Incorporation of hyperfine probes into the thin-film superconductor YBa$_2$Cu$_3$O$_{7-\delta}$ during deposition

D. W. Tom, R. Platzer, John A. Gardner, and J. Tate
Department of Physics and Center for Advanced Materials Research, Oregon State University, Corvallis, Oregon 97331-6507

Radioactive ^{111}In has been incorporated into oriented thin films of YBa$_2$Cu$_3$O$_{7-\delta}$ during a thermal coevaporation process. The hyperfine technique of perturbed $\gamma\gamma$-angular correlation spectroscopy shows that 60% of the indium substitutes at a single site in the superconductor. We obtain spectra with reasonable statistics from 2 mCi of starting material, about 1% of which is incorporated into the film. Other methods of incorporating indium into films and bulk YBa$_2$Cu$_3$O$_{7-\delta}$ have often resulted in a significant amount of indium being incorporated into impurity phases.

Perturbed $\gamma\gamma$-angular correlation spectroscopy (PAC) is a powerful method for studying the microscopic structure of materials[1] like ceramics,[2] semiconductors,[3] and high temperature superconductors.[4-6] The electric quadrupole moment of a dopant radioactive nucleus interacting with the electric field gradient (efg) at the nucleus produces a site-specific signature in the $\gamma-\gamma$ correlation function, measured as the nucleus decays. The PAC spectrum yields the strength and symmetry of the efg, and information about the homogeneity of the probes' environments. These can be affected by structural changes, diffusion of mobile species, temperature, and pressure. PAC is complementary to other techniques like x-ray diffraction (XRD) and transmission electron microscopy (TEM), in that it gives not only structural information, but also a microscopic understanding of atomic mobility. It can also be used to probe surfaces and interfaces. The radioactive probe is extremely dilute, and does not significantly alter the overall stoichiometry or structure of the material, although local relaxations are possible. A common PAC probe, ^{111}In, with a half-life of 2.8 days, requires only about 10^{12} probe nuclei which is orders of magnitude less than is required for other hyperfine techniques.

Often applied to randomly oriented powders, PAC spectroscopy yields more information when applied to oriented material like epitaxial films and single crystals.[7] It is common to incorporate radioactive indium into crystals and films by ion implantation, but the range of the indium may be limited, and the thermal processing required to anneal the radiation damage can degrade the material in ways that are often difficult to understand. A vapor phase epitaxy technique[8] has addressed this problem in GaAs. We favor the incorporation of the indium into the bulk during growth, particularly for high temperature superconductors where the temperature required for indium diffusion is comparable to the decomposition temperature. Below we describe a thin-film deposition system for high temperature superconductor, modified to allow coevaporation of radioactive indium. We show PAC spectra of two films to illustrate the characterization potential of this technique.

Thin films of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBaCuO) are evaporated from the constituent metals in a molecular oxygen environment in a system similar to that described by Berberich *et al.*[9] Yttrium, barium, and copper metal are evaporated from tantalum evaporation boats, each of which has a separate and independent evaporation rate monitor and power supply. A quartz crystal oscillator monitors the evaporation rate. A PID feedback system in a Sycon 200 STC controller, in conjunction with a triac power controller, maintains the set rate. (We measure the film stoichiometry by Rutherford backscattering or electron microprobe analysis and calibrate the set rates accordingly.) The substrate is heated by a pyrolytic graphite heater to about 650–700 °C, and is bathed in oxygen at a local pressure of about 10^{-2} Torr during deposition.

Efficiency and safety were crucial considerations in modifying the system to coevaporate radioactive material (see Fig. 1). The efficiency of the evaporation process is improved by using a cannon-shaped boat to collimate the flux. We achieve an efficiency of about 1%, so for 10 μCi in the film (about 10^{11} atoms of ^{111}In), we start with 1–2 mCi in the source. This needs bulky shielding to ensure the operators' safety. The indium itself is on a thin, copper foil
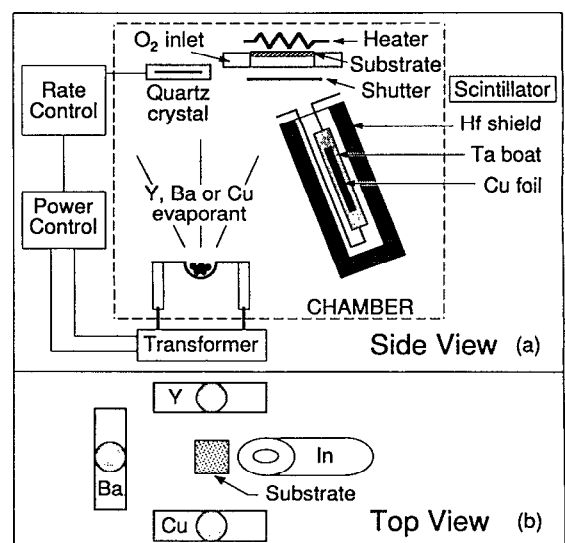

FIG. 1. Schematic of the evaporation system.

inside an evaporation boat. The boat is a 0.08-mm sheet of tantalum, welded into a 5-mm-diam cylinder with one end pinched closed. The boat is inside two ceramic tubes which insulate it from its leads and from an outer, cylindrical hafnium shield that provides >90% attenuation of the γ rays emitted from [111]In. The shield sits in an easily accessible, adjustable cradle.

After evaporation, most of the radioactivity is distributed in a 1.5-cm-diam spot directly opposite the indium source, but because the indium sticking coefficient is less than unity at these temperatures, the other evaporants and oxygen distribute a small amount of the indium in the chamber. Aluminum foil shields other components from radioactive indium wherever possible. Disposal of the foil after each deposition results in a nearly clean evaporator. The 2.8-day half-life of ^{111}In is short enough to eliminate radioactive buildup at the levels we use and the frequency at which we operate.

[111]In is received in the form of $InCl_3$ in HCl solution. A clean, outgassed piece of copper foil and the dried $InCl_3$ are placed inside a quartz tube sealed at one end. The tube is filled with hydrogen gas and sealed at the other end. A temperature gradient is established with the $InCl_3$ at about 700 °C and the copper at about 300 °C. $InCl_3$ dissociates and hydrogen combines with the chlorine to form HCl. The indium is transported to the cooler end of the tube, where it plates out preferentially onto the copper foil. This process is about 80% efficient. We break the tube, place the foil in the shielded evaporation boat, and transport the shield and its contents to the evaporator.

Once the substrate is at the proper temperature, the oxygen pressure is correct, and the yttrium, barium, and copper evaporation rates have stabilized, a shutter opens, exposing these evaporants to the substrate. At some later time, which depends on the desired probe location, we heat the boat containing the radioactive indium. A photomultiplier tube with a gamma scintillator outside the chamber monitors the ^{111}In evaporation. The indium evaporates within about 30 s, which, for this configuration, confines it to a 50-nm layer in the YBaCuO film. The resulting probe density is approximately 10^{17} cm^{-3} or 1 probe per 50 000 unit cells, assuming about 10^{11} probes are incorporated. We anneal the film *in situ* for 45 min at 475 °C with oxygen pressure at 10 Torr, and cool it to room temperature at 10 Torr. It is then removed from the evaporator and mounted in a four-detector PAC spectrometer. The entire procedure, from receipt of indium to finished film, can be as short as 10 h.

The films are characterized by standard techniques. XRD shows textured, c-axis oriented films with less than a few percent of other phases. TEM confirms the c-axis orientation and reveals that the films are twinned with the a and b axes aligned along the principal axes of the SrTiO₃ ⟨100⟩ substrate. Rutherford backscattering indicates a 50% channeling yield of both film and substrate. The transition temperatures are about 89 K, with a width of about 1 K.

Figures 2(a) and 2(b) show room temperature ^{111}In/Cd PAC spectra we obtained from two 200-nm thin

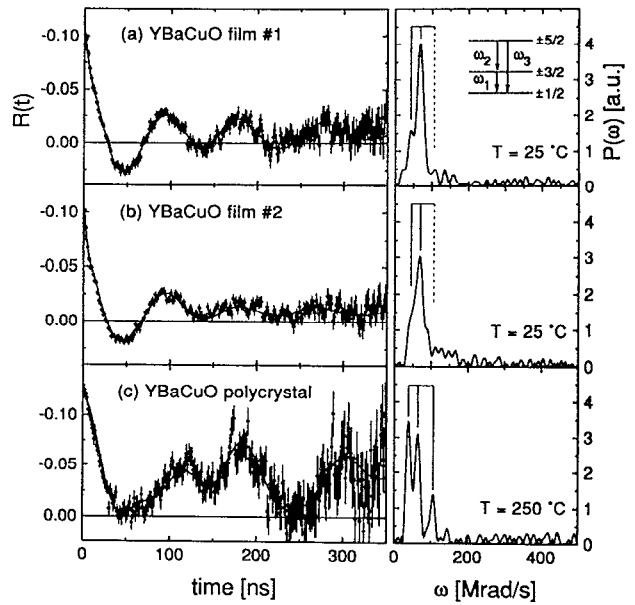FIG. 2. (a)–(b) [111]In/Cd PAC spectra of $YBa_2Cu_3O_{7-\delta}$ thin films. The c axis of the films is perpendicular to the detector plane, while the a and b axes point between the detectors in plane. (c) Spectrum of bulk, powdered $YBa_2Cu_3O_{7-\delta}$ (Ref. 10).

films of YBaCuO, and Fig. 2(c) shows a spectrum of a powder sample.[10] We give a very brief description of the PAC method to allow the reader unfamiliar with it to interpret the spectra; detailed accounts can be found elsewhere.[11] [111]In decays to an excited state of [111]Cd which in turn decays to the ground state by the successive emission of two gamma rays (172 and 243 keV). The gamma rays are detected by four scintillation detectors in a plane at 90° angular separation. Events in which the first gamma ray enters one detector and the second enters another are collected in a histogram as a function of the time between gamma-ray emissions. From these data, an experimental function $R(t) = A_{22}G_{22}(t)$ can be formed, where A_{22} is the effective anisotropy, typically ~ -0.1 here, of the $\gamma\gamma$ cascade and the function $G_{22}(t)$, the PAC time function, is unity if no electric field gradient is present at the [111]Cd nucleus during the lifetime of the intermediate state ($T_{1/2} = 85$ ns). If a static efg is present

$$R(t) = A_{22} \sum_{n=0}^{3} s_n \exp(-\Delta\omega_n t)\cos(\omega_n t), \qquad (1)$$

where ω_1, ω_2, and $\omega_3 = \omega_1 + \omega_2$ arise from the energy splitting of the $I = 5/2$ [111]Cd nuclear levels [inset, Fig. 2(a)]. Minor variations in the efg due to distant impurities and other defects are common and are well described by a small Lorentzian line broadening, which appears as exponential damping in the time domain. The amplitudes s_n depend on the symmetry and the orientation of the efg relative to the detector system and can be calculated for a given geometry.[12] If more than one site were occupied, the right-hand side of Eq. (1) would contain an additional sum over sites with each term multiplied by the appropriate fraction of probes at each site.

From a fit to the PAC time spectra, we find that 60% of the probes are located in the single site indicated in Fig. 2. The room temperature quadrupole frequency, $\nu_Q = 39$ MHz, and the asymmetry parameter, $\eta = 0.5$, are the same for both the films and the major site previously identified in powdered material.[4] The remaining 40% are subject to interactions with a broad range of frequencies. Some portion of these may be incorporated into other sites in the unit cell, twin boundaries, grain boundaries, second phases, or amorphous material. About 3% must be incorporated into a well-defined crystalline site to be detectable.

The PAC spectra of the two YBaCuO films differ from that of the bulk, powdered material in that the orientation of the film is evident. The ratio of the peak amplitudes at ω_1, ω_2, and ω_3 is as expected for each configuration. The suppression of the peak at ω_3 and the reduction in amplitude of the peak at ω_1 in the films implies that the principal axis of efg is directed between the detectors, i.e., along the a or b axes (the film is twinned) for this geometry. The spectra from the films differ from each other in that the linewidth is narrower for (a) than for (b), indicating that the probes' surroundings are more uniform in the former case. Cation disorder is a possibility in (b). Electron microprobe results also indicate that the composition of the film (a) is more homogeneous than (b). Annealing some films at 500 °C in oxygen narrowed the linewidth in the spectra and reduced the asymmetry parameter. The films may have been slightly oxygen deficient prior to annealing, so that the uptake of oxygen improved the homogeneity.

There is no evidence in the films of any signal from Y_2BaCuO_5 or $Y_2Cu_2O_5$,[13] the major impurity phases in bulk synthesis. PAC in high quality bulk, sintered $YBa_2Cu_3O_{7-\delta}$ often yields spectra dominated by these impurity phases even if they are present in quantities undetectable by x-ray diffraction. This suggests that indium preferentially diffuses into them at the high processing temperatures. The thin-film synthesis takes place at much lower temperature, so the indium is certainly less mobile once it is trapped in the "bulk" of the film, but it may be highly mobile on the surface. In the absence of a detailed mechanism for the film growth, it is difficult to determine whether the indium preferentially migrates to the impurity phases as it does in the bulk. If it does, then the films are phase pure; if not, then we give up sensitivity to impurities in exchange for information about YBaCuO.

There has been only one report of ^{111}In PAC in YBaCuO films.[5] The authors diffused ^{111}In into a YBaCuO film at 742 °C in 1 mbar of oxygen, and annealed it at 457 °C in 1 atm of oxygen for 20 h. The resulting spectrum is the same as the one we obtained using a similar 700 °C diffusion technique on high quality YBaCuO films. (Our films were severely degraded after the treatment.) The spectrum is identical to that obtained from [111]In:$Y_2Cu_2O_5$ PAC spectroscopy, and bears no resemblance to the film spectra presented here.

We have developed a reliable method for codepositing trace amounts of radioactive ^{111}In into oriented thin films and have obtained reproducible PAC spectra from ^{111}In in thin films of $YBa_2Cu_3O_{7-\delta}$. The spectra are consistent with indium substitution at a single site at which an electric field gradient is present. We see clear evidence of the orientation of the films in the PAC spectra, and conclude that the electric field gradient at the substitutional site is in the ab plane. The magnitude of the electric field gradient at this site is the same as in the bulk material. This method provides a new means to investigate the structure, orientation and oxygen mobility of different regions of the film, with the probes being confined to ~ 50-nm slices. The correlation of the PAC measurements with properties of the films under different processing conditions will certainly yield interesting information. Future investigations of the substrate-film interface and the film surface should provide a deeper insight into the growth mechanism of epitaxial YBaCuO films.

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