Role of Oxygen Pressure During Deposition on the Microwave Properties of YBCO Films

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Abstract—**We have studied the effect of oxygen pressure (PO_2) during pulsed laser deposition on the properties of YBCO films, with particular attention to the low power microwave surface resistance R_s. Above a threshold oxygen pressure the properties of the films are nearly independent of PO_2 during deposition and are typical of high quality YBCO films. The films made below this threshold pressure have increased disorder which produces a reduced T_c and an expanded c-axis lattice parameter. However, these films also have significantly reduced low temperature R_s, which is likely a direct result of the increased scattering in these films. Preliminary Raman measurements show no increase in the Y-Ba cation disorder in these low PO_2 films, so that a different disorder mechanism must be present.**

I. Introduction

High temperature superconductors such as $YBa_2Cu_3O_7$ (YBCO) are currently being used in a variety of passive microwave applications [1], [2]. Although many factors will enter into the ultimate success of these applications, the low power microwave surface resistance, R_s of the films is one critical enabling property. Much effort has gone into improving the microwave properties of YBCO films, although the exact materials properties responsible for microwave losses are still not well understood. Studies have suggested correlations between the outgrowths on the film's surface and the R_s [3], and improvements in microwave properties have been achieved with the inclusion of certain impurities [4]. However, more work is needed to understand the processing-properties relationships in these materials.

In this study we report on the effect of oxygen pressure, PO_2, during pulsed laser deposition on the properties of YBCO films, with a particular focus on the low power R_s of the films. Films were made with oxygen pressures that spanned over an order of magnitude, and except for the films made at the lowest PO_2 we observed very little change in any of the film properties. At the lowest oxygen pressures used in this study we observed a significant suppression of the critical temperature, T_c, of the films with a corresponding increase in the c-axis lattice parameter, consistent with the introduction of some form of disorder into the films. Surprisingly, despite this evidence for degraded material quality, the low temperature R_s of these films was more than a factor of 2 lower than the rest of the films in the study. These results suggest the need to understand the type of disorder introduced by low oxygen pressure and its role in determining the microwave properties of this material.

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II. Film Deposition Conditions

The films for this study were deposited by pulsed laser deposition using an excimer laser operating at 248 nm (KrF radiation) and a 10 Hz repetition rate. The laser spot passed through a primary 11 mm x 6 mm aperture, and then was focused to a spot approximately 4 mm x 2 mm at the YBCO target, striking the target at a 45° angle. The calculated energy density at the target, based on the energy measured just before the focusing lens outside the deposition system, was 1.3 J/cm^2. The laser spot was scanned over the stationary target by rastering the focusing lens, inscribing a square 12 mm on a side on the target surface. The same commercially-available high density YBCO target was used for all the films in this study except for the films made at 10 Pa (75 mTorr), which used a different target made from the same batch of YBCO powder. The targets were sanded after each deposition to remove the ablation damage.

The substrates for this study were 15 mm x 15 mm squares cut from commercially-available 0.5 mm thick $LaAlO_3$ wafers. The substrates were mounted on a resistively-heated block using silver paint, air-dried at 100 °C, and then positioned in the deposition system 65 mm away from the target. The deposition system was pumped to a base pressure near 1 x 10^{-3} Pa (1x10^{-5} Torr), and the substrate block heated to a temperature of 770 °C ± 1 °C, as measured by a thermocouple mounted inside the block 2 mm behind the

substrate. Based on temperature measurements using a thermocouple attached to a substrate on the heater block, we estimate that the substrate temperature was approximately 40 °C cooler than the measured block temperature, as has been reported by others [5].

After reaching temperature, oxygen was flowed into the system at a rate of 50 sccm, and the pressure was controlled by a throttle valve to the desired value for the deposition. Films for this study were made with oxygen pressures from 6.7 Pa (50 mTorr) to 106 Pa (800 mTorr). Over this range of pressures the laser ablation plume changes from very diffuse and much larger than the substrate size at the lowest pressures to very tightly "focused" and barely reaching the substrate at the highest pressures. The target was ablated for 1 minute before opening the shutter and beginning the deposition. Deposition rates were determined by profilometry measurements on test samples run under identical conditions. It was discovered that the deposition rate above 27 Pa (200 mTorr) was a strong function of the oxygen pressure during deposition, as shown in Fig. 1. This required a different deposition time for each oxygen pressure to deposit films with approximately the same thickness, 300 nm. Thus for this study it is not possible to completely separate the role of oxygen pressure and chemistry from the role of deposition rate, although the most dramatic changes in film properties occur at the lowest oxygen pressures, where the deposition rate is essentially constant.

After deposition, the chamber was filled with oxygen at a rate of 5.3 kPa/min (40 Torr/min). At the same time, the sample temperature was decreased at 20 °C/min to a temperature of 470 °C. The oxygen flow was stopped when the chamber pressure reached 80 kPa (600 Torr), which occurred at approximately the same time as the heater block temperature reaching 470 °C. The sample was held at 470 °C for 5 min, and then the heater switched off and the sample cooled to room temperature. Thus independent of the oxygen pressure during deposition, all the samples received the same post-deposition oxygen anneal. We have both increased and decreased the cooldown rate by over an order of magnitude, and have not observed any changes in the films properties studied here, suggesting that over this range the films achieve an equilibrium oxygen content that is not easily modified. We have also done *ex-situ* oxygen anneals in an attempt to increase the oxygen content of the films, especially the lowest PO_2 films, again with no measurable change in film properties.

III. Materials Characterization

All the films in this study were examined in a scanning electron microscope (SEM) to compare the surface morphology and the size and density of surface outgrowths, or "boulders". The films deposited with oxygen pressures above 6.7 Pa (50 mTorr) were all very similar in appearance. These films show an island growth mechanism for the YBCO [6] that has previously been identified as consistent with a Stranski-Krastanov growth mode [7]. The films all had similar island density as judged from SEM, as expected for films grown at the same temperature and to the same thickness. The exception to this was the films grown at 6.7 Pa (50 mTorr). These low PO_2 films had a significantly higher island density, and the boundary between islands appeared more distinct than in the higher PO_2 films.

The films also had submicron outgrowths on the surface. Most of the outgrowths were rectangular, with a length-width ratio of about three to one, and often grew aligned to the major substrate axes. The variation in outgrowth density between different areas of the same film was greater than the difference between films, making a careful analysis of outgrowth density versus oxygen pressure impossible. For

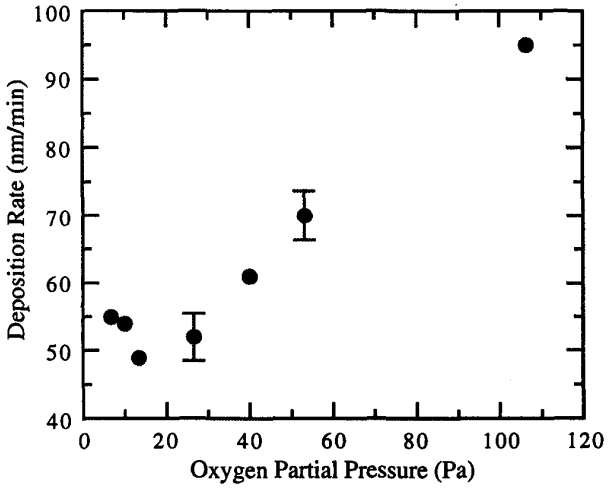

Fig. 1. The deposition rate as a function of oxygen partial pressure. Error bars were determined at two different pressures (27 Pa and 53 Pa) using rates from at least 6 different depositions.

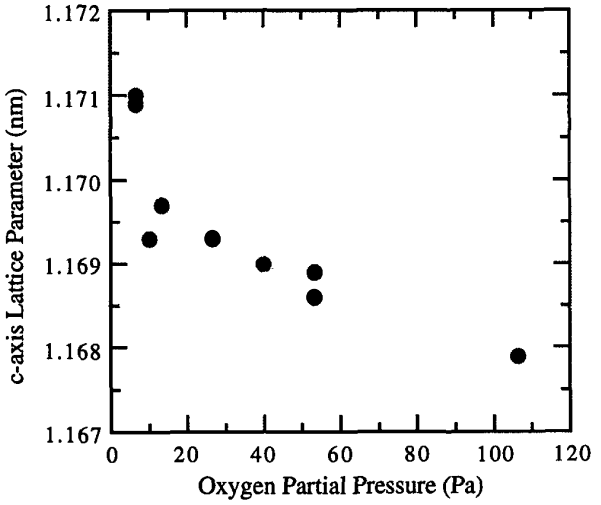

Fig. 2. c-axis lattice parameter as a function of oxygen partial pressure.

this study the outgrowth density was typically 0.3 ± 0.1 outgrowths per μm^2. In more recent work on films made from different YBCO targets, the outgrowth density was significantly lower, and there was a clear trend to lower outgrowth density with reduced PO_2 during deposition. This raises the possibility that the target used for this study was slightly off stoichiometry, resulting in an increase in second phase precipitates at the surface.

The films were analyzed in a high-resolution x-ray diffractometer to determine orientation and lattice parameter [8], [9]. All the films appear to be epitaxial, with the c-axis perpendicular to the substrate and no evidence for a-axis or other misoriented grains. The crystalline quality of the films is excellent, as judged by very narrow rocking curve widths (full width at half maximum) for the (006) line of 0.13° ± 0.03°, although some films did exhibit multiple (00ℓ)-peaks, indicative of inhomogeneities. There was no systematic dependence of the rocking curve width on PO_2. The c-axis lattice parameter was found to be a function of the PO_2 during deposition, as shown in Fig. 2. There is a monotonic increase in the c-axis lattice parameter with decreasing PO_2 during deposition, with a significant jump in the lattice parameter for the film made at the lowest pressure. The increase in lattice parameter at lower PO_2 could be due to a variety of factors, such as sub-stoichiometric oxygen content or lattice disorder.

One possible origin for the expanded c-axis lattice parameter could be cation disorder, specifically Y-Ba exchange, which has been associated with low oxygen pressure during deposition in electron-beam evaporated [10] and sputtered [11] YBCO films. To explore this, films made at 6.7 Pa (50 mTorr) and 53 Pa (400 mTorr) were examined using a Raman microprobe. The technique [12], [13] can distinguish Y-Ba exchange by the intensity of the 585 cm^{-1} peak normalized to the 340 cm^{-1} peak. However, this measurement suggested a relatively low level of Y-Ba disorder, 2-3%, in the two films measured, and did not reveal significant differences between the films. This provides strong evidence that in this case the structural disorder has another origin. Work is continuing with x-ray diffraction and Raman spectroscopy to attempt to identify the type (or types) of disorder present in these films.

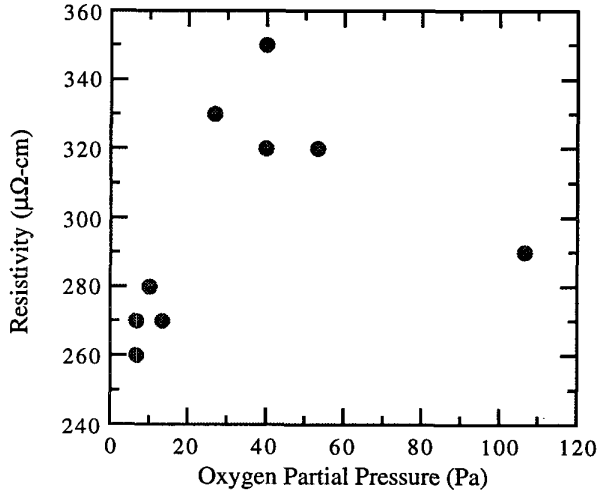

Fig. 3. Room temperature dc resistivity as a function of oxygen partial pressure.

IV. Electrical Characterization

The room temperature dc resistivity of the films was measured using the van der Pauw technique [14], and is plotted in Fig. 3 as a function of PO_2 during deposition. The low resistivity of the low PO_2 sample is somewhat surprising considering the evidence from x-ray for increased disorder in these films. The temperature dependence of the resistance was also measured on a set of control samples made under identical conditions. For all samples, the resistance decreased linearly from room temperature to just above T_c, with a resistance ratio from 300 K to 100 K of 2.9 ± 0.1, independent of PO_2 during deposition.

The superconducting transition temperature T_c and critical current J_c were both measured on the films using a single coil inductive technique operating at a fundamental frequency of

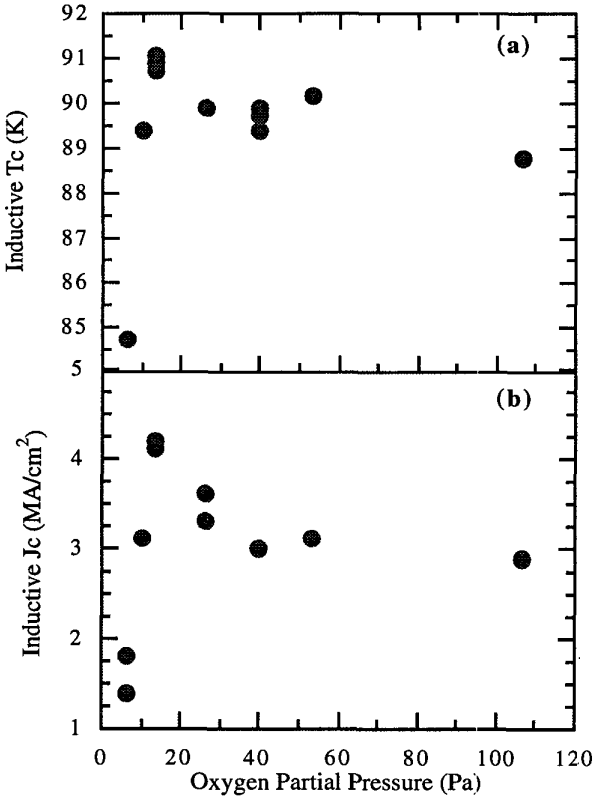

Fig. 4. Inductively measured (a) T_c and (b) J_c in zero field and at 76 K as a function of oxygen partial pressure. For similar samples the inductive J_c was typically 25% larger than the corresponding transport J_c measured on the same sample.

1 kHz [15]. The T_c was taken as the onset of change in the inductive reactance, and usually corresponds within 1 K to the zero-resistance point of a transport measurement. The critical current was measured in zero applied magnetic field with the sample immersed in liquid nitrogen (76 K at this altitude), and J_c was determined using the onset of third harmonics with increasing drive current in the coil. As shown in Fig. 4, except for the films made at the lowest PO_2, the T_c and J_c were both approximately independent of oxygen pressure during deposition. The lowest PO_2 films had a significantly suppressed T_c. The J_c is also suppressed, although since the measurement was only done at 76 K it is impossible to determine if the suppression is intrinsic to the film or due to the higher relative measurement temperature (T/T_c) for this sample. These results suggest that there is a minimum oxygen pressure during growth in our PLD system that is required to form high quality YBCO, and that oxygen in excess of this amount does not dramatically affect the low frequency properties of the films.

V. Microwave Characterization

We measured the surface resistance R_s as a function of temperature of all films using a sapphire dielectric resonator operating at 17.5 GHz [16]. The cavity is mounted on a closed-cycle cryocooler in vacuum, with temperature measured at several points using standard Si diode thermometers. The temperature of the films is estimated to be known within ± 1 K. The position of the loops used to couple microwave power into the cavity are adjusted after the cavity is at low temperature (and thus at high Q) to minimize loading of the cavity. The measurement uses a pair of films made under identical deposition conditions, and extracts R_s from the temperature-dependent quality factor of the cavity, correcting for such factors as losses in the copper walls of the cavity [16]. Each film is assumed to have the same surface resistance, so that the values of R_s reported here represent the average for the two films.

Except for the films made at the lowest PO_2, the R_s of the films was relatively insensitive to the oxygen pressure during deposition, as seen with the low frequency measurements (T_c and J_c),. Figure 5 shows the low temperature R_s as a function of PO_2. The average value for R_s for the higher PO_2 films was 0.36 mΩ ± 0.05 mΩ at 30 K and 17.5 GHz (or 0.12 mΩ ± 0.02 mΩ when scaled by f^2 to 10 GHz). These are typical values for R_s for YBCO thin films. The surprising result is that the lowest PO_2 films, which had significantly surppressed T_c, had *lower* microwave surface resistance by more than a factor of 2, with a scaled R_s at 10 GHz and 30 K of 45 μΩ. Figure 6 compares R_s as a function of temperature for the 6.7 Pa (50 mTorr) and 53 Pa (400 mTorr) films. (The 53 Pa result was representive of all the higher PO_2 films.) The curves have significantly different shapes, with the higher PO_2 films showing a plateau region near 50 K and only a gradual decrease in R_s at low temperatures, while the low PO_2 film has no plateau region and continues to decrease rapidly down to the lowest temperatures.

VI. Discussion

The results presented here clearly indicate that for our pulsed laser deposition system there is a minimum oxygen pressure during deposition which is required to form YBCO films with transition temperatures above 90 K. For our system this pressure was typically around 13 Pa (100 mTorr) independent of target and relatively insensitive to substrate temperature. For pressures above this value, up to the highest pressures examined, the properties of the films were nearly independent of the deposition pressure. In particular, the morphology, T_c, J_c, and R_s of the films were all very similar

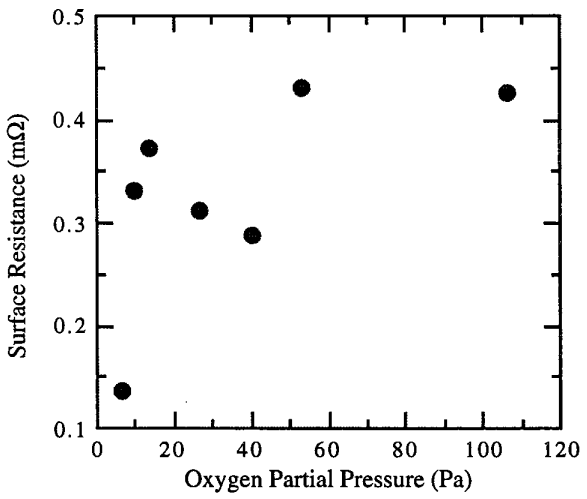

Fig. 5. Low power microwave surface resistance measured at 17.5 GHz and 30 K as a function of oxygen partial pressure.

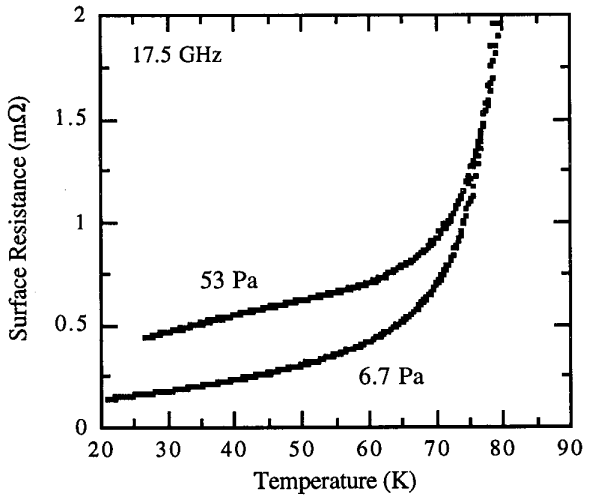

Fig. 6. Comparison of the temperature dependence of R_s for films made at 53 Pa (400 mTorr) and 6.7 Pa (50 mTorr).

and typical of well-ordered YBCO films. The shape of temperature dependence of R_s for these films all show the plateau region around 50 K.

For the films made at the lowest oxygen pressure used in this study, there was a significant change in the film quality. The decrease in T_c and the corresponding jump in the c-axis lattice parameter are consistent with the introduction of disorder into these films. This disorder is a likely cause for the improved low temperature R_s of the films, since an increase in the quasiparticle scattering rate can result in a decrease in the R_s [4]. The temperature dependence of R_s for these films is consistent with this interpretation, since the increased scattering rate would shift or eliminate the plateau region typical of better-ordered YBCO films. These films also had lower room temperature dc resistivity, suggesting that the disorder in the films has also resulted in a higher doping level. Disorder driven by low oxygen pressure has been observed before in films fabricated by post-deposition annealing [17] and *in-situ* electron-beam evaporation [10] and sputtering [11]. In the sputtering study it was shown that the disorder was Y-Ba cation exchange coupled with apical oxygen vacancies. A similar conclusion was reached in the electron-beam deposition study. These studies also showed that Y-Ba disorder can increase the doping density of the films. However, for the PLD films made here, the Raman data showed a relatively low level of Y-Ba cation disorder and no significant difference between the low and high PO_2 films. Therefore, it is likely that the specific disorder present in these films is different. Work is continuing to try to identify the specific disorder introduced into these films by the low oxygen pressure during deposition. Preliminary results with *ex-situ* oxygen annealing suggests that the disorder is not a simple oxygen stoichiometry problem.

VII. Summary

We have studied the effect of oxygen pressure during pulsed laser deposition on the properties of YBCO films, with particular attention to the low power R_s. We have found that above a threshold oxygen pressure, the properties of the films are independent of PO_2 during deposition and are typical of high quality YBCO films. For films made with PO_2 below this threshold pressure, disorder is introduced into the films, which produces a reduced T_c and an expanded c-axis lattice parameter. However, these films have significantly reduced low temperature R_s, which is likely a direct result of the increased scattering in these films. The specific disorder present in the films is being investigated, although preliminary Raman measurements suggest that Y-Ba cation disorder is not present. As a clearer picture of the interaction between disorder and R_s is acquired, it may be possible to tailor the disorder in the films so as to reduce R_s without suppressing T_c.

Acknowledgment

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References

[1] Z. Y. Shen, *High-Temperature Superconducting Microwave Circuits*, Artech House, Boston, 1994.

[2] J. Gallop, "Microwave application of high-temperature superconductors," Supercond. Sci. Technol., vol. 10, pp. A120-A141, 1997.

[3] Y.J. Tian, L. Li, L.P. Guo, J.Z. Liu, Z.X. Zhao, S.F. Xu, H.B. Lu, Y.L. Zhou, Z.H. Chen, D.F. Cui and G.Z. Yang, "Correlation between distribution of outgrowths and microwave surface resistance for $YBa_2Cu_3O_7$," Appl. Phys. Lett., vol. 65, pp. 2356-2358, 1994.

[4] D.A. Bonn, S. Kamal, K. Zhang, R. Liang, D.J. Baar, E. Klein, and W.N. Hardy, "Comparison of the influence of Ni and Zn impurities on the electromagnetic properties of $YBa_2Cu_3O_{6.95}$," Phys. Rev. B, vol. 50, pp. 4015-4063, 1994.

[5] A. C. Westerheim, A. C. Anderson, M. J. Cima, "Substrate temperature measurements using ultrasonically bonded Platinel II thermocouples," Rev. Sci. Instrum., vol. 63, 2282, 1992.

[6] F. J. B. Stork, J. A. Beall, A. Roshko, D. C. DeGroot, D. A. Rudman and R. H. Ono, "Surface resistance and morphology of YBCO films as a function of thickness," IEEE Trans. Appl. Supercond., vol. 7, pp. 1921-1924 1997.

[7] A. Roshko, F. J. B. Stork, D. A. Rudman, D. J. Aldrich, and P. A. Morris Hotsenpiller, "Comparison of heteroepitaxial $YBa_2Cu_3O_{7-x}$ and TiO_2 thin film growth," J. Crystal Growth, vol. 174, pp. 398-408, 1997.

[8] S. B. Qadri, E. F. Skelton, M. S. Osofsky, V. M. Browning, J. Z. Hu, P. R. Broussard, M. E. Reeves, and W. Prusseit, "Microscopic X-Ray characterization of inhomogeneities in YBCO crystals with sharp superconducting transitions," Physica-C, vol. 282-287, pp. 93-96, 1997.

[9] S. B. Qadri, E. F. Skelton, P. Broussard, V. C. Cestone, M. S. Osofsky, M. E. Reeves, and W. Prusseit, "Structural inhomogeneities in thin films of $YBa_2Cu_3O_{7-d}$ and their effects on their superconducting properties," Thin Solid Films, vol. 308-309, pp. 420-424, 1997.

[10] V. Matijasevic, P. Rosenthal, K. Shinohara, A.R. Marshall, R.H. Hammond, and M.R. Beasley, "Reactive coevaporation of YBaCuO superconducting films," J. Mater. Res., vol. 6, pp. 682-698, 1991.

[11] J.L. MacManus-Driscoll, J.A. Alonso, P.C. Wang, T.H. Geballe, and J.C. Bravman, "Studies of structural disorder in $ReBa_2Cu_3O_{7-x}$ thin films (Re-rare earth) as a function of rare-earth ionic radius and film deposition conditions," Physica C, vol. 232, pp. 288-308, 1994.

[12] G. Gibson, J.L. MacManus-Driscoll and L.F. Cohen, "Raman microscopy as a local probe of structural defects and oxygen content in HTS thin films," IEEE Trans. Appl. Supercon., vol. 7, pp. 2130, 1997.

[13] G. Gibson, L.F. Cohen, R.G. Humphreys and J.L. MacManus-Driscoll, Phys. C, in press.

[14] L.J. van der Pauw, "A method of measuring specific resistivity and hall effect of discs of arbitrary shape", Philips Research Reports vol. 13, pp. 1-9, 1958.

[15] J. H. Claassen, M. E. Reeves, and R. J. Soulen, "A contactless method for measurement of the critical current density and critical temperature of superconducting films," Rev. Sci. Instrum., vol. 62, pp. 996-1004, 1991.

[16] J. Krupka, M. Klinger, M. Kuhn, A. Baranyak, M. Stiller, J. Hinken and J. Modelski, "Surface resistance measurements of HTS films by means of sapphire dielectric resonators", IEEE Trans. Appl. Supercond., vol. 3, pp 3043-3048, 1993.

[17] R. Feenstra, T.B. Lindemer, J.D. Budai, and M.D. Galloway, "Effect of oxygen pressure on the synthesis of $YBa_2Cu_3O_{7-x}$ thin films by post-deposition annealing", J. Appl. Phys., vol. 69, pp. 6569-6585, 1991.