MECANISM DE CREŞTERE ŞI PROPRIETĂȚI ALE FILMELOR SUBȚIRI DE $YBa_2Cu_3O_{7-\delta}$ DEPUSE PRIN ABLAȚIE LASER PE (001) $SrTiO_3$
GROWTH MECHANISM AND PROPERTIES OF $YBa_2Cu_3O_{7-\delta}$ THIN FILMS DEPOSITED BY LASER ABLATION ON (001) $SrTiO_3$

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Filme subțiri monocristaline de $YBa_2Cu_3O_{7-\delta}$ cu proprietăți supraconductoare au fost crescute epitaxial prin ablație laser pe substraturi de $SrTiO_3$ (001). Morfologia suprafeței filmelor a fost studiată prin difracție prin reflexie de electroni cu energie înaltă (DREEI) la presiuni mari, microscopie de forță atomică (MFA) şi microscopie electronică de baleiaj (ME), în timp ce proprietățile structurale au fost analizate prin difracție de raze X (DRX). Pentru parametrii optimizați de creştere, filmele rezultate au o suprafață cu o rugozitate de ~ 10-15 nm, conform rezultatelor obținute de la MFA şi ME. Creşterea filmelor, de tip Stransky-Krastanov, este influențată de proprietățile interfeței substrat-film, datorită prezenței stresului epitaxial. Din punct de vedere al proprietăților electrice, filmele sunt supraconductoare, cu valori ale temperaturii critice de T_c=85-91 K. Sunt prezentate rezultate obținute asupra fabricării şi proprietăților electrice ale joncțiunilor Josephson tip rampă cu electrozi din $YBa_2Cu_3O_{7-\delta}$ şi barieră din $PrBa_2Cu_3O_{7-\delta}$.

High quality, single phase c-axis oriented $YBa_2Cu_3O_{7-\delta}$ thin films with superconducting properties were grown by laser ablation on (001) $SrTiO_3$ substrates. The surface morphology of the films has been investigated by means of high-pressure reflection high energy electron diffraction (RHEED), atomic force microscopy (AFM), and scanning electron microscopy (SEM), while the structural properties were studied by X-ray diffraction (XRD). Deposition under optimum conditions produces films with relatively smooth surface, with a roughness of about 10-15 nm, as confirmed by AFM and SEM data. The growth follows a Stransky-Krastanov mechanism governed by the substrate-film interface properties due to presence of epitaxial strain. The films show good superconducting properties with T_c values of 85-91 K. Results on the fabrication and electrical transport properties of ramp-type Josephson junctions with $YBa_2Cu_3O_{7-\delta}$ electrodes and $PrBa_2Cu_3O_{7-\delta}$ barrier are presented.

Keywords: *$YBa_2Cu_3O_{7-\delta}$, pulsed laser ablation, morphology, X-ray diffraction, ramp-type Josephson junctions.*

1. Introduction

$YBa_2Cu_3O_{7-\delta}$ (YBCO) is one of the most studied high critical temperature superconducting (HTSc) materials with a p-type conduction. It has an orthorombic symmetry for its superconducting phase (a=3.823 Å, b=3.887 Å, and c=11.680 Å), with the maximum T_c of 92 K for the optimum oxygen doping ($\delta\approx0$). In the form of thin films, *c*-axis oriented YBCO films are thermodynamically preferred to the *a*-axis ones and are, therefore, most often used for the construction of devices based on Josephson junctions. However, *c*-axis oriented planar YBCO-based devices are difficult to fabricate due to the extremely low value of its coherence length in the *c*-axis direction, ξ_c, e.g., $\xi_c\approx3$ Å, about ¼ of the *c*-axis length, that makes difficult tunneling along the c-axis. This problem was partialy solved by the development of ramp-type Josephson junctions in which the tunneling takes place along the *a-b* plane. Also, studies on the fabrication of YBCO based Josephson junctions have been hampered by the fact that this material grows following a 3D (islands) growth mechanism, with a negative effect on the films morphology and, as a result, on the interface quality in case of the heterostructures incorporating YBCO.

Pulsed laser ablation (PLD) is one of the techniques used with success for the preparation of this material [1]. In PLD a material is transported from a target of the same material to a cold support (the substrate) via a plasma plume resulted from the interaction of a laser beam with the target [2]. This method can be used to solve the problem of YBCO film's roughness because it gives the user the possibility of controlling the film's growth parameters (growth temperature and gas pressure, laser energy density on the target). By selecting the proper substrates with similar crystal structure and thermal expansion coefficient with the ones of the film, the epitaxial strain induced by substrate in the film is reduced, favoring a 2D growth mode, with few or no 3D islands, reducing the film roughness.

In this paper we present the results of studies on growth mode, morphology, structure and transport properties and their evolution with deposition parameters for YBCO thin films grown by PLD on (001) $SrTiO_3$ substrates. They were analyzed *in-situ* and in real time by high-pressure RHEED, and ex-situ by AFM and XRD. The electrical properties were measured in the 80-300 K range in liquid nitrogen by using the standard

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dc four-probe method; for the ramp-type junctions, the current-voltage (I-V) characteristics were measured in the 4.2-80 K range, in a cryostat with liquid He.

2. Experimental

A computer controlled PLD system (laser excimer, KrF, λ=248 nm) equipped with *in-situ* high-pressure (up to 0.50 mbar) RHEED was used for the experiments [2]. The growth and film thickness were controlled *in-situ* by monitoring the RHEED intensity oscillations of the specular spot. The RHEED gun was operated at 40 keV and 1.3 mA with the electron beam focused to the surface (of the substrate or of the film) at a glazing incidence angle of 1-1.5^o along [100] or [110] crystallographic directions. (001) $SrTiO_3$ single crystal substrates with miscut angle in range of 0.1-1.2^o were used as template. The substrates were cleaned in organic solvents (acetone and ethanol) and subsequently chemically and/or thermally treated. For chemical treatment a HF buffered solution was used in order to obtain a reproducible TiO_2 single-terminated surface [2, 3]. The thermal treatment was done at 950-1000 ^oC, in an O_2 flow. The substrates were then thermally attached to a heater block using Ag paste. The main deposition parameters for the YBCO thin films grown on $SrTiO_3$ are given in Table 1. The films thickness was in range of 50-150 nm. After deposition, the YBCO films were annealed under 1 bar O_2 successively for 15 min. at 750^{o}C and 650^{o}C, respectively, followed by 1 h annealing at 450^{o}C. The first two annealing steps have the aim of partial relaxation of the strain between the film and the substrate, and therefore improving the oxidation of the film during the final annealing step at 450^{o}C. The last, low temperature annealing step has the aim of oxidizing the film in order to induce the phase transition from the as-deposited, non-superconducting, tetragonal symmetry, to the orthorhombic symmetry, superconducting.

Table 1

Deposition parameters for $YBa_2Cu_3O_{7-x}$ thin films grown on (001) $SrTiO_3$ substrates. / *Parametrii de depunere a filmelor subțiri de $YBa_2Cu_3O_{7-x}$ crescute prin ablație laser pe substraturi de $SrTiO_3$ (001).*

Target composition *Compoziția țintei*	$YBa_2Cu_3O_{7-\delta}$ (polycrystalline)
Substrate / *Substrat*	(001) $SrTiO_3$
Substrate temperature *Temperatura substratului*	750-800 ^oC
Deposition pressure *Presiunea de depunere*	(18-25)$\times 10^{-2}$ mbar
Laser repetition rate *Frecvența laserului*	1-5 Hz
Deposition gas *Gazul de depunere*	O_2
Target-substrate distance *Distanța țintă-substrat*	50-65 mm
Laser energy density on target *Densitatea de energie a laserului pe țintă*	1.30-2.50 J/cm^2

3. Results and discussions

3.1. Initial growth and surface morphology

The in-plane cell parameters of YBCO are slightly smaller than those of the $SrTiO_3$ substrate (heteroepitaxial growth); therefore the film is expected to be under compressive strain. Beside strain, the evolution of the growth front will be determined by growth parameters, such as temperature and pressure, as well as by the miscut angle of the substrate. These parameters will determine the diffusion length of the ad-atoms on the surface and, finally, a bidimensional (2D) or island (3D) growth mode. The RHEED data showed that the YBCO films undergo a transition from a layer-by-layer like (2D) to island growth (or a typical Stranski-Krastanov growth mode) [5] at the initial stage of the growth. This conversion takes place faster when deposition is done on substrates with smaller miscut angle (therefore, an increased substrate terrace length), e.g, 0.05-0.2^o. After this conversion the YBCO films show predominantly a 3D growth mode, as confirmed by the decrease in the RHEED intensity and also by the presence of 3D islands in AFM image of the film (Fig. 1a) and of 3D diffraction dots on the corresponding RHEED pattern (see Fig. 1b). An increased in film roughness is also observed with reduced value for the miscut angle. This is explained by the fact that the deposited material does not have enough time to find a terrace edge or to diffuse to the edge of an island (reduced interlayer diffusion); therefore, the film grows following a 3D growth mode.

Laser energy density on target has an important influence on surface and transport properties of the YBCO films. However, a too low laser energy density leads to an incomplete surface chemistry resulting in surface outgrowths enriched with copper oxides, as was observed for some samples from Energy Dispersive X-ray Microanalysis (EDX) data. SEM, EDX, and XRD data also showed the presence of needle-like outgrowths on the films surface corresponding to *a*-axis growth, consistent with the reduced laser energy (see Fig. 1c). A decreased concentration of droplets on the films surface was obtained after optimization of the deposition parameters (i.e., the distance target-substrate, laser energy density on target).

3.2. Structural analysis. X-ray Diffraction

The structural properties of the $YBa_2Cu_3O_{7-\delta}$ thin films were strongly dependent on the growth parameters, such as deposition temperature and pressure, substrate-target distance, or laser energy density on target. Post-deposition annealing conditions (oxygen pressure, annealing temperature and time) also determined the final structural and transport properties of the films by

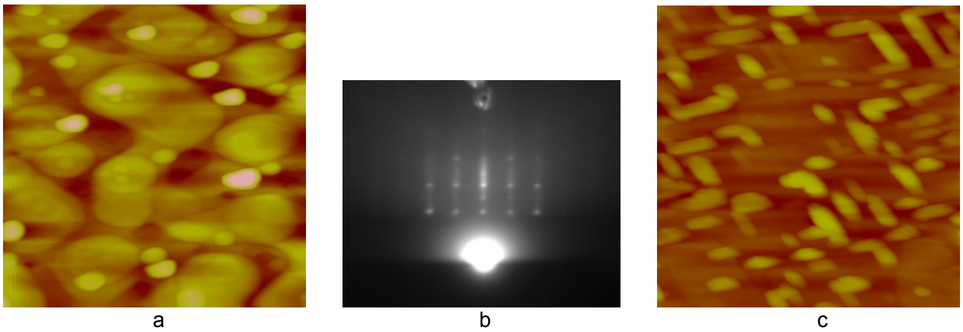

Fig. 1 - AFM micrographs (topographic mode) and RHEED pattern of two distinct c-axis $YBa_2Cu_3O_{7-\delta}$ thin films grown on (001) $SrTiO_3$: a) AFM image (1×1 μm^2) of a film showing the presence of 3D islands; b) corresponding RHEED pattern of the film from a); formation of dots characteristic to a 3D growth mode can be observed; c) AFM image (1.5×1.5 μm^2) of a film showing the presence of a-axis outgrows (needle like) on the surface / *Imagini de la microscopul de forta atomica (MFA) si spectru DREEI a două filme subţiri de $YBa_2Cu_3O_{7-\delta}$ depuse prin ablaţie laser pe $SrTiO_3$ (001): a) imagine MFA (1×1 μm^2) indicând prezenţa de insule 3D; b) spectru DREEI corespunzător filmului prezentat în a); se poate observa formarea unui spectru de difracţie caracteristic unei creşteri tip insule 3D; c) imagine MFA (1,5×1,5 μm^2) a unui film indicând prezenţa de cristale $YBa_2Cu_3O_{7-\delta}$ de formă aciculară, caracterizate de orientare diferită faţă de restul filmului (cu axa a perpendicular pe suprafaţa substratului).*

influencing the oxygen composition and their crystallinity. The XRD data showed that the films are epitaxialy grown, with c-axis perpendicular to the substrate surface. However, in some films the presence of a-axis oriented YBCO was observed, although in small amount (less then about 10 %), confirming the results from AFM. This was the case for films grown on reused $SrTiO_3$ substrates, when the former YBCO layer was chemically removed (in a 0.5 vol.% HNO_3 solution), resulting in a relatively rough $SrTiO_3$ surface. The formation of the a-axis YBCO was also observed for the films grown at temperatures lower than about 750°C. By increasing the deposition temperature and/or the energy of the adatoms (by increasing the laser energy and/or by reducing the target-substrate distance) this problem could be avoided. All YBCO films grown at 780-800°C were single phase, c-axis oriented. A typical θ-2θ XRD pattern for a single phase YBCO thin film epitaxialy grown by PLD on (001) $SrTiO_3$ is given in Fig. 2. Only (00*l*) reflections can be observed, as a result of the preferential c-axis orientation of the film. From omega scans (rocking curves), values of full width at half maximum (FWHM) of 0.09-0.12° for (005) reflection were measured, indicating highly crystalline films. The two-axis ω-2θ scans around any of the (00*l*) reflections showed the formation of a single domain film (in the c-axis direction), as shown in Fig. 3 for the (007) plane. From XRD data it was concluded that the fully oxidized $YBa_2Cu_3O_{7-\delta}$ thin films have an orthorhombic symmetry, with in-plane cell parameters of a ~ 3.825 Å and b ~ 3.885 Å, while the c axis value was found to be c ~ 11.685 Å, similar with the literature data.

3.3. Electrical properties

The electrical properties of the films were measured by the conventional dc four-probe method in liquid nitrogen, for the R vs. T data, and in He, for the transport properties of the junctions. The The measurements showed that the films have a transition temperature T_C of 85-91 K, the highest values being obtained for films deposited at temperatures of 790-800 °C. A typical resistive measurement for an $YBa_2Cu_3O_{7-\delta}$ thin film is shown Fig 4. The film was grown at 800 °C, at a deposition pressure of 0.25 mbar O_2 and post-deposition annealed for 1 h at 450°C under an oxygen pressure of 1 bar.

In order to study the tunneling of charge carrier between two superconducting electrodes separated by a thin non-superconducting barrier, Josephson junction in ramp-type configuration were fabricated and their transport properties

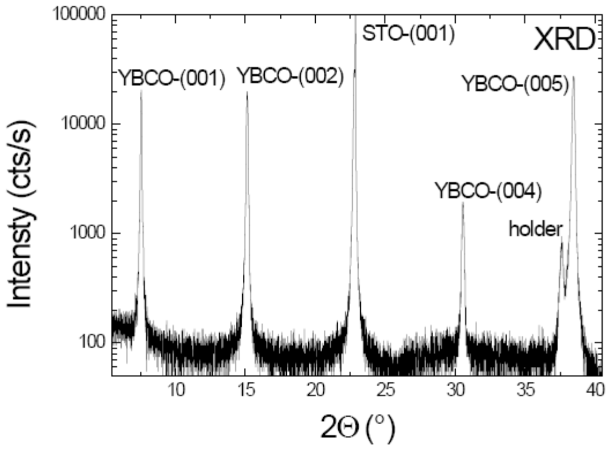

Fig. 2 - θ-2θ XRD pattern of single-phase c-axis $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin film epitaxialy grown by PLD on (001) $SrTiO_3$ showing only (00*l*) reflections. The Al reflection is coming from the sample holder/ 3a. θ-2θ XRD pattern of single-phase c-axis $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin film epitaxialy grown by PLD on (001) $SrTiO_3$ showing only (00l) reflections. The Al reflection is coming from the sample holder. / *Spectru de difracţie de raze X (θ/2θ) al unui film subtire monocristalin de $YBa_2Cu_3O_{7-\delta}$ (YBCO) crescut prin ablaţie laser pe $SrTiO_3$ (001) indicând prezenţa numai a liniilor de difracţie a planelor (00l). Linia de Al aparţine suportului probei.*

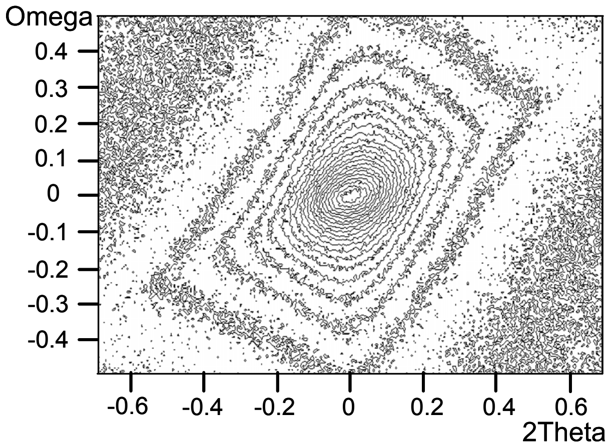

Fig. 3 - XRD ω-2θ (2-axis) scan of the (007) reflection of a $YBa_2Cu_3O_{7-\delta}$ thin film epitaxialy grown by PLD on (001) $SrTiO_3$ showing the formation of a single domain in the c-axis direction. / *Spectru de difracție de raze X ω-2θ (scală logaritmică) a planului (007) pentru un film subțire de $YBa_2Cu_3O_{7-\delta}$ crescut epitaxial prin ablație laser pe $SrTiO_3$ (001) indicând formarea unui singur domeniu în direcția axei c.*

studied. Fabrication steps of this type of junction are given in Refs. [6-8]. In Fig. 5 is shown the current-voltage (I-V) characteristic of a 5 μm wide ramp-type junction fabricated from 150 nm thick $YBa_2Cu_3O_{7-\delta}$ electrodes separated by a 25 nm thick $PrBa_2Cu_3O_{7-\delta}$ barrier, with insulating properties. From this figure it can be concluded that while tunnelling of charge carriers (Cooper pairs) takes place, the shape of the curve indicates that the barrier is not uniform due to, most probably, a relatively rough bottom $YBa_2Cu_3O_{7-\delta}$ electrode, resulting in shortcuts in the barrier between the electrodes. Experiments are in

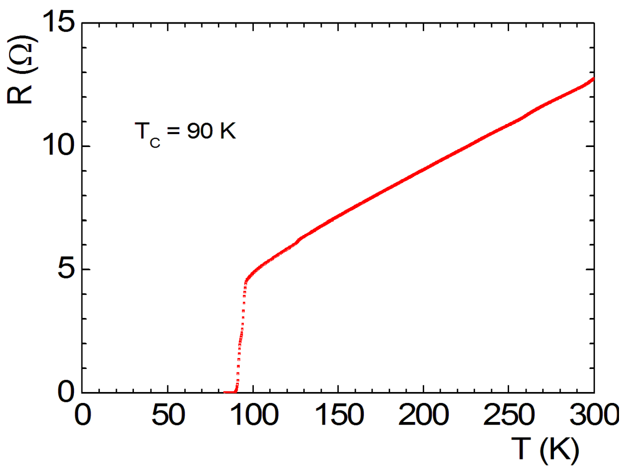

Fig. 4 - Temperature dependence of resistance for a $YBa_2Cu_3O_{7-\delta}$ thin film grown at 780°C, 0.25 mbar O_2, cooled down in oxygen (1 bar) and annealed for 1 h at 450°C. / *Dependența rezistență electrică - temperatură pentru un film subțire de $YBa_2Cu_3O_{7-\delta}$ crescut la 780°C, 0,25 mbar O_2, răcit în oxygen (1 bar) şi tratat termic la această presiune pentru 1 h la 450°C.*

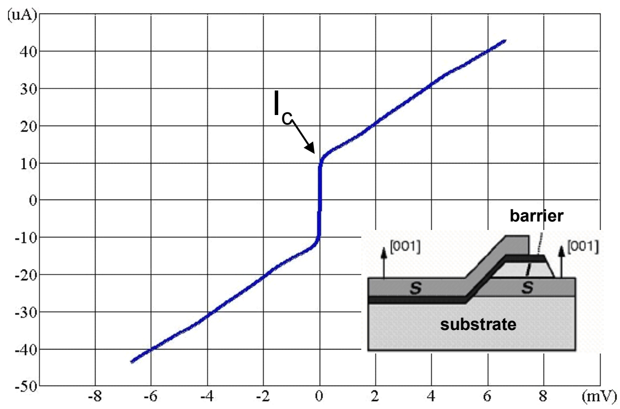

Fig. 5 - I-V characteristic at 4.2 K for a 5 μm wide Josephson junction, in ramp-type configuration, based on the $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_3O_{7-\delta}/YBa_2Cu_3O_{7-\delta}$ structure (150 nm thick $YBa_2Cu_3O_{7-\delta}$ electrodes and 25 nm thick $PrBa_2Cu_3O_{7-\delta}$ barrier). The I_c value is 11 μA. / *Caracteristica curent-tensiune (I-U), la 4,2 K, pentru o joncțiune Josephson tip rampă cu lățimea de 5 μm şi structura de tipul $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_3O_{7-\delta}/YBa_2Cu_3O_{7-\delta}$. În acest caz grosimea electrozilor de $YBa_2Cu_3O_{7-\delta}$ este de 150 nm, iar grosimea barierei de $PrBa_2Cu_3O_{7-\delta}$ este de 25 nm). Insert: reprezentare schematică a joncțiunilor Josephson tip rampă (S=supraconductor). Valoarea curentului critic, I_c, pentru aceasta joncțiune este de 11 μA.*

progress in order to improve the fabrication process of the junctions.

4. Conclusions

Pulsed laser ablation has been used to fabricate high quality, epitaxially grown c-axis oriented $YBa_2Cu_3O_{7-\delta}$ thin films on (001) $SrTiO_3$ single crystal substrates. The surface morphology of the films has been investigated *in-situ* by means of high-pressure RHEED and *ex-situ* by AFM and SEM. Structural characterization of the films was done by means of XRD, while electrical properties have been investigated by resistive measurements. Deposition under optimum conditions (laser energy densities, deposition temperature and pressure) resulted in single phase films, c-axis oriented, with relatively smooth surface. A Stranski-Karstanov growth mode was observed from RHEED data, the growth being governed by the film-substrate interface properties (presence of strain), resulting in an increased surface roughness (i.e., the step density at the surface is increased) with film thickness. From the point of view of electrical properties, the films showed superconductivity with typical T_c values of ~85-90 K, while the $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_3O_{7-\delta}/YBa_2Cu_3O_{7-\delta}$ ramp-type Josephson junctions showed tunneling of the Cooper pairs between the superconducting electrodes. Futher experiments are required in order to improve the fabrication process of the junctions, with focus on improving the barrier thickness homogeneity.

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MANIFESTĂRI ŞTIINŢIFICE / SCIENTIFIC EVENTS

International Conference on Manufacturing Science and Engineering (ICMSE 2011), China, Guilin, 9 -11 April 2011

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The International Conference on Manufacturing Science and Engineering is the premier forum for the presentation of new advances and research results in the fields of Manufacturing Science and Engineering. The conference will bring together leading researchers, engineers and scientists in the domain of interest from around the world. The 1st International Conference on Manufacturing Science and Engineering (ICMSE 2009) was successfully held from Dec. 26 -28, 2009 at Zhuhai, China. Delegates from 11 countries or districts attended this conference. All accepted papers were published on Advanced Materials Research journal and have been indexed in EI Compendex databases. The 2nd International Conference on Manufacturing Science and Engineering (ICMSE 2011) will take place in Guilin, China, 2011. All accepted papers will also be published on international journal Advanced Materials Research and will be indexed in EI Compendex and Thomson ISI databases (See TTP's Conference List). Selected excellent papers will be published on international reputation journals.

2nd International Conference on Nanotechnology: Fundamentals and Applications (ICNFA2011), Canada, Ottawa, 27 – 29 July 2011

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The International Academy of Science, Engineering and Technology (International ASET) and the University of Ottawa organize the 2nd International Conference on Nanotechnology: Fundamentals and Applications. As globalization leads to increasing interaction among regions and peoples of the world, it is important to encourage multi-disciplinarity in emerging scientific topics such as nanotechnology.

The aim of the 2nd International Conference on Nanotechnolgy: Fundamentals and Applications is to gather scholars from all over the world to present advances in the field of nanotechnology and to foster an environment conducive to exchanging ideas and information.

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