Growth and applications of superconducting and nonsuperconducting oxide epitaxial films

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Abstract. Growth and characterization of high-temperature-superconducting $YBa_2Cu_3O_7$ and several metallic-oxide thin films by pulsed laser deposition is described here. An overview of substrates employed for epitaxial growth of perovskite-related oxides is presented. Ag-doped $YBa_2Cu_3O_7$ films grown on bare sapphire are shown to give $T_c = 90$ K, critical current $> 10^6$ A/cm² at 77 K and surface resistance $= 450\,\mu\Omega$. Application of epitaxial metallic $LaNiO_3$ thin films as an electrode for ferroelectric oxide and as a normal metal layer barrier in the superconductor–normal metal–superconductor (SNS) Josephson junction is presented. Observation of giant magnetoresistance (GMR) in the metallic $La_{0.6}Pb_{0.4}MnO_3$ thin films up to 50% is highlighted.

Keywords. Epitaxial thin films; metallic oxides; high-T_c films; SNS junction; $LaNiO_3$; $La_{1-x}Pb_xMnO_3$: ferroelectric oxides; ferromagnetic oxides.

1. Introduction

Since the discovery of superconductivity at high temperature in $La_{2-x}Ba_xCuO_4$ (Bednorz and Muller 1986) and subsequently in $YBa_2Cu_3O_{7-x}$ ($T_c = 90$ K) (Wu et al 1987), extensive efforts have been made to fabricate thin films of these materials because of the high possibility of their use in electronic devices. Even though a large number of Bi- and Tl-based oxides are known to give superconducting transition temperature $T_c > 90$ K, the majority of efforts in the thin-film area still continue to be on the growth of $YBa_2Cu_3O_{7-x}$ (YBCO) films because of the relative ease with which YBCO films can be fabricated in situ with correct composition. Further, thin films give high critical current density (J_c) routinely at 77 K. Chaudhari et al (1987) were the first to show that J_c as high as 10^6 A/cm² can be achieved in epitaxially grown YBCO films on $\langle 100 \rangle$ $SrTiO_3$ (STO) substrates. Pulsed laser deposition (PLD) is the most successful technique among the commonly used methods to fabricate good quality high-T_c thin films. PLD has also been extended to grow a variety of epitaxial nonsuperconducting oxide thin films for superconductor–insulator–superconductor (SIS) and superconductor–normal metal (metallic oxide)–superconductor (SNS) trilayer heterojunctions. These types of multilayer structures are required to realize Josephson junctions for superconducting quantum interference device (SQUID) fabrication.

The fabrication of trilayer junctions using YBCO films as superconductor and $PrBa_2Cu_3O_7$ (PBCO) as insulating barrier was reported for the first time by Rogers et al (1989). The trilayer junction fabricated by them did show Josephson-junction (JJ) behaviour, but the current (I)–voltage (V) characteristic of the junction was unlike the I–V characteristic of SIS junction fabricated out of the classical superconductors and insulating barriers such as Nb–Al_2O_3–Nb. Subsequent attempts to make SIS

junctions using other insulating layer like $NdGaO_3$, or $NdAlO_3$ also showed only the SNS type of $I-V$ characteristics. Therefore attempts were made to fabricate SNS Josephson junctions with perovskite-related metallic oxides as the N-metal barrier layer (Char *et al* 1993). Thus fabrication of epitaxial thin films of perovskite-related metallic oxides itself became an important aspect of research in conjunction with high-T_c oxides. Further, perovskite-related metallic oxides could also be used as electrodes for ferroelectric oxide capacitors. Another advantage of epitaxial oxide thin films was that they are essentially single-crystal-like materials and unusual properties such as giant magnetoresistance (GMR) in lanthanum manganates could be realized (Searle and Wang 1970).

Realizing the importance of this area of research, we have set up a PLD system (Dijkkamp *et al* 1987; Inam *et al* 1988; Srinivasu *et al* 1991) in our laboratory to fabricate high-temperature-superconducting and related oxide thin films. In this article, we will present an overview of the substrates employed for epitaxial growth of perovskite-related oxide thin films and some of the recent results that we have obtained on (a) Ag-doped $YBa_2Cu_3O_{7-x}$ (Ag-YBCO) thin films, (b) fabrication of epitaxial metallic $LaNiO_3$ thin films, (c) fabrication and properties of YBCO/$LaNiO_3$/YBCO trilayer junctions, (d) $LaNiO_3$ thin-film electrodes for $Bi_2VO_{5.5}$ ferroelectric oxide, and (e) giant magnetoresistance in epitaxial $La_{0.6}Pb_{0.4}MnO_3$ thin films.

2.   Experimental

The PLD experiments for the growth of $YBa_2Cu_3O_7$, $LaNiO_3$ and other related oxide films were carried out using KrF ($\lambda = 248$ nm) excimer laser with a 300 mm focal length quartz lens for focusing the laser beam. The excimer pulse had maximum energy of 1000 mJ with a pulse width of 25 ns and 1–10 Hz of variable repetition rate. The laser fluence was varied from 1·5 to 2·5 J/cm^2 by varying the laser pulse energy and quartz attenuators. A schematic diagram of the experimental set-up is given in figure 1. For thin-film deposition, the substrates were held on the surface of the heater face plate by Ag paste and the temperature on the surface of the heater was measured using a chromel–alumel thermocouple fixed onto it by Ag paste. The temperature difference between the heater face plate and the substrate top surface was about 30–40°C which was calibrated by fixing another thermocouple on the top surface of substrate. The oxygen pressure during film deposition was maintained at about 200–450 m torr depending on the material. The deposition temperature was optimized separately for each material, and it was about 780°C for YBCO. The growth and structural properties of high-temperature-superconducting oxide and other oxide films have been reported in detail in our earlier publications (Srinivasu *et al* 1991; Hegde *et al* 1993, 1994; Satyalakshmi *et al* 1993; Prasad *et al* 1993).

The YBCO/LNO/YBCO trilayer structure was fabricated by depositing YBCO film first on the complete surface of STO and subsequently depositing LNO on the previously deposited YBCO film by masking one side of the film by silver foil. This was followed by the deposition of YBCO on the central region of LNO by masking the remaining portion with silver foil. The structural characterization of all the individual films as well as of the trilayer was carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The conductivity measurements were carried out by a four-probe method
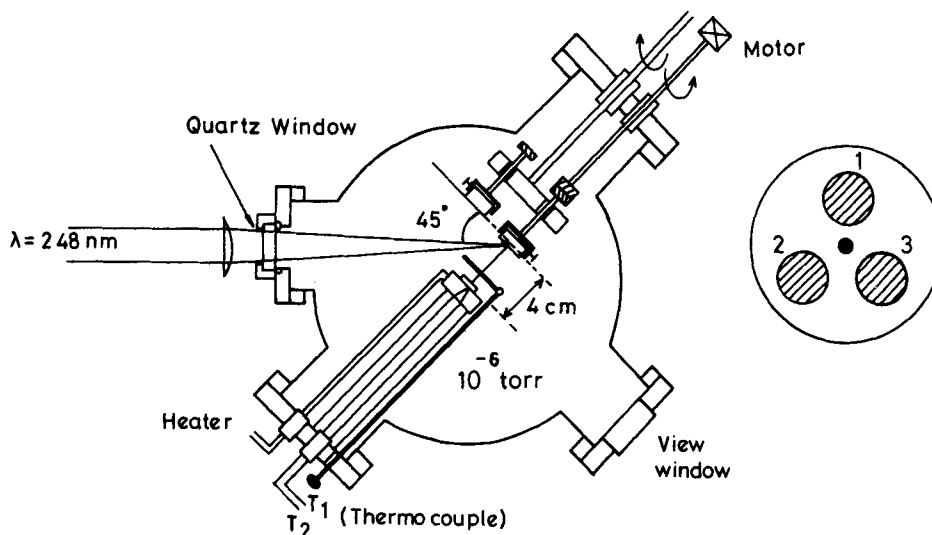
Figure 1. Triple target pulsed laser deposition system.

and the $I-V$ characteristics of the trilayer were determined using laser-patterned mirobridges.

3. Substrates for epitaxial growth of $YBa_2Cu_3O_7$ (YBCO) and related oxide films

As mentioned earlier, the breakthrough to realize high T_c, and high J_c came only when the YBCO epitaxial thin films were grown on $SrTiO_3$ (100) single-crystal substrate by Chaudhari *et al* (1987). Ability to grow *in situ* YBCO films in the as-deposited condition giving T_c 90 K by introducing oxygen during the deposition was a significant step towards the use of YBCO films for high-T_c applications (Inam *et al* 1988). A large number of single-crystal substrates have been employed to fabricate YBCO and other oxide films. YBCO has the lattice parameters $a = 3.83$ Å, $b = 3.89$ Å and $c = 11.65$ Å. General criteria for the epitaxial growth of these high-T_c oxide films are summarized below:

 (i) The substrate should have structural compatibility, i.e. possess cubic and perovskite-related structure.
 (ii) The lattice parameter of the substrate should be within 5% of the lattice parameters of high-T_c oxides.
 (iii) These substrates should have thermal expansion coefficients close to that of YBCO itself. Otherwise, due to thermal shock during cooling, the grown films are known to develop microcracks leading to discontinuity in the films.
 (iv) The substrate should be chemically and structurally stable at the processing temperature of YBCO, which is generally around 750–800°C.
 (v) The substrate material should be chemically compatible in terms of the nature of chemical bond.

In table 1, we summarize the structure, lattice parameters, thermal expansion coefficient and dielectric constant of a variety of substrate materials. The single crystals

Table 1. Structure, lattice parameters and physical properties of substrates for epitaxial growth of $YBa_2Cu_3O_7$ thin films.

Substrate material	Crystal structure	Lattice parameters (Å)	Thermal expansion coefficient $(10^{-6}/K)$	Dielectric constant
$SrTiO_3$	Cubic (perovskite)	$a = 3.905$	9.4–10.8	7300
$LaGaO_3$	Orthorhombic (distorted perovskite) $(GdFeO_3)$	$a = 5.482$ $b = 5.526$ $c = 7.78$ $(^*a_0 = 3.892)$	10.6	25
$LaAlO_3$	Rhombohedral (distorted perovskite)	$a = 5.364$ $c = 13.11$ $(a_0 = 3.788)$	10	16
YSZ	Cubic (fluorite)	$a = 5.16$ $(a_0 = 3.65)$	9.2–10.3	27
MgO	Cubic (NaCl)	$a = 4.212$	13.8	14
Al_2O_3 (sapphire)	Trigonal	$a = 5.14$ $(a_0 = 3.64)$	5	10
Si	Diamond	$a = 5.43$ $(a_0 = 3.83)$	6.7	12
$KTaO_3$	Cubic (perovskite)	$a = 3.989$	—	—
$BaTiO_3$	Tetragonal (perovskite)	$a = 3.99$ $c = 4.03$	19	> 2000
$LaSrGaO_4$	Tetragonal (K_2NiF_4)	$a = 3.843$ $c = 12.861$	—	—
$Y_3Fe_5O_{12}$	Garnet	$a = 12.376$ $(a_0 = 4.125)$	—	—
$YbFeO_3$	Orthorhombic $(GdFeO_3)$	$a = 5.36$ $b = 5.50$ $c = 7.77$ $(a_0 = 3.86)$	—	4–5
$BaFe_{12}O_{19}$	Barium orthoferrite	$a = 5.88$ $c = 23.22$ $(a_0 = 4.158)$	—	—
$MgAl_2O_4$	Cubic Spinel	$a = 8.059$ $(a_0 = 4.029)$	76	—
$YBa_2Cu_3O_7$	Triple Perovskite	$a = 3.83$ $b = 3.89$ $c = 11.65$	12	—

$^*a_0$, Pseudocubic parameter

of these materials have been employed to grow epitaxial thin films of YBCO. Single crystals of these materials cut in the $\langle 100 \rangle$ direction generally support c-axis growth. Thus $\langle 100 \rangle$ surface of the substrate supports epitaxial growth, the a–b plane of YBCO aligned parallel to $\langle 100 \rangle$ of the substrate. Some of these substrates are also used for the growth of perovskite-related metallic and ferroelectric oxide thin films.

Among these materials, $SrTiO_3$ (STO) is a widely used substrate for the growth of YBCO and it is known to give the highest critical current density (10^6 A/cm^2 at

77 K) for epitaxial YBCO films. This is due to the very small lattice mismatch between YBCO and STO. STO is a good lattice-matched substrate, but due to the large dielectric constant, the films grown on this substrate are not good for microwave applications. $LaAlO_3$ (LAO) single crystal is a commonly used substrate because it is relatively less expensive and high-J_c, 90 K YBCO films on LAO are routinely grown. $LaGaO_3$ is the best known substrate for YBCO thin-film growth but it is not readily available and it is expensive. Both MgO and YSZ are relatively less expensive but both have about 5% lattice mismatch with reference to YBCO because of which growing high-quality YBCO film is difficult compared to the films on $SrTiO_3$. Al_2O_3 (sapphire) is the best-suited substrate for microwave applications. But due to the large lattice mismatch and Al diffusion into YBCO at high temperature making YBCO nonsuperconducting, it is difficult to grow high-J_c, high-T_c YBCO films on sapphire. However, high-quality YBCO thin films have been successfully grown on sapphire by employing a yttria-stabilized zirconia (YSZ) barrier layer on Al_2O_3. This minimizes the interaction between YBCO and Al_2O_3. We have grown Ag-doped YBCO on bare sapphire with excellent T_c (90 K) and J_c (10^6 A/cm^2). The results are presented here in the next section.

Silicon is a unique material. There is a famous saying at IBM Laboratories: 'If one can use Si for any electronic applications, don't use any other!' But due to the large thermal mismatch and also the weaker bonding between covalent silicon lattice and the ionic oxides, growth of YBCO on bare silicon has not been successful so far. However, with $MgAl_2O_4/BaTiO_3$ oxide layers as buffer layers on Si(100), the growth of YBCO, with $T_c = 85$ K, coated with these buffer layers has been achieved (Wu et al 1989).

$LaSrGaO_4$ is an important substrate material for the growth of a-axis-oriented YBCO films. This is one of the important single-crystal substrates which supports high-quality a-axis growth of YBCO without any template buffer layer. It is important to note that oxides which are magnetically ordered, such as garnets and orthoferrites are also known to support the epitaxial growth of YBCO with T_c as high as 90 K (Ramesh et al 1989). Spinels such as $MgAl_2O_4$ are also found to be good lattice-matched material for the growth of YBCO, but it has been mainly used as a material for buffer layer. Search for new substrates, new barrier-layer materials and substrates for a-axis-oriented growth against c-axis-oriented growth of YBCO is still an active area of research.

4. Results and discussion

4.1 *Ag-doped YBCO films on sapphire*

High-quality epitaxial YBCO films with c-axis perpendicular to the (100) cut substrate plane can be characterized by the slope of R vs T curve. If R_{300}/R_{100} is greater than 3, T_c of 90 K and J_c around 10^6 A/cm^2 at 77 K are generally obtained.

Sapphire is the most important substrate which has extremely low loss in the microwave region. High-T_c films in the form of strips are used as transmitting lines without loss in the microwave region. However, growing high-quality, high-J_c, 90 K YBCO films having low surface resistance is difficult on bare sapphire due to the large lattice mismatch and chemical interactions of Al with YBCO. We have overcome
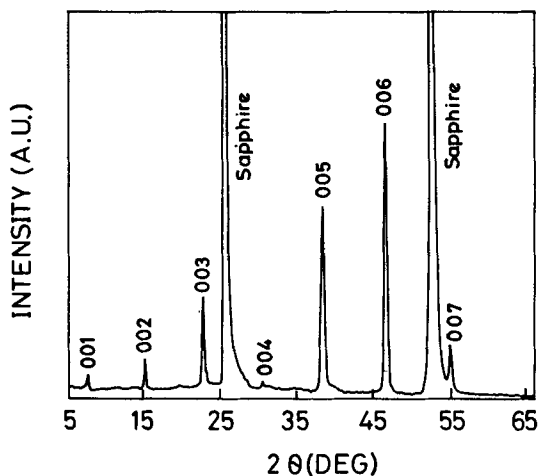
Figure 2. CuK θ–2θ scan of 7%-Ag-doped $YBa_2Cu_3O_7$ films on sapphire.
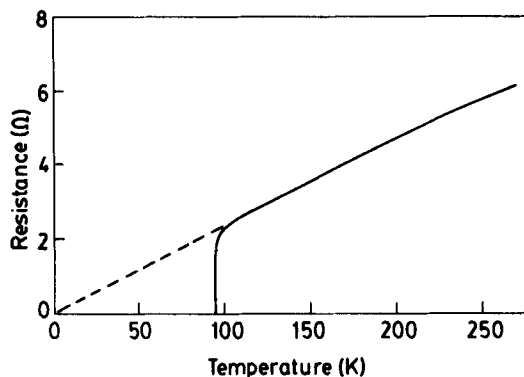

Figure 3. R vs T plot of the above film showing $R_{300}/R_{100} \sim 2 \cdot 9$ and $T_c = 90$ K.

this problem by growing 7%-Ag-doped YBCO films on bare sapphire. Silver addition lowered the growth temperature from 780°C to 730°C in the PLD system. A typical *c*-axis-oriented Ag-doped film grown on sapphire is shown in figure 2. Figure 3 shows R vs T plot of Ag-doped YBCO films. The film showed T_c of 90 K. R_{300}/R_{100} was about 2·9. Transport critical current of these films was about $1 \cdot 2 \times 10^6$ A/cm^2 at 77 K. Microwave surface resistance of Ag-doped films was about 450 $\mu\Omega$ at 10 GHz at 77 K. The T_c, J_c values of Ag-doped YBCO films on bare sapphire reported here are the highest and surface resistance value is the lowest compared to values reported in the literature. Details of the study will be published elsewhere (Dhananjay Kumar *et al*, to be published). We are now using these high-T_c, Ag-doped YBCO films for microwave applications.

4.2   *Metallic LaNiO₃ thin films*

Metallic oxide films are finding application as the normal metal barrier in the SNS-type Josephson junctions, and electrodes for superconducting, insulating and ferro-

electric oxides. Among the perovskite-related oxides, we have found that $LaNiO_3$ (LNO) is perhaps the best material for these applications (Hegde *et al* 1994). Epitaxial $LaNiO_3$ thin films have been routinely grown in this laboratory on a variety of substrates such as $LaAlO_3$, $SrTiO_3$, MgO, YSZ, $SiO_2/Si(100)$ and Al_2O_3. Typical *R* vs *T* plots of a few films are given in figure 4. Resistivity of these $LaNiO_3$ films is of the order of 300–400 $\mu\Omega\cdot$cm. We have grown (100)-oriented $LaNiO_3$ thin films on $SiO_2/Si(100)$ substrate for the first time even though SiO_2 layer on Si(100) is amorphous. The reason for an oriented growth of $LaNiO_3$ on amorphous SiO_2 is not clear to us. The θ–2θ scan of $LaNiO_3$ over YBCO films is shown in figure 5. Observation of only (100) and (200) $LaNiO_3$ lines on the epitaxial YBCO films on $LaAlO_3$ (100) indicates epitaxial growth of LNO on YBCO. The contact conductance between metallic $LaNiO_3$ and superconducting YBCO thin films has been measured by a modified four-probe method and the value is $1\cdot4 \times 10^4$ ohm^{-1} cm^{-2} at 77 K, which is about the same as that of Ag and Pd with YBCO films.
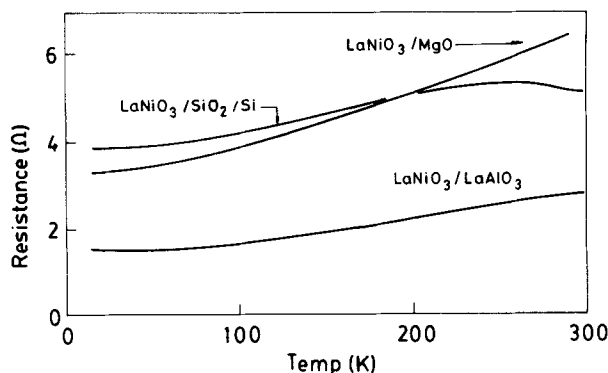

Figure 4. *R* vs *T* plot of $LaNiO_3$ films on different substrates.
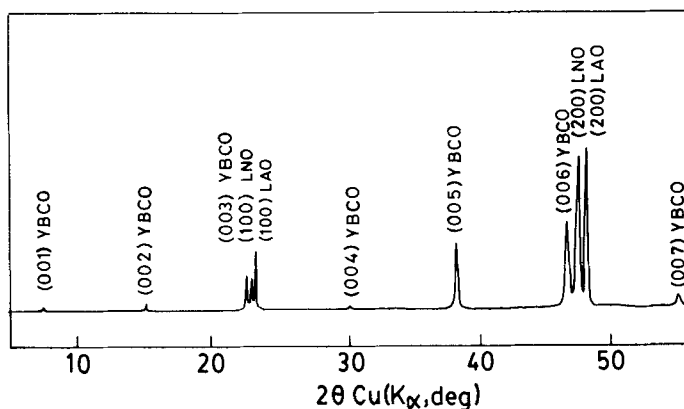

Figure 5. CuK_α X-ray θ–2θ scan of $LaNiO_3$ (LNO) films grown on $YBa_2Cu_3O_7$ (YBCO) films deposited on $LaAlO_3$ (LAO) substrate.

4.3   *LaNiO₃ as a normal metal barrier for SNS junction*

YBCO/LNO/YBCO trilayer structures were fabricated in the planar form with LNO barrier thickness of the order of 1000 Å. The CuK_α X-ray θ–2θ scan of YBCO/LNO/ YBCO/STO trilayer structure is similar to that given in figure 5. This indicates that the third (YBCO) layer grown LNO is also c-axis-oriented.

In order to measure the I–V characteristics of the above structure, a 100 μm wide and 330 μm long microbridge was patterned by laser irradiation. Figure 6 shows the I–V characters of the junction at 77 K. The T_c of the YBCO film across the LNO barrier was about 86 K and J_c of the junction at 77 K was 300 A/cm². The coherence length ζ_n in the normal metal (LNO) region was found to be 125 Å, which was calculated using the formula

$$J_c(d) = J_{co}\exp(-d/\zeta_n),$$

where d is the barrier thickness.

The figure of merit of the Josephson junction R_nA is found of the order of $10^{-9}\Omega\cdot cm^2$, which is comparable to the values reported for SNS junctions fabricated using YBCO superconducting films with different metallic-oxide films as barrier layers (Char *et al* 1993).

4.4   *LaNiO₃ films as electrodes for ferroelectric oxides*

The main problem of integrating ferroelectric thin films into devices is the difficulty of growing single-crystal-like films with proper electrode materials. Recent developments in oxide thin film fabrication reveal that perovskite-related metallic oxides can act as good electrodes for ferroelectric oxides (Ramesh *et al* 1991). Since we have already
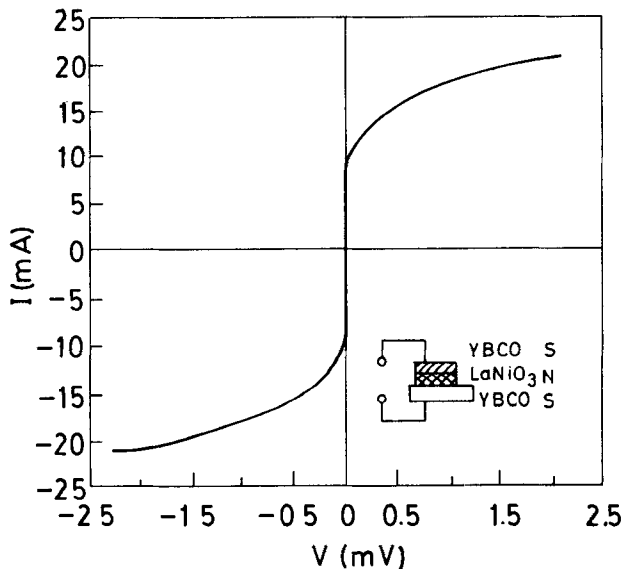

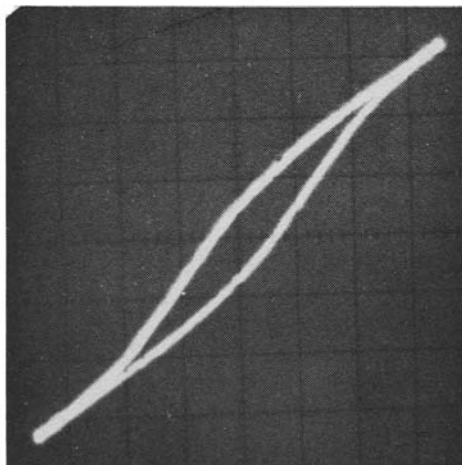**Figure 6.** *I–V* characteristics of YBCO/LNO/YBCO junction.

Figure 7. Hysteresis loop of ferroelectric $Bi_2 VO_{5.5}$ film in the $LaNiO_3/Bi_2 VO_{5.5}/LaNiO_3/SiO_2/Si$ trilayer configuration.

developed processes for $LaNiO_3$ films, we considered it worthwhile to explore this material as an electrode for $Bi_2 VO_{5.5}$ ferroelectric oxide (Prasad *et al* 1993).

$Bi_2 VO_{5.5}$ thin films were grown on $LaNiO_3/SrTiO_3(100)$ as well as $LaNiO_3/SiO_2/Si$. $LaNiO_3$ metallic film here acted as the bottom electrode. Experiments were carried out with both Au as well as $LaNiO_3$ as the top electrode. The trilayer $LaNiO_3/Bi_2 VO_{5.5}/LaNiO_3$ film with the $LaNiO_3$ electrodes indeed showed the ferroelectric hysteresis loop shown in figure 7. Such a loop could be obtained with just 5 V across the ferroelectric oxide layer. The remanent polarization (P_r) is of the order of $10^{-7} C/cm^2$. This clearly demonstrates the utility of $LaNiO_3$ as an electrode material. Characteristic ferroelectric property in the form of the hysteresis loop seen here further suggests the growth of stoichiometric $Bi_2 VO_{5.5}$ thin film. It has also been shown that the trilayer growth is indeed epitaxial (Hegde, unpublished).

4.5 *Giant magnetoresistance in* $La_{0.6} Pb_{0.4} MnO_3$ *thin films*

Giant magnetoresistance (GMR) effect was first observed in $(Fe/Cr)_n$ multilayer thin films. Here, large negative resistance is observed when magnetic field is applied and such an effect is likely to be useful for magnetoresistive 'read' heads in information storage devices. Lanthanum manganates doped with Ca, Sr, Ba and Pb are known to show ferromagnetic ordering at temperatures below 320 K and $La_{0.67} Ba_{0.33} MnO_3$ thin films did show over 50% GMR (Von Helmort *et al* 1993). We considered it worthwhile to pursue this aspect and here we report GMR in $La_{0.6} Pb_{0.4} MnO_3$ thin films.

The films of $La_{0.6} Pb_{0.4} MnO_3$ were prepared by PLD with almost similar conditions as the $LaNiO_3$ films. In figure 8, we show the $\Delta R/R_0$ vs H of $La_{0.6} Pb_{0.4} MnO_3$ thin films. Thus for the first time we show here that over 40% GMR is seen in $La_{0.6} Pb_{0.4} MnO_3$ thin films at room temperature. Details of this experiment are published elsewhere (Sundar Manoharan *et al* 1994).

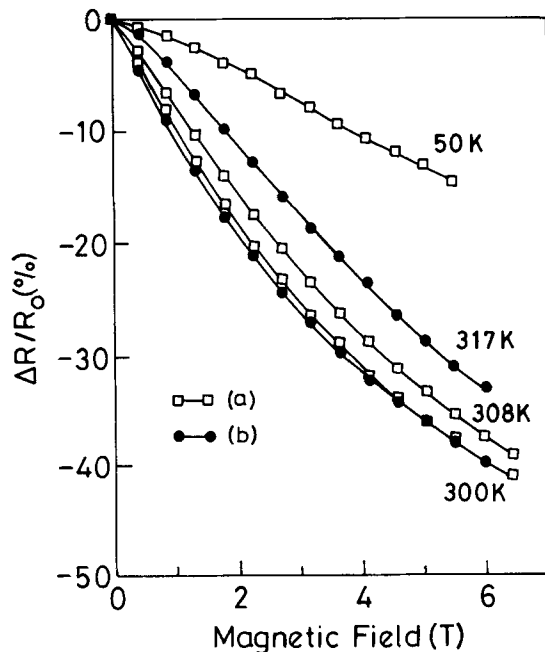**Figure 8.** Giant magnetoresistance $\Delta R/R_0$ vs magnetic field for ferromagnetic films of (a) as-deposited epitaxial $La_{0.6}Pb_{0.4}MnO_3$ and (b) partially oxygen-desorbed $La_{0.6}Pb_{0.4}MnO_3$.

5. Conclusions

We have presented in this article fabrication of epitaxial thin films of Ag-doped YBCO on sapphire, $LaNiO_3$ metallic oxide, ferroelectric oxide and ferromagnetic $La_{0.6}Pb_{0.4}MnO_3$ oxide by pulsed laser deposition and some of their properties. The results presented here indicate that PLD is a versatile technique to fabricate a variety of oxide thin films for various applications. We expect to bring out some practical devices such as microwave transmitters, SQUIDS, ferroelectric switches and ferromagnetic switches out of these oxide thin films.

Acknowledgements

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