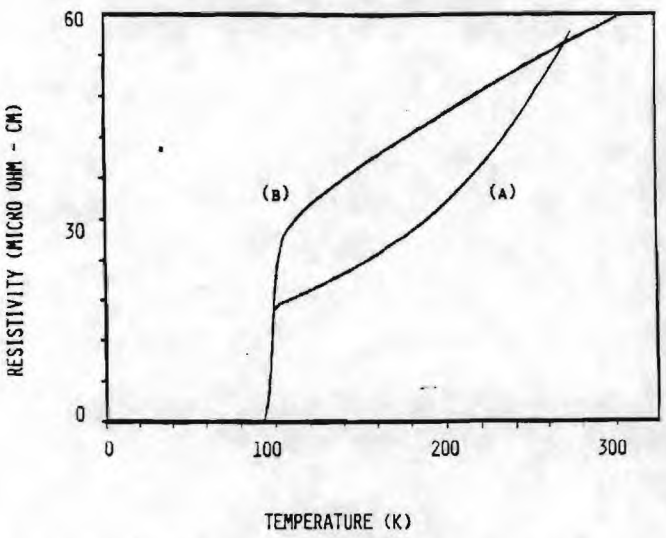


FIG. 2. Resistivity vs temperature for films on MgO (100) substrates: (a) as-deposited film: (b) post-annealed film.

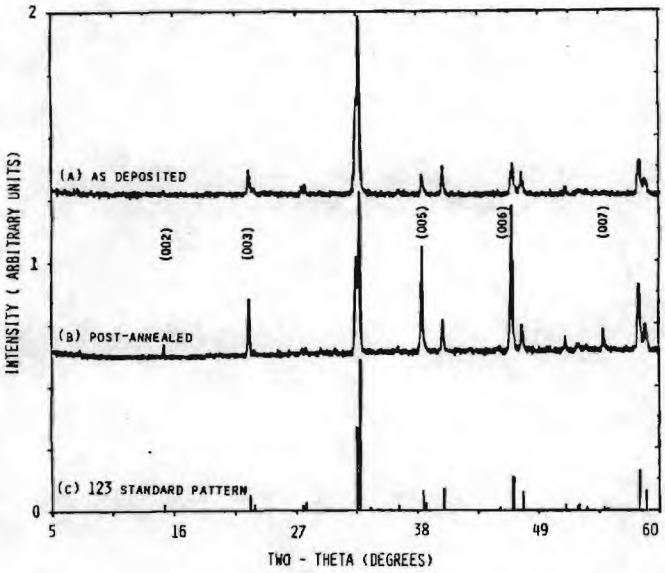


FIG. 3. X-ray diffraction patterns: (a) as-deposited film on MgO (100), (b) post-annealed film on MgO (100), (c) $Y_1Ba_2Cu_3O_{7-\delta}$ standard powder diffraction pattern.

It has been shown that the aerosol injection method can be used to produce oxide-superconductive films in ambient atmosphere by rf plasma evaporation. Besides the experimental setup shown in Fig. 1, we also have tried other configurations, i.e., mist or powder injection in the flame region, and powder injection in the rf plasma region. It is observed that films deposited by aerosol injection methods are more uniform than that of the powder methods which are usually a hybrid plasma spray procedure. It is observed that films deposited by the ionized vapor from the plasma region are more homogeneous than that from the flame region. It is believed that oxygen is ionized into the O_2^+ state in the plasma region. The positive oxygen ion may be helpful in the formation of the superconductive

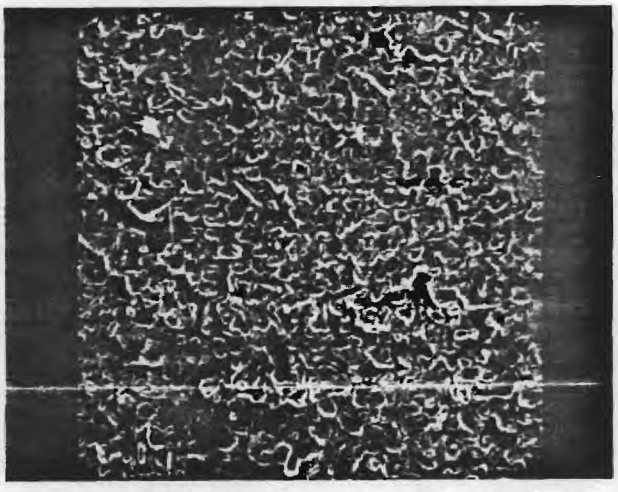


FIG. 4. SEM (second electron mode) photo of the "as-deposited" $Y_1Ba_2Cu_3O_{7-\delta}$ film. (Length of the photo is 22 μm.)

$Y_1Ba_2Cu_3O_{7-\delta}$ structure.[3] It is also observed that when the substrate holder is electrically grounded, the as-deposited film is superconductive.

Currently, we are working on the optimization of the deposition conditions. Critical current measurements are also under way.

This work was partially supported by the U.S. Air Force Rome Air Defense Center, the New York State Institute of Superconductivity, and the Center for Advanced Ceramic Technology at Alfred University. We wish to thank Professor L. David Pye, John Simmins, B. Chen, M. Pitsakis, M. Rodriguez, J. Hao, and N. Burlingame for many valuable contributions.

[1] See, for example, A. W. Sleight, Science **242**, 1519 (1988).
[2] B. Oh, M. Naito, S. Arnason, P. Rosenthal, R. Barton, M. R. Beasley, T. H. Geballe, R. H. Hammond, and A. Kapitulnik, Appl. Phys. Lett. **51**, 852 (1987); M. Hong, S. H. Liou, J. Kwo, and B. A. Davidson, Appl. Phys. Lett. **51**, 694(1987); D. Dijkkamp, T. Venkatesan, X. D. Wu, S. A. Shaheen, N. Jisrawi, Y. H. Min-Lee, W. L. McLean, and M. Croft, Appl. Phys. Lett. **51**, 619 (1987).
[3] S. Witanachchi, H. S. Kwok, X. W. Wang, and D. T. Shaw, Appl. Phys. Lett. **53**, 234 (1988).
[4] K. Terashima, K. Eguchi, T. Yoshida, and K. Akashi, Appl. Phys. Lett. **52**, 1274 (1988).
[5] A. Koukitu, Y. Hasegawa, H. Seki, H. Kojima, I. Tanaka, and Y. Kamioka, Jpn. J. Appl. Phys. **28**, L1212 (1989).
[6] J. J. Cuomo, C. R. Guarnieri, S. A. Shivashankar, R. A. Roy, D. S. Lee, and R. Rosenberg, Adv. Ceramic Mater. **2**, 442 (1987).
[7] W. T. Elam, J. P. Kirkland, R. A. Neiser, E. F. Skelton, S. Sampath, and H. Herman, Adv. Ceramic Mater. **2**, 411 (1987).
[8] M. Ishii, T. Maeda, M. Matsuda, M. Takata, and T. Yamasunua, Jpn. J. Appl. Phys. **26**, L1959 (1987).
[9] T. K. Vethanayagam, J. A. T. Taylor, and R. L. Snyder, in *Thermal Spray Technology: New Ideas and Processes*, Proceedings of National Thermal Spray Conference, edited by D. L. Houck, Oct. 1988, Cincinnati, Ohio (ASM International, Metals Park, Ohio, 1989), pp 233–237.