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DEPOSITION TECHNIQUES FOR HIGH-T_C SUPERCONDUCTING YBCO THIN FILMS

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ABSTRACT

Many application of high temperature superconductor in advance technology usually require the superconductor in the form of thin films. In this paper attempts has been made to summarize the most popular growth techniques such as Co-evaporation sputtering, laser ablation, and chemical vapor deposition of high-T_c superconducting thin films.

Keywords: deposition parameters, substrate, $YBa_2Cu_3O_{7-x}$, molecular beam epitaxy

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I INTRODUCTION:

. Thin film technology [1] is important in the electronic research in superconductivity. There are many ways to prepare high quality thin films by highly reproducible fabrication process such as electron beam evaporations, molecular beam epitaxy, sputtering, laser ablation and metal organic chemical vapor deposition on oriented substrate materials like $SrTiO_3$, MgO, $LaAlO_3$ and YSZ. The microstructure of the films depends on grain size, grain orientation and grain boundary weak-links, which in turn critically depend upon the complexity of the growth process and the quality of the substrate used.

Vacuum deposition technique can be grouped in two main categories: Physical vapor deposition (PVD) and Chemical vapor deposition (CVD). In physical vapor deposition, a film is deposited by the condensation of a vaporized form of the target material on to the substrate. The critical parameters are physical (temperature, pressure, voltage applied etc). In chemical vapor deposition, the reactant gases (precursors) are pumped into a reaction chamber (reactor) and they undergo a chemical reaction at the substrate. The key parameters are chemical (reaction rates, gas transport, diffusion etc). The different techniques can be divided into three groups: deposition from a single source, simultaneous deposition from multiple sources and sequential deposition from multiple sources

There are two major categories of growth techniques, which can be utilized: in-situ and ex-situ film growth. In-situ high-T_c superconducting films are superconducting when they are removed from the growth chamber. In-situ films are deposited onto a heated substrate. The presence of oxygen and substrate temperature of about 700°C to 750°C is essential for crystallization of tetragonal YBCO during deposition. The tetragonal to orthorhombic phase transition is allowed to take place at certain ambient in between 550°C- 450°C for few hours before cooling down the system to room temperature. In situ formation of YBCO results in layer by layer crystallization, yielding epitaxial layers exhibiting smooth surface morphologies. Hence the fabrication of multilayer’s is possible. On the other hand, in ex situ method, proper ratio of Y, Ba and Cu are deposited on to a substrate held at relatively low temperature (200°C to 400°C). The resulting precursor film is therefore usually in a structurally amorphous state and the film crystallization must be performed in a subsequent annealing steps taking place at elevated temperatures around

800^oC to 900^oC.Annealing in the presence of oxygen is performed in the furnace outside the vacuum chamber in which the tetragonal to orthorhombic phase transition is allowed to take place by keeping films at around 450^oC-550^oC for few hours.

A substrate heater which would operate in vacuum and under oxygen up to 900^OC is required. In order to ensure good thermal contact between heater and substrate a suitable method of heat transfer has to be chosen. Silver pastes are used for better thermal contacts between substrate and heater.

II CO-EVAPORATION

Co-evaporation is the first multiple source growth technique used to produce high-T_c thin films [1]. In this technique, a separate source is required for each metal to be deposited and each source must have real -time rate control of deposition. Further more, the composition of the film will vary across the substrate unless its dimensions quite small compared to its distance from the sources. The deposition of superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) thin films by electron beam co-evaporation (figure 1) of metals Y, Ba and Cu has difficulty of performing the evaporation in relatively high ambient pressure of O_2 necessary to promote in-situ growth of the film. The deposition rate is typically 0.1-1 nm/s.

The most successful ex-situ deposition by this technique is the BaF_2 process, which uses BaF_2 instead of Ba metal source [2]. The precursors films are stable in air, whereas precursor films that contain Ba metal tend to react to form carbonate that are difficult to dissociate during the post anneal. Molecular beam epitaxy (MBE) [3,4] technique used for in-situ deposition of high quality epitaxial growth of YBCO via the interaction of one or several molecular or atomic beams that occurs on a surface of a heated crystalline substrate using co-evaporation of constituent elements. Solid materials are placed in evaporation cells to provide an angular distribution of atoms or molecules in a beam. MBE takes place in ultrahigh vacuum with lower deposition rate less than 3000nm per hour that allows the film to grow epitaxially.

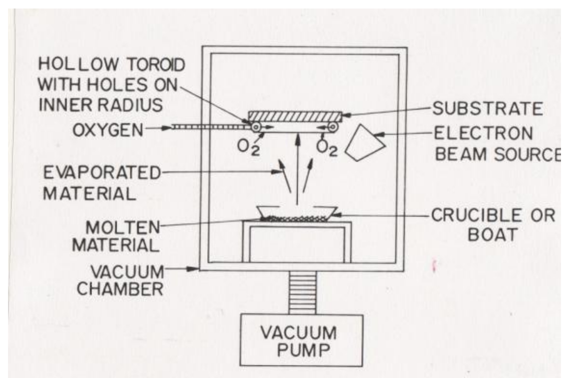

Figure 1 Schematic view of basic electron beam evaporation process for production of YBCO thin film from single source

III SPUTTERING

In sputtering, positive ions from a glow discharge, after acceleration across the cathode dark space, strike the target and remove neutrals, ions and secondary electrons by momentum transfer. The target species then deposit onto a heated substrate that is located near the target. The glow discharge is initiated and self sustained by applying a suitable voltage across anode and cathode and by adjusting the pressure of an inert sputtering gas such as argon in the range from a few to few hundred milli torr. Energy can be imparted to the growing film by substrate heating and biasing. Sputtering can be performed using either multiple targets[5] or a single oxide target [6].

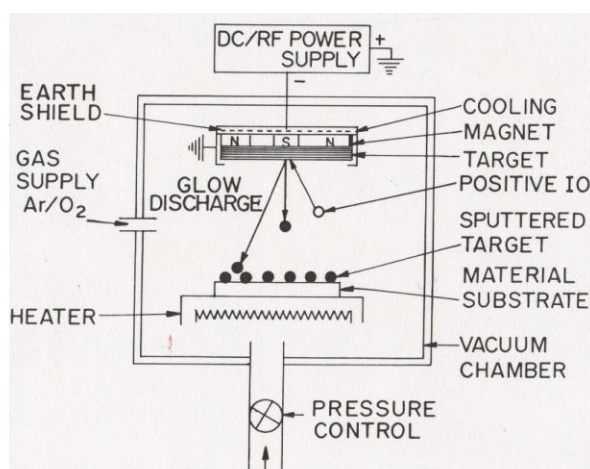

Figure 2 Schematic view of sputtering process positive argon atoms in the plasma is accelerated towards the negative target where they dislodge group of atoms. Some of these atoms are deposited on to the substrate to form the film.

Mostly, planer circular magnetron guns are being used at present for the deposition of high-T_c superconducting thin films. In magnetron guns, the magnetic field usually enters and leaves the target normal to the target face so as to avoid sputtering from the target edges and to maximize the transverse field component. The secondary electrons in magnetrons are accelerated by the potential difference between the cathode and plasma, they acquire curved trajectories under the influence of the transverse magnetic field prior to bombarding the anode or the substrate, are thermalised to energies of $\approx$ 1 eV because of the ionization and collision process. However, an electron escaping along the magnetic field lines, after emerging from the cathode, can impinge directly on the substrate with the full potential of the cathode. Planer magnetron sputtering cathodes (figure 2) are most popular but suffer from a non-stoichiometric transfer of the elements from the target to the substrate.

Dc sputtering requires conducting targets consisting of metallic constituents or stoichiometric superconducting phases that have fairly high normal state conductivity. According to ternary phase diagram of Y_2O_3, CuO and BaO, the phases surrounding the conducting $YBa_2Cu_3O_{7-x}$ orthorhombic phase are either semiconducting or insulating. The conducting and semiconducting phases on the target surface will continue to sputter while the insulating phase will remain. This will consequently change the composition of sputtered films.

Rf sputtering allows the deposition of insulators as well as other materials. Insulating composite targets can be sputtered in a rf glow discharge because the rf-voltage that can impart energy to oscillating electrons can be coupled through any kind of impedance.

In on-axis geometry, the substrate faces the target [7]. This configuration gives reasonable deposition rates (0.1 nm/s), but the deposition of stoichiometric thin films is very difficult on a substrate exactly facing the plasma ring region [8], mainly due to re-sputtering of the deposited film by negative oxygen ions, which results in a film with non-stoichiometric composition. Negative oxygen ions are formed at YBCO target due to the large difference in electro negativities between oxygen and barium. To avoid re-sputtering of the growing film by negatively charged energetic oxygen ions special precaution are taken using high sputtering pressure (because the harmful ions could be thermalised due to large number of collisions by the

time they reach the substrate), substrate position in an off-axis configuration, much stronger magnets in the magnetron source and low sputtering power.

The main modification in off-axis [9, 10] deposition is the change of substrate orientation in relation to the plasma. The surface of the substrate lies parallel to the plasma axis and the material deposition can only take place if the species inside the plasma have a significant velocity component perpendicular to their main expansion direction. This is possible because of high deposition pressure. For light particles such as atoms, ion and molecule, these impact results in a Brownian like motion of the particles leading to a material deposition on the substrate in spite of off-axis configuration. The material deposition occurs only via a diffusion process out of the plume. An important advantage of the off-axis deposition geometry is the probability of in-situ double sided film preparation, since the substrate is fixed in a frame having both surfaces open for simultaneous deposition and homogeneous heating by radiation from a heater [11]. The major drawback of the off-axis geometry is the relatively low deposition rate.

In hollow cathode sputtering system [12] the target consists of hollow cylinder and the substrate is placed at some distance from one end with its surface normal to the axis of the cylinder. An axial magnetic field confines the plasma to the inside of the target enabling one to achieve high sputtering rates while keeping the substrate free of negative ion bombardment. A disadvantage of the technique, however, is that it requires large, cylindrical targets which are difficult to fabricate (with diameters greater than 50-75 mm). A dc hollow cathode sputtering system are used for deposition of large area high quality YBCO thin films from hollow stoichiometric target of 75mm outer diameter and 67mm inner diameter with thickness of 20mm[13].

Ion beam sputtering (IBS) has been chosen to overcome certain drawbacks associated with magnetron sputtering, (such as energetic ion bombardment and non-uniformity) and with laser ablation, (such as droplet deposition). In IBS films grow nearly unaffected by energetic primary and secondary ions because they are located away from the sputtering plasma. The ion beam is carefully confined to the target, which is kept at floating potential so that the majority of the sputtered species has kinetic energies much below the sputtering threshold and O- ions cannot be launched from the target. Due to two to three orders of magnitude lower total pressure less gas is

trapped at the grain boundaries and surface diffusion of condensing film constituents is less impeded, thus, YBCO crystallization can occur at distinctly lower growth temperature [14].

IV LASER ABLATION

The in-situ pulsed laser deposition (PLD) [15, 16] technique is one of the simplest and most versatile methods for deposition of YBCO thin films. The relatively low number of control parameters, as well as the stoichiometric removal of constituent species from the target during deposition makes the PLD technique (figure 3) particularly attractive for growth of complex multicomponent material. The essential process of PLD consists of melting and evaporating the target material with the pulsed laser beam. In PLD of YBCO thin films, a short periodic focused laser pulse strikes the surface of the target which is a solid bulk YBCO. The evaporated material expands perpendicular to the target surface forming so called plume comes in contact with surface of heated substrate kept away from the YBCO target. The plume which consist building blocks of the YBCO lattice, cover the substrate. The result is the fabrication of thin films of YBCO material with the same chemical structure as the target. PLD offers numerous advantages including film stoichiometry closed to the target, high deposition rate, low contamination level and non–equilibrium processing. The accessible experimental parameters are substrate temperature, the energy of the atom flux, the relative and certain arrival rate of atoms for compound films and the pressure in the chamber.

The basic experimental design for thin film deposition by laser ablation [17] is similar to other physical vapor deposition process. An excimer laser which operates using a mixture of Kr, F_2, He and Ne generates pulses with a wavelength varying from 193nm to 308 nm is used for target ablation. The growth chamber contains substrate holder with heater block, a rotating target holder and a shutter. The oxygen pressure during deposition is regulated using mass flow controller and a micro valve. The substrate is generally positioned at 2.5-4.5 cm from the target and heated at 700^oC-800^oC depending upon the system. The laser target interaction deepens on the laser properties such as pulse duration, intensity, wavelength, and the target properties such as vaporization energy, absorption depth, specific heat and thermal conductivity. Laser deposition does not have a problem with negative ion bombardment as in case of sputtering.

The target is rotated slowly to prevent it from being pierced by the laser beam, which has energy density in the range 1.22- 1-5 J/cm^2. The stoichiometry of the deposited film depends on a number of parameters besides target composition such as background gas pressure, laser energy density, and substrate temperature. Reasonable deposition rates of 0.1-0.5 nm/s are possible with PLD, but the area of uniform deposition is typically very small. [18]. The film produced is relatively pinhole free. The films ablated at short wavelengths laser beam were smoother with fewer particulate and showed lower normal state resistivity.

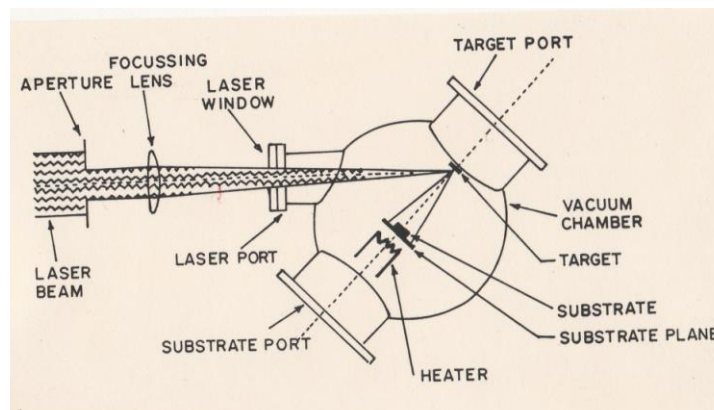

Figure 3 An apparatus for YBCO thin film growth by pulsed laser ablation

V Metal Organic Chemical Vapor deposition (MOCVD)

The in-situ growth of $YBa_2Cu_3O_{7-x}$ (YBCO) superconducting thin films by MOCVD process (figure 4) uses chemically reactive gases to deposit thin films on the substrate. In this technique [19, 20] the growth process involves preparation of organo-metallic precursors, which slowly sublime when heated to 100°C to 300°C. The organo-metallic vapors are then swept into the reaction chamber by a carrier gas onto the heated substrate, where the formation of the desired compound takes place by its pyrolysis and recombination of the atomic or molecular species. MOCVD chamber maintained at 600°C-800°C and at a pressure of 1-10mm of Hg. Growth rates and the uniformity in composition and thickness are controlled by the transport phenomena of heat, mass and momentum transfer in the reaction zone. The volatile compounds for the metallic constituents of superconductors, beta- diketonate complexes such as acetylacetonates and dipivaloylmethanates have been successfully used as source metal organic complexes. The quality of the films grown is affected by the deposition temperature, substrate material and post deposition annealing procedure. There is possibility of depositing high-T_c material over large area using this technique.

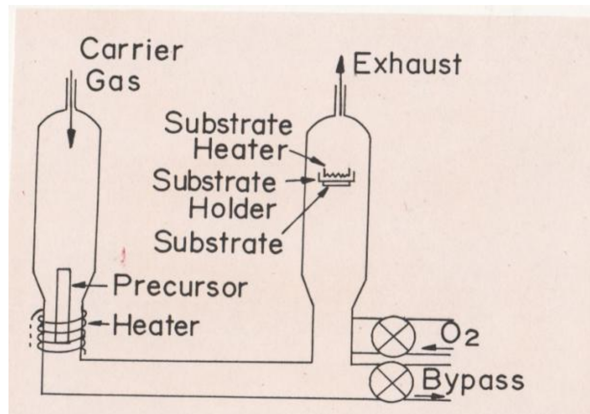

Figure 4 An apparatus for film growth by solid source metallorganic chemical vapor deposition

VI CONCLUSIONS

The fabrication of homogeneous high quality YBCO thin films on large area substrates is the first essential steps on the way to commercial high temperature superconductor devices. Control of composition and the preferred orientation of the films is perhaps the most challenging aspects of high- T_c thin films growth. We need a growth method in which the composition can be controlled in-situ with increasing precision. There is great need of development of system for double sided and large area film deposition, in particular a heater that allows the substrate to be at uniformly heated at higher fixed temperatures. It is mandatory to eliminate high angle grain boundaries in thin films by innovative deposition scheme. The attention should be given to the properties of low angle grain boundaries in high quality films. The thermal contact of substrate with heater is made with silver paste, which is not practical beyond 5cm diameter. Another issue is the oxygen concentration; it is desirable to investigate which oxygen concentration optimizes the device performance. There is large impact of defects and growth morphology on physical properties such as microwave surface resistance, critical current, critical thickness and interface resistance. Subsequently, technological processes have to be developed to control the morphology and creation of adequate defects in order to tune the physical properties of the films according to the requirements.

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