Journal of Superconductivity, Vol. 10, No. 3, 1997

Comparison of High-Pressure dc-Sputtering and Pulsed Laser Deposition of Superconducting $YBa_2Cu_3O_x$ Thin Films

P. B. Mozhaev,[1,2] P. V. Komissinski,[1] N. P. Kukhta,[1] A. Kühle,[2] G. A. Ovsyannikov,[1] and J. L. Skov[2]

Received February 15, 1997

Superconducting $YBa_2Cu_3O_x$ thin films were deposited on $NdGaO_3$ (110) substrates using two different techniques: dc sputtering at high oxygen pressure and pulsed laser deposition. The structure, electrical properties, and surface morphology of the obtained films were compared. The superior crystal quality of dc-sputtered films fabricated at the same temperature and at oxygen pressure of the same range as for laser-deposited films can be explained by a lower deposition rate providing time for recrystallization processes. The re-evaporation becomes significant for dc sputtering at high deposition temperatures and results in Ba-deficient films. The high mobility of atoms on the surface of the growing film during laser deposition helps in the formation of smooth c-oriented areas of the film.

KEY WORDS: Pulsed laser deposition; high-pressure dc-sputtering; thin film growth.

1. INTRODUCTION

Among the different high-critical-temperature superconducting $YBa_2Cu_3O_x$ (YBCO) thin film deposition techniques, pulsed laser deposition and different sputtering methods are popular due to the high reproducibility of the obtained film parameters (critical temperature and current, element contents). Pulsed laser deposition yields almost uniform transport of ablated atoms to the substrate and results in high crystal quality films with stoichiometry close to the target element contents. Compared to other sputtering techniques, high pressure dc sputtering gives films of the best structure and electrical properties [1]. The electrical properties of thin YBCO films obtained with pulsed laser deposition and rf sputtering were compared in [2]. The surface morphology of laser-deposited and dc-sputtered films was compared using STM in [3]. For adequate comparison of deposition techniques the films must be fabricated on the same substrate and the thermodynamic deposition parameters (substrate temperature, oxygen pressure) should be chosen as close as possible to offset the differences in the film formation process. We used pulsed laser deposition and high-pressure dc sputtering to deposit YBCO thin films on $NdGaO_3$ (110) substrates [4,5]. Optimization sequences were carried out to obtain films of high electrical properties; the optimal temperature and oxygen pressure were found to be almost the same for both techniques. We studied the crystal quality of the obtained films as the most direct evidence of the processes in the growing film. In this paper we compare these two techniques of fabrication of superconducting thin films.

[1]Institute of Radio Engineering and Electronics, Russian Academy of Sciences, Moscow, 103907, Russia.
[2]Physics Department, Technical University of Denmark, Lyngby, DK-2800, Denmark.

2. EXPERIMENTAL

Details of the deposition setup can be found elsewhere [4,5]. In brief, we used a KrF excimer laser with energy density on the target about 1.2 J cm. The laser beam was scanned across the stoichiometric YBCO ceramic target surface with a turnable mirror, driven in orthogonal directions by two motors. The pressure in the chamber was held at 1 mbar with a constant oxygen flow of 10 sccm. The substrate was

0896-1107/97/0600-0005$12.50/0

positioned 42.5 mm from the target and was heated to 810°C with a halogen lamp. At the chosen conditions the visible ablation plume was just touching the substrate surface [6]. After deposition, an oxygenizing procedure was carried out, including rapid cooling to 400°C in 1 mbar of oxygen, slow cooling to 350°C (annealing) in 2 hours in 1 bar of oxygen, and fast cooling to room temperature.

For dc sputtering the deposition pressure was 4 mbar with a constant flow of oxygen of 40 sccm. The target -substrate distance was 20 mm. the discharge current density on the target surface was 12- 16 A,/ cm', and the discharge voltage was about 270 V. The chosen geometry and discharge power made the glowing area around the cathode slightly touch the substrate surface. The substrate holder was heated to 750-850°C with a ThermoCoax element. The oxygenating sequence included rapid cooling to about 400°C in 4 mbar without turning the discharge off. annealing at the chosen temperature for 1 hour in I bar of oxygen, and fast cooling to room temperature. In both techniques. to enhance the thermal contact the substrate was glued to the substrate holder with silver paint. Optimization procedures for both techniques were carried out to obtain the best electrical properties.

The structure of the obtained films was examined by X-ray diffractional analysis. θ 2θ-Scans were used to determine phase composition. The c-axis lattice constant was calculated using (001) peak positions for l from I to IO using the method of [7]. Rocking curves (o-scans) of the (005) peak were used for evaluation of the crystal quality of the film. Film surface morphology was observed in a scanning electron microscope (SEM). Element contents were estimated by X-ray microanalysis. The electrical properties of the films were studied using a four-probe technique. To determine the critical current densities. sets of narrow bridges (4-15 μm) were made in the films with conventional photolithography and wet etching techniques.

3. RESULTS

For adequate comparison of the deposition techniques were tried to keep the conditions on the substrate surface as close as possible. The oxygen pressure was in the same range (1 and 4 mbar): the optimal temperature of the sample holder in both cases was determined to be about 800°C. We tried to minimize the ion bombardment of the growing film both in dc sputtering (the substrate is positioned outside the glowing area around the cathode) and during pulsed laser deposition (the plume height is slightly less than the target-substrate distance).

Both laser-deposited and dc-sputtered films showed zero resistance temperatures T_{c0}'s up to 9 1 K. The width of the superconducting transition AT, (determined by the IO-90% levels of the resistance at the transition) of the laser-deposited films was about 1.5 K, and that in the dc-sputtered films less than I K (Fig. I). The critical current density at 77 K in the absence of magnetic field in both sets of films was up to 5 . 10^6 A/cm^2 (2 mV/cm criterion). The specific resistance at room temperature of both types of films was the same, about 350 $\mu\Omega \cdot$ cm in the best films. The residual resistance ratio RR = $R(300\ \mathrm{K})/R(100\ \mathrm{K})$ in both cases was about 3.

The films deposited at optimal conditions showed element composition close to the stoichiometric Y $Ba_2Cu_3O_x$. Deviations from optimal dc-sputtering parameters lead to decrease of T_{c0} due to the Ha depletion of the films (Fig. 2). Laser-deposited films showed almost stoichiometric element contents even for films with lower T_{c0}'s, showing the influence of crystal structure on the superconducting properties of the film.

The SEM observations of the films obtained with both techniques showed the presence of particles on the films surfaces (Fig. 3) that can be divided into

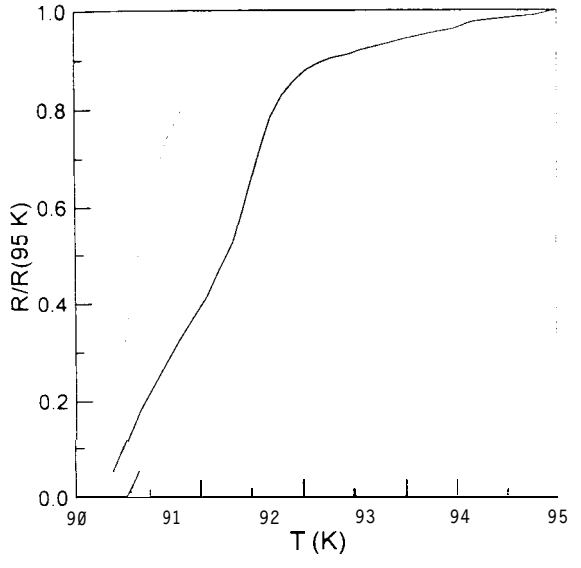

Fig. I. Temperature dependences **of resistance** near the superconducting transition **for: solid** line—laser-deposited film. deposition rate 36 nm/min; **dotted** line—laser-deposited **film.** deposition rate **7** nm/ **min** ; **dashed line** –high-pressure **dc-sputtered** film. deposition **rate I** nm/min.

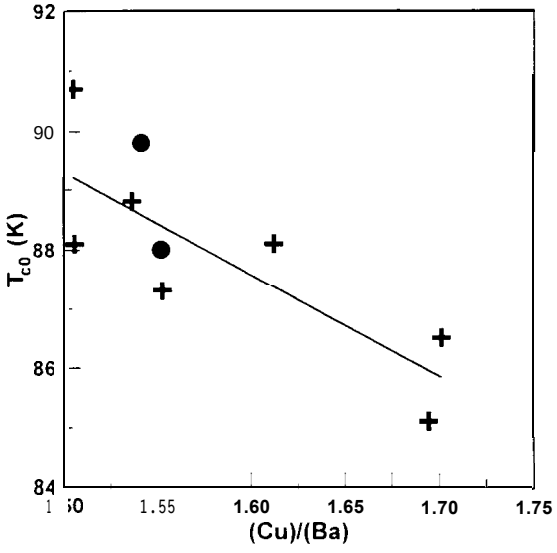

Fig. 2. Dependence of zero-resistance temperatures T_{c0} on copper-to-barium content ratio determined by X-ray microanalysis. Crows dc-sputtered films obtained al deposition temperatures 750-840 C and constant discharge current: circles. laser-deposited films at 780 and 810 C The line is a linear fit of experimental points for dc-sputtered films The copper-to-yttrium content ratio is constant for all samples

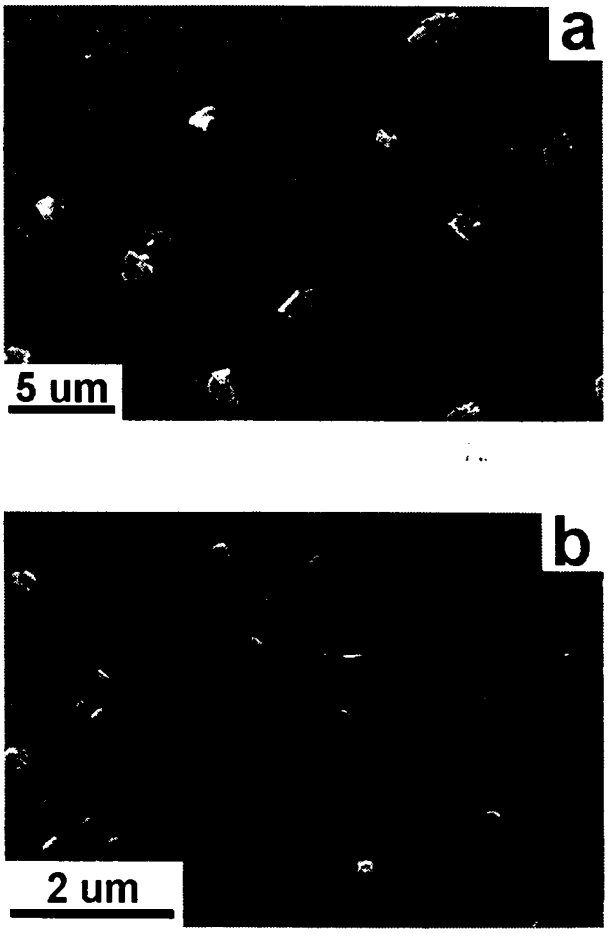

Fig. 3. SEM micrographs of $YBa_2Cu_3O_x$ thin film on NdGaO (110) substrate: (a) by dc sputtering at high pressure: (b) by pulsed laser deposition. Nonoriented (a, b) and oriented elongated (b) outgrowths can be seen on the film surface. The deposition temperature is 810 C.

nonoriented crystal faceted outgrowths (typical size 0.7 0.5 μm for laser-deposited films. I 2 μm for dc-sputtered films). probably crystallites of nonsuperconducting phases [II]. and oriented elongated outgrowths along the [I I I] directions of the substrate with typical size (50 100 nm) × (0.3 I μm), probably a-oriented grains of the YBCO [5,8,9]. The densities of both types of particles on the film surfaces vary strongly from sample to sample depending on deposition conditions. The densities of nonoriented particles range from 10^5 to 10^8 cm^{-2}; the densities of oriented outgrowths vary from 10^6 to 5 10^9 cm^{-2}. Our results are in good agreement with [3], where clusters of 100 nm diameter and density 3 10^7 and 2 IO" cm^{-2} were observed on dc-sputtered and laser-deposited films. respectively. The greater size of the nonoriented particles on the surface of the dc-sputtered films can result from the higher overall nonstoichiometry of these films [2]. On the surface of laser-deposited films large (0.5- 2 μm diameter) spherical particles with density on the film surface about 10^5 cm^{-2} can be seen. These droplets are never observed on dc-sputtered films and seem to be the molten parts of the target, exploded during ablation [2]. Observations of the films at high magnification showed differences in the submicrometer scale morphology of the smooth c-oriented areas of the films (Fig. 4). The dc-sputtered films exhibit parallel steplike features (terraces) of very low height, probably resulting from a layer-b>,-layer growth mechanism [8,10]. The laser-deposited films show a very smooth surface with some caverns. The formation of such smooth surfaces can he explained with high atom mobilities on the growing film surface. leading to increase of the terrace breadth [8]. Holes on the surface of the laser-deposited films with densities about IO' cm^{-2} were observed in [I I] resulting from the 1/3 film unit cell steps on the $SrTiO_3$ substrate surface. The typical size of the caverns we observed is about 0.1 μm, which is close to the size of the antiphase boundary region observed in [I I]. but their density is much lower. from 10^6 to 10^8 cm^{-2}.

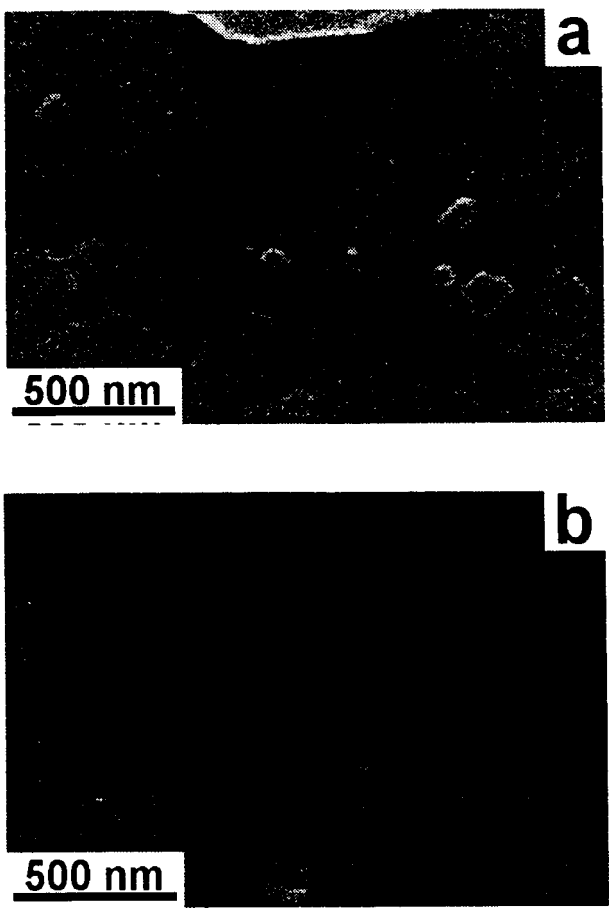

Fig. 4. SEM micrographs **of the c-oriented** areas **of** $YBa_2Cu_3O_x$ thin **films on** $NdGaO_3$ **(I 10) substrates: (a)** high **pressure** dc-sputtered film; (b) laser-deposited film. Both **films were gown at** 810 **C. Terraces on the dc-sputtered film can be** seen.

Films with the best superconducting properties (T_{c0}, AT,) obtained with the two techniques were chosen for comparison of the crystal quality of the film. The $\theta/2\theta$ X-ray diffraction patterns showed the presence of the $YBa_2Cu_3O_x$ phase only for both techniques. The contents of the nonsuperconducting oxides (nonoriented particles on the film surface) are too low to be detected by the X-ray diffractional analysis. The films are mainly oriented with the c-axis normal to the substrate surface (c-oriented); some parts of the films are u-oriented. The c-axis lattice constant shows nearly the same value in both sets of films, 11.67 -11.69 Å for dc-sputtered films and 11.68 I I .7 Å for laser-deposited films. The a-oriented part can be estimated roughly using the ratio of intensities of the (100) and (003) peaks: IR = $I(100)/I(003)$ [9]. This ratio varies for both sets of films from nearly zero to 1, depending on the deposition conditions [4,5]. A clear correlation between the density of the oriented outgrowths and the intensity of the (100) peak can be found to very high values of IR. confirming the nature of elongated outgrowths as the u-oriented grains of Y BCO. One of the reasons for formation of the u-oriented grains in the YBCO film can be the diffusion of Ga into the growing film at high temperatures [9]. The products of reactions between Ga and Y BCO, such as $BaGaO_3$, can act as seeding centers for the u-oriented grains. This supposition is confirmed by the increase of the IR with the increase of the substrate temperature during deposition [5]. When the IR becomes higher than 1, the oriented outgrowths disappear from the film surface. assuming the film itself has become mainly u-oriented. The crystal quality of the films was determined using $\theta/2\theta$- and co-scans of the (005) YBCO peak vicinity (Fig. 5). The $\theta/2\theta$-scans obtained from the dc-sputtered films show clear $K_{\alpha 1}/K_{\alpha 2}$ splitting. After subtraction of the $K_{\alpha 2}$ peak the (005) FWHM of the dc-sputtered films is found to be less than 0.15". The laser-deposited films always show a single peak, its width being about 0.25" (0.2 after $K_{\alpha 2}$ peak subtraction). The thicknesses of the studied films were nearly the same in the range 80 120 nm, resulting in the broadening of the (005) peak of 0.12-0.08°, in accordance with the equation $\Delta(2\theta) = \lambda/(t \cdot \cos 0)$ [12], where $\lambda = 1.54$ Å is the wavelength of $CuK_{\alpha 1}$ radiation, t is the thickness of the film, and θ is the Bragg reflection angle of the studied peak. The measured width of the (005) peak is close to the estimated broadening due to the small thickness of the film, assuming high crystal quality of the film. The difference can be explained as the influence of crystal lattice defects and variations of the c lattice constant due to stresses in the film [I?]. The

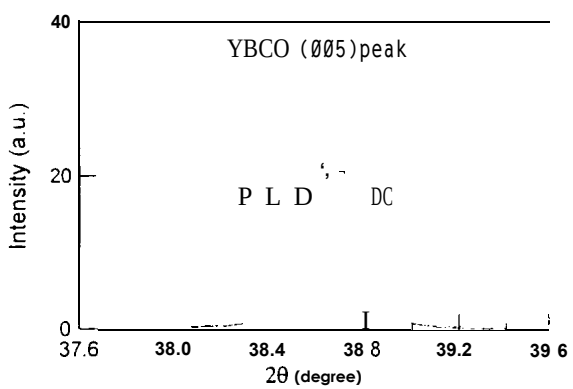

Fig. 5. X-ray $\theta/2\theta$**-diffractogram of the** vicinity of the (005) $YBa_2Cu_3O_x$ **peak. Solid line: dc-sputtered** film; dashed line **I** ser-deposited film.

FWHM of the ω-scan of the YBCO (005) peak also gives smaller values for the dc-sputtered films (0.45') compared to the laser-deposited films (0.55"). The difference of the (005) FWHM found from $\theta/2\theta$- and o-scans probably results from misorientation of the crystal domains.

4. DISCUSSION

During dc sputtering the atoms are transported from the target to the substrate due to diffuse scattering of sputtered atoms in the working atmosphere. The intense scattering provides isotropic spreading of all elements. resulting in stoichiometric flow of atoms on the substrate surface. The deposition rate is low, resulting in films of 100 nm after 2 h of deposition (1 nm 'min). During pulsed laser deposition the atom transport is realized in two different ways: mainly with the "supersonic" expansion due to overheating of the ejected cloud over the target surface by the laser beam. and to a smaller extent by a diffusive process similar to that of the dc-sputtering technique. The energy of atoms of the supersonic part is much higher than of diffusive ones and the travel time from target to substrate is very small [13]. The possibility of moving large amounts of material in a short time determines the high deposition rate of pulsed laser deposition. in our case about 0.6 Å/pulse which for a repetition rate of 10 Hz yields an average deposition rate of 36 nm, min. Comparing the two techniques, two differences can be pointed out: (I) the deposition rate and (2) the energy of atoms coming to the substrate.

During the slow dc-sputtering deposition the initial nonstoichiometric areas resulting from fluctuations in the atom How to the substrate can be dissolved at high temperature of film growth. This would enhance the crystal quality of the dc-sputtered films. showing smaller broadening of the X-ray diffraction peaks and more narrow superconducting transition widths. To check the influence of deposition rate we deposited films using pulsed laser deposition with lower repetition rate (2 Hz), resulting in a deposition rate of about 7 nm/min. The obtained films showed width of the superconducting transition about 1 K and the (005) peak FWHM (co-scan) about 0.5'. The $\theta/2\theta$-scan of the (005) peak showed the $K_{\alpha 1}/K_{\alpha 2}$ splitting, though not as clear as for the dc-sputtered films. The values of ΔT_c and FWHM (005) confirm the intermediate crystal quality of the obtained films between dc-sputtered and laser-deposited films. The main part of the mass transport during laser deposition comes to the substrate surface within a few milliseconds after the laser pulse. The conditions for sticking of these atoms are the same at pulse repetition rates of IO and 2 Hz, so the difference in the crystal quality should be explained by the prolonged relaxation period between the pulses. One can assume that the effect of some recrystallization process at the high temperature during deposition is to decrease the density of lattice defects in the film.

The low deposition rate during dc sputtering has the disadvantage of increasing the influence of resputtering and re-evaporation. At typical deposition temperatures about 800°C the Ba evaporation rate exceeds by some orders of magnitude the evaporation rates of Cu and Y [14], which leads to formation of Ba-deficient films (see Fig. 2). Resputtering due to negative oxygen ion bombardment of the growing film also leads to nonstoichiometric film formation [I]. These processes are almost negligible in the pulsed laser deposition technique.

The high energy of "supersonic" atoms coming to the substrate surface during the pulsed laser deposition helps in the formation of the smooth c-oriented areas of the films (Fig. 4).

Differences in the deposition processes make the use of the two techniques convenient for different purposes. The perfect crystal structure of the dc-sputtered films make them excellent for monolayer applications. such as bicrystal Josephson junctions. microwave passive elements, etc. The use of this technique for multilayer structures is restricted by long deposition periods. which can lead to strong interdiffusion between the layers. The pulsed laser deposition technique suits these purposes much better. because of its higher deposition rate and the smooth surface of the main c-oriented areas of the film.

5. CONCLUSIONS

A comparison of the structural and electrical properties of thin superconducting $YBa_2Cu_3O_x$ films. manufactured using pulsed laser deposition and dc sputtering at high pressure, was carried out. For adequate comparison the deposition parameters (substrate material and temperature, oxygen pressure) of different techniques was chosen as close as possible. Both methods allow production of high crystal quality films with superior electrical parameters. The dc-sputtered films showed higher crystal quality due to the smaller deposition rate favoring formation of films with low density of defects. The long deposition time

during dc sputtering leads to Ba deficiency in the films grown at high temperatures. The very smooth surface of the c-oriented parts of laser-deposited films probably results from the high atom mobility on the growing film surface.

ACKNOWLEDGMENTS

This work was supported in part by the Russian Foundation for Basic Research, "Superconductivity" division of the Russian State Program "Modern Problems of Condensed Matter Physics," the INTAS Program of EU, the INCO-Copernicus program of EU, and by the Danish Research Academy. The authors would like to thank Dr. J. Bindslev-Hansen and Dr. Z. G. Ivanov for useful discussions.

REFERENCES

1. U. Poppe, J. Schubert, R. R. Arons, W Evers, C. H. Freiburg, W Reichert, K . Schmidt, W Sybertz, and K Urban, *Solid State Commun.* **66**, 661 (1988).
2. H.-U. Habcrmeier. G. Beddies, B. Leibold, G Lu, and G Wagner, *Physica C* **180**, 17 (1991)
3. J Burger. P. Bauer. M. Veith, and G . Saemann-Ischenko, preprint (I99 I).
4. P. B. Mozhaev. A. Kühle, G. A. Ovsyannikov, J. L. Skov, and P. Bodin. *Supercond: Phys., Chem., Tech.* 8. 288 (1995). (in Russian).
5. P. B. Mozhaev. G. A. Ovsyannikov. S. N. Polyakov. E. K. Kov'ev. and N. P. Kukhta, in: Proceedings of EUCAS 1995. Edinburgh. Scotland, 3–6 July, 1995, D. Dew-Hughes, ed. (IOP Publishing Ltd., Institute of Physics Conference Series. No. 148, 1995). Vol. 2. pp. 907-912.
6. A. Kühle, J. L. Skov. S. Hjorth, I. Rasmussen. and J. Bindslev-Hansen. *Appl. Phys. Lett.* 64. 3178 (1994).
7. M. S. Raven. E. E. Inametti, Y. M. Wan. and B. G. Murray. *Supercond. Sci. Technol.* 7. No. 7. 462 (1994).
8. D. Bhatt, S. N. Basu, A. C. Westerheim. and A. C. Anderson. *Physica C* 222. 283 (1 994).
9. Ju A. Boikov, Z. G. Ivanov, E. Olsson. V. A. Danilov. T. Claeson. M. Shcheglov, and D. Erts, *Solid State Phys.* 37. 880 (1995).
10. M. Ece. E. G. Gonzalez. H.-U. Habermeier. and B. Oral. *J. Appl. Phys.* 77, 1646 (1995).
11. J. C. Martinez, B. Dam, B. Stauble-Pumpin, G. Doornbos, R. Surdeanu, U. Poppe, and R. Griessen. preprint (to be published in *J. Low Temp. Phys.*, 1996).
12. J. P. Gong. M Kawasaki, K. Fujito, R. Tsuchiya, M. Yoshimoto, and H. Koinuma, *Phys. Rev. B* 50, No. 5, 3280 (1994)
13. Y. Nakata, W. K. A. Kumuduni, T. Okada, and M. Maeda, *Appl Phys. Lett.* 64, 2599 (1994).
14. *Methods of Experimental Physics*, L. Marton, ed., Vol. I (Academic Press. New York and London. 1959)