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Theoretical model of heat exchanges during the rapid thermal annealing of YBaCuO thin films

J.M. Depond, J.C. Martin, F. Carrié, E. Caristan and A. Kreisler [a], C. Martin and D. Tétard [b]

[a] Laboratoire de Génie Electrique de Paris (LGEP) - Universités Paris 6 et Paris 11 - URA n°127 du CNRS
SUPELEC - Plateau de Moulon, 91192 GIF SUR YVETTE CEDEX, FRANCE

[b] Laboratoire de Matériaux Céramiques et Traitements de Surface (LMCTS) - URA n° 320 du CNRS
Université de Limoges - Faculté des Sciences - 123 avenue Albert Thomas, 87060 LIMOGES CEDEX, FRANCE

Abstract

A rapid thermal annealing technique used to process *ex situ* YBaCuO thin films previously rf-sputtered on industrial substrates is analysed and interpreted in terms of thermal conductivities. A key result is that a dominant contribution of indirect conduction heating is observed instead of the expected direct radiation heating. An experimental validation of the model to optimize the superconducting properties of the film is described.

1. Purpose of the study

We have developed an original process to obtain *ex situ* YBaCuO superconducting thin films on industrial substrates such as silicon or polycrystalline zirconia (fig. 1). After deposition by rf-sputtering, the sample undergoes several rapid thermal annealing (RTA) cycles, a regular treatment in semiconductor technologies, to acquire final superconducting characteristics, typical of granular thin films ($T_{R=0}$≈85 K, J_c≈3000 A/cm^2). As opposed to long thermal annealing and to the now widespread *in situ* technique, RTA limits the interdiffusion between film and substrate (particularly for silicon wafers) and further enhances YBaCuO grain growth in a fast step after deposition.

The whole set of RTA parameters has been optimized for a 0.5 to 1 µm thick YBaCuO film deposited on 1.3 mm thick 3 or 8 mol % yttria stabilized polycrystalline zirconia (YSZ) (fig. 1). However, RTA brings into play a lot of non-equilibrium processes which makes necessary detailed analysis and thermal modelling to improve the optimization of the annealing parameters for a thin film deposited on other substrates such as 0.1 mm thick YSZ or very reactive silicon.

After a rapid presentation of the RTA technique, we analyse it in terms of heating processes and present a set of modelling equations. We then show some results of numerical computations and parameter determination, leading to a successful application of the model. Finally, possible foreseen refinements of our model are discussed.

2. Rapid thermal annealing (RTA)

A typical RTA cycle lasts about 5 minutes and is formed of three segments (fig. 1, insert): (i) fast heating from room temperature to a typical value of 920°C within 10 seconds under a neutral atmosphere (flowing argon); (ii) dwell during 60 seconds under the same atmosphere; (iii) inertial cooling during a few minutes down to room temperature under flowing oxygen.

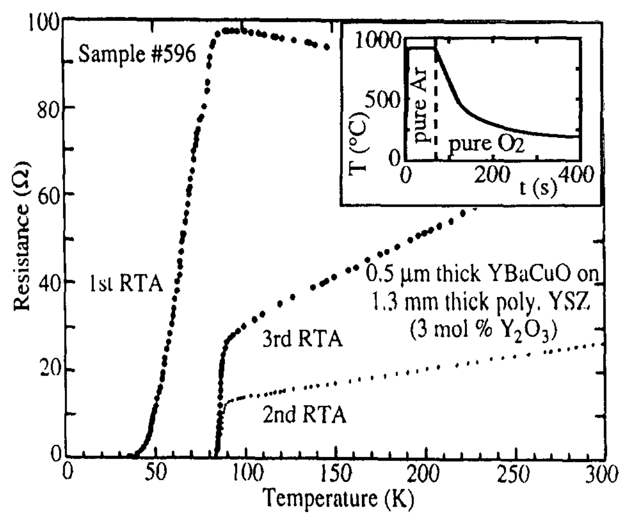

Figure 1. Optimization of superconducting characteristics by the RTA cycle (insert) developed at LGEP (after refs. 1 and 2)

Such temperature dynamics are accessible owing to the radiative type of the furnace which makes use of infrared quartz heating tubes allowing to reach 1000°C within 3 seconds. However, the samples which are placed on a 100 mm diameter 0.5 mm thick silicon wafer (fig. 2) are also heated by conduction.

3. Thermal modelling of the RTA

We have worked out a thermal model of the RTA based on the laws of thermal conduction. In a first step, we have determined a set of hypotheses which describes

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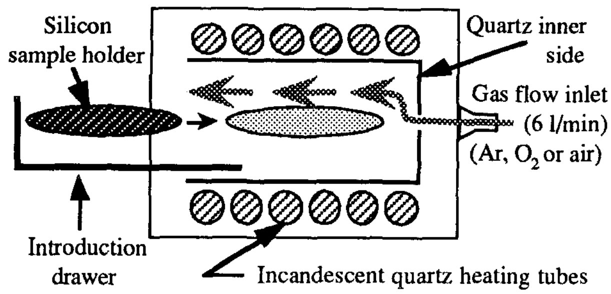

Figure 2. Sketch of the RTA furnace (ADDAX model R1000, Grenoble, France)

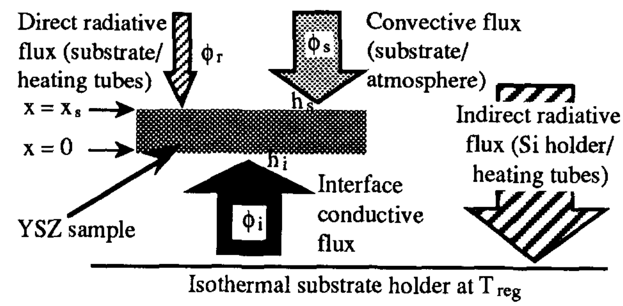

Figure 3. Model of heat exchanges inside the RTA furnace

all the heat exchanges occurring inside the radiative furnace. In a second step, we have written a code based upon a relaxation method referring to measurements done on a 1.3 mm thick YSZ sample.

3.1. Hypotheses

The starting hypothesis is that, in the sample, the only heat propagation mode is conduction (eqn. 1). The other hypotheses are (see figs. 2 and 3):

(i) Long distance effects, such as perturbations due to the inner sides of the furnace and possible convection vortices are neglected .

(ii) The position of the gas inlet on the same level as the sample and the continuous gas flow during the whole RTA prevent surface convection phenomena. Therefore the heat exchange between the sample and the atmosphere can be modelled by a simple perpendicular flux (eqn. 4).

(iii) The thinness of the silicon sample holder (0.5 mm), the very high thermal diffusivity of silicon at RTA temperatures ($\approx$ 0.3 cm^2/s), the uniform illumination produced by the incandescent tubes and the position of the regulator thermocouple sensor (directly placed onto the wafer) allow to consider the holder as an isothermal plane at the regulation temperature T_{reg}, even for relatively short RTA time scales. So we model the contact between the sample and the silicon wafer by a simple perpendicular conducting exchange flux with a known isotherm (eqn. 3).

(iv) The absorptivity of YSZ in the range of incandescent tube wavelengths is lower than 10% and allows to neglect radiation absorption. This involves that no internal heat source has to be considered and that the furnace behaves as a conductive device during the RTA. We have admitted that the radiation is only absorbed by the upper side of the sample which can be represented by a perpendicular heat exchange surface (eqn. 4).

We have first developed a 1D modelling justified by the observed homogeneous temperature surface distribution. Moreover, as we had to determine the exchange flux coefficients of the model, we have primarily worked with substrates without YBaCuO film. YBaCuO would induce a new heat exchange interface (see part 5).

3.2. Equations and boundary conditions

The general equation to solve is the conduction heat propagation in a homogeneous and isotropic solid:

$$\operatorname{div}\left[- K(T)\,\overrightarrow{\operatorname{grad}}\, T \right] + \rho\, C_p \frac{\partial T}{\partial t} - p = 0 \qquad (1)$$

where K is the thermal conductivity, ρ the volumic mass, C_p the specific heat of the propagation medium; all these parameters are temperature dependent. p is the power delivered by possible internal sources.

Hypothesis (iv) yields $p = 0$ and, introducing an intermediate variable $\Theta(T)=\left(1/K_0\right)\int_{T_0}^{T} K(\tau)\,d\tau$ where T_0 is a reference temperature and $K_0 = K(T_0)$, we have to solve:

$$\Delta\Theta - \frac{1}{\alpha(\Theta)}\frac{\partial \Theta}{\partial t} = 0 \qquad (2)$$

where $\alpha = K_0/\rho\, C_p$ is the thermal diffusivity.

Our hypotheses yield two equations for the boundary conditions. First

$$-K(T)\left.\frac{\partial T}{\partial x}\right|_{x=0} = -K_0 \left.\frac{\partial \Theta}{\partial x}\right|_{x=0} = \phi_i = h_i \left(T_{reg} - T_{x=0}\right) \qquad (3)$$

at the sample holder/substrate interface. ϕ_i is the conductive flux and h_i the interface heat exchange coefficient. Secondly

$$-K(T)\left.\frac{\partial T}{\partial x}\right|_{x=x_s} = -K_0 \left.\frac{\partial \Theta}{\partial x}\right|_{x=x_s} = \phi_s + \phi_r \qquad (4)$$

on the surface of the substrate. $\phi_s = h_s\,(T_{x=x_s} - T_{reg})$ is the convective flux between the sample and the furnace atmosphere with h_s the heat exchange coefficient. $\phi_r = \sigma F_\varepsilon F_g\,[(T_{x=x_s})^4 - (T_{tube})^4]$ is the radiative flux between the sample and the incandescent tubes where σ is the Stefan-Boltzmann constant, F_ε the emissivity function and F_g the form factor associated with the sample. This flux disappears with the tube extinction, i.e. when cooling stops to be linear with temperature. Cooling then becomes really inertial.

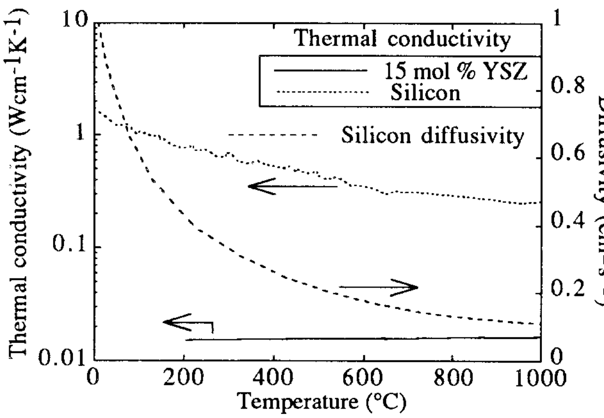

Figure 4. Thermal properties of 15 mol % YSZ and Si according to Touloukian and Dewitt [3]

3.3. Principles of the computation

The problem is solved by an iterative method, i.e. a relaxation algorithm. We use a Simultaneous Over Relaxation technique with Chebyshev acceleration to solve:

$$\alpha(\Theta)\Delta\Theta - \frac{\partial \Theta}{\partial t} = \frac{\partial \Theta}{\partial \tau} \qquad (5)$$

with τ a relaxation variable.

This leads to solve after an obvious discretisation:

$$\frac{\alpha(\Theta_i^{n,s})\Delta t}{(\Delta x)^2}\left[\Theta_{i+1}^{n,s}-\Theta_{i-1}^{n,s}\right] - \left[\frac{2\alpha(\Theta_i^{n,s})\Delta t}{(\Delta x)^2}+1\right]\Theta_i^{n,s}+\Theta_i^{\infty,s-1}=0 \qquad (6)$$

where n is an iterative index (associated with $\Delta\tau=1$, the relaxation time step), i a spatial index (associated with the geometrical net step Δx) and s a time index (associated with the time step Δt). These two latter steps are linked by a law of acceleration of convergence $\alpha(\Theta)\Delta t \approx (\Delta x)^2$.

3.4. Parameter Determination

The model needs some basic data such as emissivity, thermal conductivity and diffusivity of the substrate in the 20 to 1000°C range (fig. 4) and also the heat exchange coefficients h_i and h_s. The latter bring a real difficulty because they are not measurable in our case.

We have chosen an alternative way to access these data by running the code in a fixed case (a 1.3 mm thick 8 mol % YSZ substrate) until reobtaining the experimental values. Such a method needs a good knowledge of the thermo-physical properties of zirconia. Unfortunately we have noted that there are great discrepancies between the data available from literature and our room temperature measurements (performed at LMCTS by a flash method [5]). So we have taken the following assumptions: (i) 8 mol % YSZ having an opaque white polished aspect and being weakly absorbing in the far

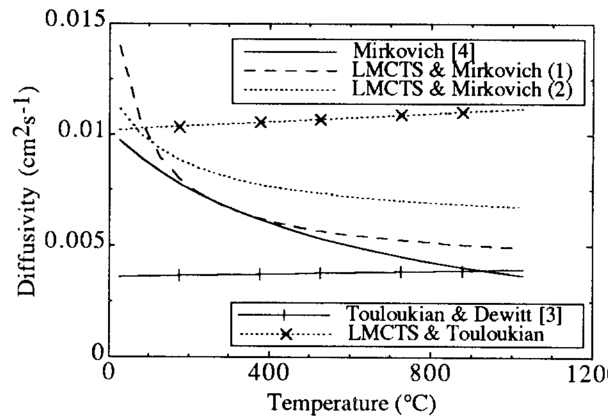

Figure 5. Diffusivities of 8 mol % YSZ deduced from our measurements (LMCTS) and data from literature

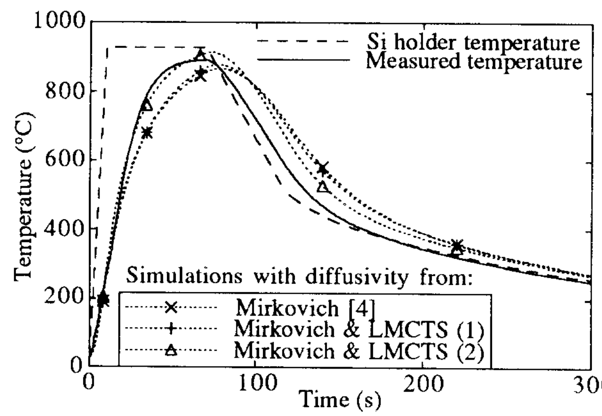

Figure 6. RTA profiles for various simulations; (1) & (2) refer to diffusivities shown in figure 5

infrared range, we fixed the YSZ emissivity function at $F_\varepsilon \approx 0.2$ through the whole incandescent tube spectrum; (ii) the linear thermal conductivity law given by Touloukian and Dewitt is assumed to be valid (fig. 4); (iii) the YSZ diffusivity, function of both the composition and fabrication technique, follows the $\alpha(T) \equiv 1/(A+BT) + C$ law generally valid for ceramics, where A, B and C are constants.

Several extrapolations based on LMCTS room temperature measurements and on Mirkovich's data, referred to as (1) and (2) in figure 5 have been attempted.

The results of the simulation are obviously related to the choice of the function $\alpha(T)$ (fig.6).

However, there are common results to all the calculations: (i) $F_\varepsilon F_g \approx 10^{-3}$ which shows the weak influence of direct radiative heating; (ii) $h_i > h_s$ i.e. the thermal coupling between the substrate and its holder is larger than between the substrate and the atmosphere; this is expected because of the thin gaseous layer at the interface substrate/holder which leads to a simple thermal resistance; (iii) $h_i + h_s \approx 1.5\ 10^{-2}$ which shows a low heating efficiency, understandable by the mainly indirect type of heating. By indirect, we mean that the sample is mainly heated by conduction from the Si wafer holder

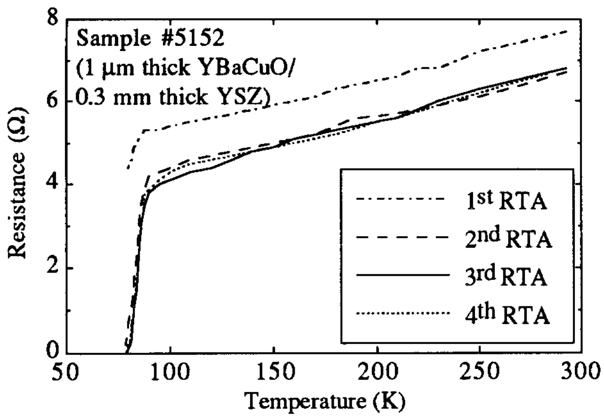

Figure 7. R(T) characteristics after several RTA cycles in the case of the optimized profile for thin YSZ substrates

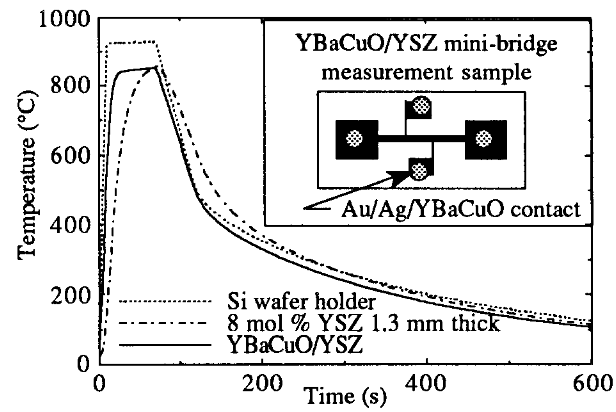

Figure 8. Surface temperatures with and without YBaCuO; the insert shows the geometry used for the electrical tests

which itself is totally heated by radiation from the incandescent tubes.

4. Application of the model

This modelling has allowed to confirm the rapidity of the thermal response of a 0.3 mm thick 8 mol % YSZ substrate, similar to that of a 0.5 mm thick silicon substrate. We have implemented a new RTA cycle tailored to this thin YSZ substrate by applying as reference temperature the surface temperature which was computed for a 1.3 mm thick YSZ substrate submitted to an optimized RTA cycle. In this preliminary study, the YBaCuO film thermal effects have been neglected.

For a film deposited on such a thin YSZ substrate, figure 7 shows R(T) plots confirming the improvement of film characteristics by application of cumulated RTA cycles so modified with respect to the much thicker YSZ substrate case. The YBaCuO film shows needle shaped grains, typical of a RTA process. Nevertheless some blistering occurs as also observed with films deposited on silicon based substrates [2,6]. In the present case however, the blisters are mechanically stable. We explain this blistering by a radiative heat influx into the YBaCuO thin film: the substrate being very thin, there is no thermal inertia to slow down the heating of the film, in opposition to the thick YSZ substrate case; moreover, the substrate being semi-transparent, radiative heating from the silicon holder is possible; finally, YBaCuO is highly absorptive in the incandescent tube spectrum range at the prescribed heating temperatures. Such properties explain the necessity of a lower dwell temperature and an intermediate dwell for silicon substrates, whose thermo-physical properties are not unlike those of thin YSZ.

5. Concluding remarks

We have developed a thermal model of rapid thermal annealing for obtaining *ex situ* superconducting YBaCuO thin films on various substrates. We have found that for thick 8 mol % YSZ substrates, the dominant heating mode is in fact a conductive rather than a radiative heating mode. Moreover, this modelling has allowed us to optimize new RTA cycles adapted to thin YSZ substrates.

We are presently involved in the experimental determination of the h_i and h_s heat exchange coefficients by various methods (lacquer temperature indicators or thin film thermocouples). The thermo-physical properties of 8 mol % YSZ in the 20 to 1000°C range will be measured and its emissivity in a large spectrum will be determined. All these data will enter an elaborate 3D version of the model.

The following step will be the introduction of the not negligible thermal effects of the YBaCuO film (fig 8). In fact, due to the changes undergone by YBaCuO during the RTA cycle, the knowledge of all the thermo-physical properties of each state and phase should be known. Moreover, the YBaCuO film creates a new interface and therefore need of an extra heat exchange coefficient, badly defined in the case of a granular film. However, insofar as only average effects will be accessible through measurements, a simplified behaviour of the film should be sufficient to model an optimum RTA cycle within ±10°C, a satisfactory accuracy for the dwell temperature.

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