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Nanostructured oxide thin films for sustainable development

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Abstract

In the effort to emancipate mankind from fossil fuels dependence and minimize the CO_2 emissions, efficient transport and conversion of energy is required. Advanced materials such as superconductors and thermoelectrics are expected to play an important role in sustainable science and development. We propose an overview of our recent progress on nanostructured thin films of superconducting and thermoelectric oxides. Superconducting properties of $YBa_2Cu_3O_x$ and thermoelectric properties of Al-doped ZnO are described in relation to preparation techniques, experimental conditions, substrates used, structure and morphology. We especially discuss a nanoengineering approach for the enhancement of energy transport and energy conversion efficiency of oxide thin films compared to their corresponding counterpart of bulk materials.

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Keywords: superconductors; thermoelectrics; thin films; oxides; pulsed laser deposition; artificial pinning centers; nanodefects; phonon scattering

1. Introduction

These days, mankind has been starting to face many difficult issues: energy problems, environmental problems, water shortage problems and so on. It is a common feeling that new advanced materials will play an important role in the current challenge to develop alternative and sustainable energy technologies to reduce considerably our dependence on nuclear and fossil fuels and eliminate greenhouse gas emissions [1, 2].

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In particular, superconducting [3] and thermoelectric [4] materials seem fit to solve the energy puzzle since they can provide efficient energy transport and conversion, respectively.

Superconductors can transport electrical current without dissipation if cooled down at the appropriate temperature. Superconducting bulks and single crystals are quite important for the study of the basic physical properties, however for practical applications, such as direct current transport or winding of magnets, development of superconducting wires and tapes is strongly required. In order to be disclosed to the practical applications (lossless current transportation, winding of magnets and so on), superconducting materials should possess not only T_c, but also J_c (critical current density) and pinning force ($F_p = J_c \times B$, where B is the external magnetic field) as large as possible to cover a wide range of intended applications. Introduction of nanosized artificial pinning centres (APCs) was widely used to strongly enhance J_c and F_p of high temperature superconductors (HTSC) like $YBa_2Cu_3O_x$ (YBCO, T_c = 92 K) in magnetic field [6, 7]. Main advantage of HTSC towards conventional superconductors like NbTi or Nb_3Sn is the possibility to use nitrogen (boiling point: 77K) instead of helium (boiling point: 4.2K) as coolant. Impressively, in the past ten years or so, the nano-engineering approach to control microstructure, distribution, concentration and dimensionality of APCs has been demonstrated to be a powerful tool to produce YBCO thin films with excellent performances. Comprehensive review on the state of the art characteristics of YBCO wires and tapes can be found in [8].

Thermoelectrics can convert heat into electrical energy without moving parts. Efficient, small and light-weight thermoelectric modules are instrumental for recycling waste heat in a wide range of temperatures: gases from industrial plants, car engines, and even domestic stoves. In order to improve the efficiency of the thermoelectric conversion, the adimensional figure of merit $ZT = \sigma S^2 \times T/\kappa$ (where σ = electric conductivity, S = Seebeck coefficient; T = temperature and κ = thermal conductivity) must be increased. To date, the best performance is given by alloys like Bi_2Te_3 or Sb_2Te_3, whose key feature is the presence of natural nanosized defects which act as efficient phonon scatterers for the depression of κ and the consequent increase of ZT [9]. On the other hand, oxides have been recognized as promising candidates for practical utilization as thermoelectric materials since they are more stable than metallic materials in oxidizing environments over wide temperature range [10]. Indeed, oxides possess important characteristics, such as their benign nature, abundant supply, and cost effectiveness. More recently, researchers start to focus of thermoelectric oxide thin films which are easier to be functionalized at the nanoscale with respect to the bulk oxides. Overview on the recent status of research on thermoelectrics oxide thin films can be found here [11].

This contribution will briefly highlight our recent progresses on high quality nanostructured films of superconducting and thermoelectric oxides with strongly enhanced properties for sustainable energy applications

2. Experimental procedure

A Lambda Physik KrF excimer laser (λ = 248 nm) was used for fabrication of $YBa_2Cu_3O_7$ (YBCO) superconducting thin films doped with $BaSnO_3$ (BSO), Y_2O_3 and BSO+Y_2O_3 on $SrTiO_3$ (STO) substrates. The Pulsed Laser Deposition (PLD) conditions were: energy density E = 5 J/cm^2, deposition temperature (T) = 800 ºC, oxygen partial pressure (pO_2) = 200 mTorr, repetition rate (f) = 10 Hz, substrate to target distance (d) = 60 mm. For the deposition of pure YBCO thin film, a pristine YBCO target was ablated for 6000 laser pulses while for YBCO films added with nanodefects, YBCO+BSO mixed targets (YBCO added with x wt% of the BSO phase, being x 2, 4, 6 and 8%) and YBCO+Y_2O_3 surface-modified targets (in this case a slice of Y_2O_3, which percentage of total target area is denoted as A%, is suck on the surface of the target for periodical ablation and A% was varied as 2.5, 5.44, and 9.22%) were used. YBCO+BSO+Y_2O_3 films were prepared in multilayer fashion, alternating YBCO+BSO and YBCO+Y_2O_3 layers by periodic switching of the two targets.

Superconducting transition temperature (T_c), J_c/B characteristics (T=77 K, $B//c$, B=0~9 T) and $J_c/B/\theta$ angular dependences (T =77 K, B = 1 T, being θ the angle between B and c axis of ther film) were measured by physical properties measurement system (PPMS, Quantum Design, USA). The thermoelectric 2%Al-doped ZnO (AZO) thin films were grown on STO, Al_2O_3 and fused silica substrates by the PLD technique using a Nd:YAG laser (λ = 266 nm). The PLD conditions were: E = 4.2 J/cm^2, T = 300-600 ºC, pO_2 = 200 mTorr, f = 10 Hz, d = 35 mm. 2 % Al was found as the best doping in bulk. The electrical conductivity versus temperature (σ–T) characteristic was measured by a conventional four-probe technique from 300 to 600 K with a homemade apparatus. The Seebeck coefficient was

measured by a commercially available system (MMR Technologies, USA) The crystallinity and the orientations of both superconducting and thermoelectric thin films (θ–2θ scans, rocking curves, Φ scans) as well as *c* axis lengths were determined by XRD (Bruker D8 Discovery). Cross-sections of all films were analysed by transmission electron microscopy (TEM, JEOL).

3. Results and discussion

3.1. Superconducting thin films

Nanoengineering approach with the incorporation of nanosized artificial pinning centres has been considered to improve the pinning performance of YBCO thin films.

At first, we tried adding BSO to YBCO films grown on STO substrates by PLD [12]. By ablation of mixed BSO-YBCO targets with increasing BSO content (2~8 wt%), we obtained high quality YBCO thin films incorporating BSO in form of nanorods, which are classified as one-dimensional APCs (1D-APCs). YBCO films added with 4 wt% BSO have huge F_p^{MAX} = 28.3 GN/m^3 (77K, 3T, B//c). However, J_c is intrinsically anisotropic with the direction of applied magnetic field (with a maximum for B//c axis) and this is a critical issue for practical applications, since the value of J_c is desired to be constant in all directions of applied magnetic field.

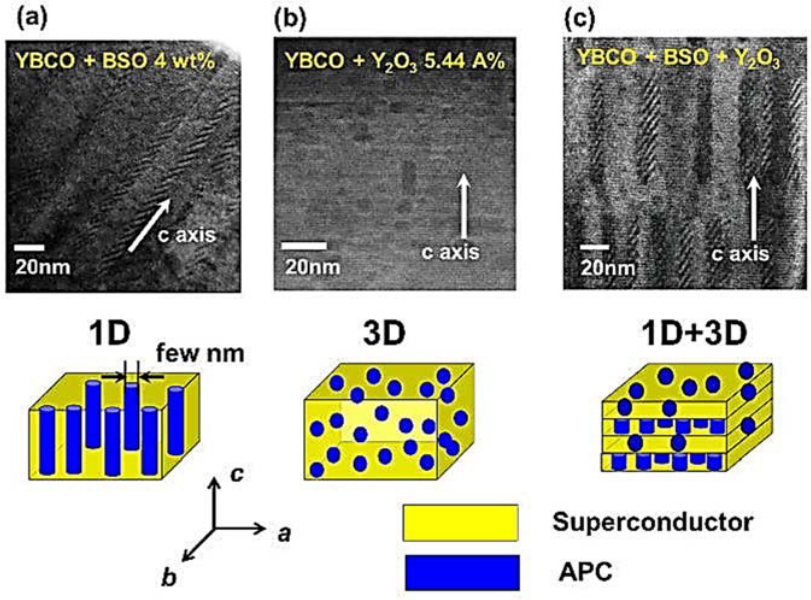

Fig. 1. Typical TEM-cross-sectional images (first row) and schematic representations (second row) of YBCO films added with artificial pinning centers (APCs) of various dimensionality: (a) 1D-APCs: YBCO with 4wt% c-axis aligned BSO nanorods; (b) 3D-APCs: YBCO with randomly dispersed 5.44 A% Y_2O_3 nanoparticles; (c) 1D+3D APCs: YBCO multilayer added with alternating 1D-APCs (BSO nanorods) and 3D-APCs (Y_2O_3 nanoparticles)

To solve this issue, we tried the incorporation of Y_2O_3 nanoparticles (three-dimensional APCs, 3D-APCs) inside the YBCO film. Areas of Y_2O_3 sectors on YBCO target were increased (2.51%, 5.44% and 9.22% of the YBCO pellet area). Randomly distributed Y_2O_3 particles, whose density was proportional to the area of sector, were incorporated in YBCO films. Consistent with the microstructure, J_c was isotropic. The 5.44 A% Y_2O_3 added sample presented F_p^{MAX} =14.3 GN/m^3 (77K, 3T, B//c)) which is significantly large, though inferior to the value reported in YBCO- BSO films with the same conditions. We further used the single vortex dynamics model to account

for vortex pinning in the samples. The 5.44A% Y_2O_3 -YBCO film result shows a good agreement with the model fit up to B = 4 T [13].

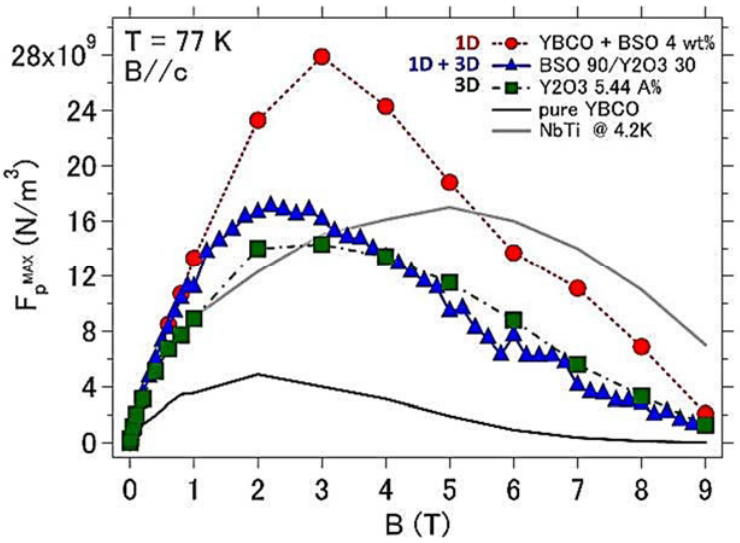

Fig. 2. Global pinning force ($F_p = J_c \times B$) at 77K (B//c) of YBCO films added with APCs of various dimensionalities: 1D-APCs (YBCO +4wt% BSO; 3D-APCs (YBCO+5.44 A%)Y_2O_3 nanoparticles; 1D+3D APCs (YBCO+BSO+Y_2O_3). F_p of pure YBCO film is reported as reference; F_p of NbTi tape (at 4.2K) is plotted as a milestone.

Ultimate approach was combination of advantages of 1D- and 3D-APCs pinning, with coexistence of BSO nanorods and Y_2O_3 nanoparticles. Multilayered films, alternating YBCO+Y_2O_3 and YBCO+BSO layers were prepared in PLD chamber by switching YBCO+ ~2A% Y_2O_3 and YBCO+ 4wt% BSO targets. Different combinations, varyingthe thickness of layers, were tried. Best result was obtained with the combination [(90 nm YBCO+BSO) / (30 nm YBCO+Y_2O_3)] × 3 presenting F_p^{MAX} =17.6 GN/m^3 (77K, 2.2T, B//c) [14].

3.2. Thermoelectric thin films

Several oxides are promising for thermoelectric applications [10] : the best performance for bulk oxide so far (has been reached by doped *p*-type $Ca_3Co_4O_9$ [15] and *n*-type ZnO [16]: ZT ~ 0.45 at 1000K in both cases.

In our research on thermoelectric oxide thin films we focused at first on ZnO, a semiconductor with wide direct band gap (3.3 eV), well known for its versatile applications (optics, solar cells, electrodes, gas sensors, biophysics, etc.). ZnO can also be regarded as low-cost, nontoxic, stable thermoelectric material for space applications, solar- thermal and electrical-energy production.

Epitaxial thin films of $Zn_{0.98}Al_{0.02}O$ (AZO) films were fabricated by PLD on several substrates: $SrTiO_3$ (STO), Al_2O_3 and fused silica. TEM images reported in Figure 3 demonstrate typical columnar growth of the films on STO and Al_2O_3, while films grown on silica present thin natural buffer layers with randomly oriented grains. As summarized in Figure 4, at T_{dep} = 400 °C, films deposited on silica always shows higher values of ZT in comparison with films deposited on Al_2O_3 and STO: at T = 600 K, $(ZT)_{silica}$ = 0.045, $(ZT)_{STO}$ = 0.03 and $(ZT)_{Al2O3}$ = 0.04. Furthermore, all the films have larger ZT in comparison with the correspondent bulk material: (ZT)bulk = 0.013. Since the values of σ and S did not change dramatically on the different substrates, we attribute the enhancement of ZT values of the thin films to the fact that the values of κ of ZnO films at room-temperature are smaller than the value of corresponding bulk (25~35 W/m×K [17, 18). In numbers, κ_{STO} = 6.5 W/m×K [11], κ_{Al2O3} = 6.90 W/m× K [11] and κ_{silica} = 4.89 W/m×K [19]. The depression of κ in thin films is due to several factors: enhanced phonon scattering by intrinsic defects of the films (point defects, dislocations, impurities, pores); phonon scattering at the grain

boundaries; phonon scattering at the interface between film and substrate.

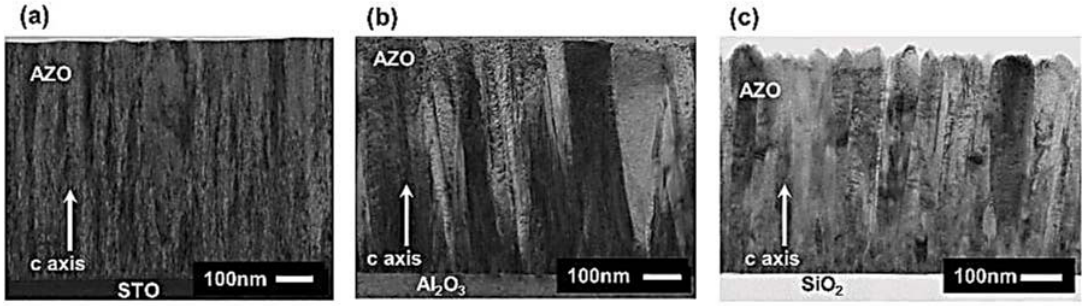

Fig. 3. Typical TEM-$_{cross}$-sectional images of AZO thin film grown on several substrates at 400 °C: (a) STO; (b) Al_2O_3; (c) fused silica: natural buffer layer can be observed on the SiO_2 substrate..

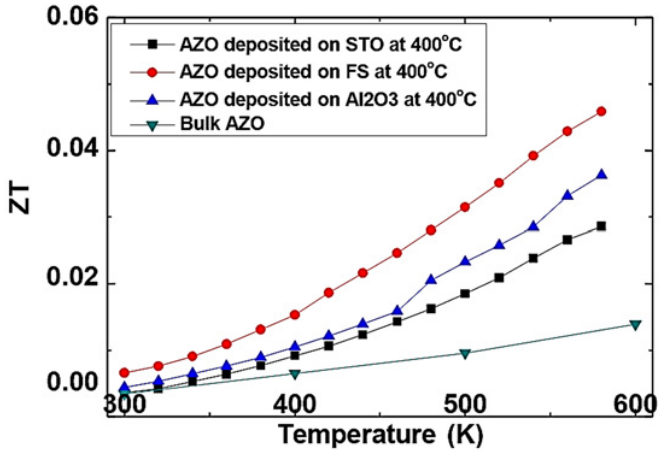

Fig. 4. Figure of merit ($ZT = \sigma S^2 \times T/\kappa$) of AZO films deposited on several substrates at 400 °C. Behavior of the corresponding bulk material is reported for comparison

4. **Outlook and perspective**

The results presented in this paper indicate that the nanoengineering approach by PLD method can produce a variety of complex nanocomposite oxide thin films with unique properties for sustainable applications. High-quality films of superconducting oxides ($YBa_2Cu_3O_x$: YBCO) and thermoelectric oxides (Al-doped ZnO: AZO) were prepared and characterized.

In the case of YBCO thin films, the nanoengineering approach is at very advanced level: satisfactory control of nanodefects size and distribution was achieved. The additions of several kinds of APCs are very effective in the enhancement of performances: large in-field pinning forces (Fp) at 77K and B//c was obtained. Highlights are FpMAX = 28.3 GN/m^3 (3T) in YBCO added with 1D-APCs (4 wt% BSO nanorods); FpMAX = 14.3 GN/m^3 (3T) in YBCO added with 3D=APCs (5.44% Y_2O_3 nanoparticles); FpMAX =17.6 GN/m^3 (2.2T) in YBCO 1D+3D-APCs multilayers, alternating BSO nanorods and Y_2O_3 nanoparticles. Despite such encouraging results, the performance of superconducting thin films still requires a breakthrough in order to realize full practical application. In particular, the irreversibility field (Birr) needs to be improved. For example, a typical values of Birr (77K) for our YBCO-BSO film is about 11T [12]. Recently, Xu et al reported Birr = 14.8T (77K) for MOCVD (Y,Gd)BCO doped with 15% vol Zr, although FpMAX = 14 GN/m^3 (at 6T) is about half the value obtained by us in the YBCO-BSO [20]. Therefore,

further exploration to expand the Fp and Birr values if one had to have real applicable superconducting oxide thin films.

In the case of AZO thin films, promising values have been obtained, such as $\kappa = 4.89$ W/m×K (300K) = ZT (600K) = 0.045 for AZO grown on silica. However, these values are still too low for the practical applications First attempt preparing a tiny module based on 5 AZO and 5 $Ca_3Co_4O_9$ thin films legs was successful, though the output power was small: 29.9 pW with $\Delta T = 230$ °C) [21]. Further decrease of □ (to the range of 1-2 W/m×K) and increase of ZT up to 2 at 1000K are the requirements for efficient recovery of waste heat [11] and improvement of module performance [21]. For these purposes, it is necessary to introduce and control additional artificial nanodefects to the films, following a similar path as for the superconducting oxide films

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