

Thermal diffusivity measurements of sub-micron organic dye thin films using a high temperature superconductor bolometer

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The thermal diffusivity of a thin organic dye layer deposited atop thin films of the high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is measured using a pulsed laser flash method. Here, the underlying superconductor acts as a highly sensitive temperature transducer after appropriate conversion of the transient voltage response from 7 ns optical pulses. Film surface temperature decays for several thicknesses of the dye layers were evaluated; these decays exhibited a linear dependence of the time at half temperature maximum versus thickness squared. Three dimensional finite difference modeling was used to study and extract the thermal diffusivity values of the thin organic layers as well as to investigate the transient temperature distributions within the dye and superconductor areas. © 1998 American Institute of Physics. [S0003-6951(98)01145-0]

The laser flash method introduced by Parker *et al.*¹ has become a routine and well characterized method for determining the thermal diffusivity of a variety of materials. Early measurements involved the use of thermocouple detectors at the rear face of relatively thick samples (>1 mm). Recently, however, efforts in the areas of microelectronics and material sciences have focused on the miniaturization of electronic components. These developments have placed new demands on measurement systems that allow for *in situ* measurement capabilities of small dimension films and materials. A wealth of techniques that make use of laser pulse heating for thermal analysis have emerged for which a number of excellent reviews can be found including photothermal spectroscopy (photopyroelectric spectroscopy),² photoacoustic spectroscopy,³ photothermal deflection (mirage effect),⁴ and picosecond time-resolved thermorefectance (forced Rayleigh scattering).⁵

Dielectric materials such as organic and polymeric films have been shown to be studied effectively using the photopyroelectric effect with pyroelectric detectors such as polyvinylidene difluoride (PVDF) and lead zirconium titanate (PZT).⁶ While adequate for film thickness values on the micrometer scale, pyroelectric detectors have never been used for the study of thermal energy transport issues on sub-micron scales. In an effort to extend the laser flash method to smaller distance scales, the exquisite sensitivity of a high temperature superconductor thin film microbridge for the detection of the temperature decay of illuminated dye layers deposited directly onto the surface of the high- T_c film has been used. Devices made from this type of system have previously been shown to be effective wavelength-selective optical sensors where the absorbed energy of the dye enhances the bolometric response over the response of the bare superconductor.⁷⁻⁹ Here, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) thin

film acts as a temperature transducer for the thermal decay of optically excited molecular overlayers. In this letter, we describe an extension of the laser flash method to the study of organic dye layers of sub-micron thickness values. Film thickness dependence of the thermal wave propagation characteristics are evaluated. Additionally, the transient temperature distributions are examined with finite difference modeling studies. Although rhodamine 6G (Rh6G) is the focus of this article, in principle, any chromophoric material could be monitored using appropriate wavelengths of radiation that are absorbed strongly by the thin film structure.

The pulsed laser ablation method was used to deposit a number of 1500 Å thick YBCO(001) thin films on MgO(100) substrates which were subsequently patterned into microbridge devices with bridge dimensions of 150 μm × 6 mm. The Rh6G layers were deposited by vacuum sublimation on exposed regions of the microbridge. Here, the thickness was controlled by a combination of temperature (150–200 °C) and vapor exposure time. Liquid nitrogen was placed in the cold finger to help obtain a smooth dye morphology and to avoid degradation losses in the superconductor film caused by oxygen loss. Electrical characterization of the YBCO microbridge before and after dye deposition reveals that little damage occurs to the high- T_c element during the deposition of the dye layer. A typical final device consisted of two dye layers covering different regions of the microbridge. Each dye pad was deposited near outer regions of the microbridge and the central region was left uncoated to serve as a control. The thickness of each dye laser was determined from multiple scans of a profilometer.

Measurement of the transient response of the dye-coated device was carried out using the doubled line (532 nm) from a Nd: yttrium aluminum garnet (YAG) pulsed laser with a 7 ns pulse width and a repetition rate of 10 Hz, Fig. 1. Laser radiation was focused onto one end of a multimode optical fiber which traversed the vacuum shroud of the cryostat. The other end of the fiber was brought to within ~0.5 mm of the

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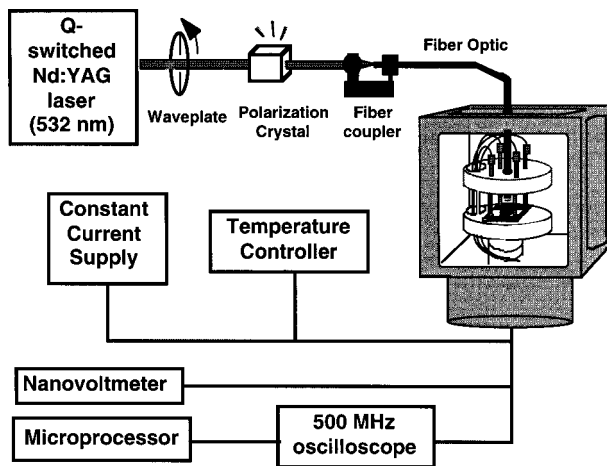


FIG. 1. A schematic of the measurement apparatus is provided. Here, the laser is focused onto a fiberoptic bundle which carries light through the shroud of a cryostat to within ~ 0.5 mm of the structure surface. Resistance vs temperature and voltage vs time measurements are collected with nanovoltmeter and oscilloscope, respectively.

sample surface. The incident power was varied by changing the polarization angle of a waveplate that was used in conjunction with a calcite polarization crystal before coupling to the fiberoptic element. Electrical contact to the high- T_c film was made using a four-point geometry onto gold contacts (contact resistance $< 1 \Omega$) which had been previously deposited onto the four corners of the superconductor film. In all electrical measurements, the microbridge was biased using a constant current source and the length of the measuring cable was chosen to minimize problems with reflections. Prior to measurement of the transient response, a resistance versus temperature curve was collected at the same bias current used during transient response measurements, typically around 10 mA.¹⁰ Accurate knowledge of the transition temperature (± 0.02 K) and resistance values accompanying the superconducting transition enable conversion of the transient voltage to transient temperature profiles.

The pulsed optical response of the uncoated region of all the YBCO microbridges displayed similar behavior observed for early work in this area.¹¹ However, the 7 ns input pulse width was too slow to measure the true bolometric response time of the uncoated YBCO region. Nonetheless, a measured delay in the transient rise time was introduced by the molecular overlayer. This delay was sufficiently long for dye layers having thickness values $> \sim 2500 \text{ \AA}$ that the contribution from the laser pulse profile could be neglected. Figure 2 shows the normalized transient voltage as a function of time recorded for four different thickness values of Rh6G dye layers. For dye layers thicker than 2500 \AA , the thermal diffusivity was determined using the method of Parker *et al.*¹ Likewise, the diffusivity obtained from the rear surface of an infinitesimally short heat pulse uniformly absorbed in a small layer at the surface is given by

$$\alpha = \left(1.38 \frac{L^2}{\pi^2 t_{1/2}} \right). \quad (1)$$

Here, $t_{1/2}$ is the rise time associated with an increase in one-half the temperature maximum and L is the dye layer thickness. An Rh6G diffusivity value was obtained from the slope of a linear fit of the thickness of Rh6G squared versus rise

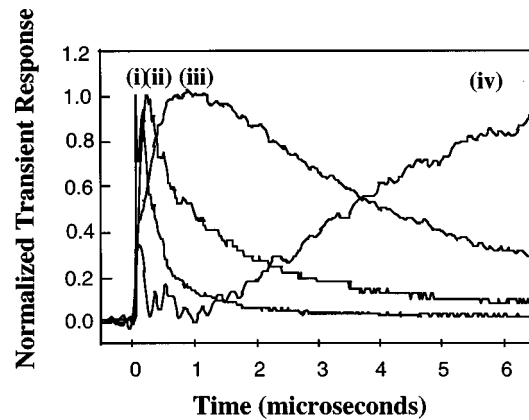


FIG. 2. Normalized transient voltage response of selected thicknesses of Rh6G on a YBCO thin film: (i) Uncoated YBCO, (ii) 3500 \AA Rh6G, (iii) 7000 \AA Rh6G, and (iv) 24000 \AA Rh6G.

time at half-maximum, Eq. (1). The Rh6G diffusivity value determined of $\alpha_{\text{Rh6G}} = 1.4 \times 10^{-3} \text{ cm}^2/\text{s}$ is in agreement with that expected for a dielectric material in this temperature range ($80\text{--}82 \text{ K}$).¹²

In order to develop a detailed picture of the flow of heat through the structure, laser illumination and subsequent thermal decay was simulated using three-dimensional finite difference modeling.¹³ The heat balance equation for node i which has M_i neighbors is given by

$$C_i \frac{T_i^{n+1} - T_i^n}{\Delta t} = P_i^n + \sum_{m=1}^{M_i} {}_i K_{a_m} (T_{a_m}^n - T_i^n), \quad (2)$$

where C_i is the heat capacitance associated with the i th node, $T_{a_m}^n$ is the temperature of the m th neighbor of the i th node at time t_n , P_i^n is the heat generation rate, ${}_i K_{a_m}$ is the conductance between nodes i and m , and Δt is the time step of $t_{n+1} - t_n$. For internal nodes, M_i is six, whereas nodes lying on the surface of the model will not have six neighbors. The transient heat flow is solved using the Crank–Nicolson implicit procedure¹⁴ due to the method's accuracy and time step stability which allows for efficient computation. For a structure containing N nodes, N equations and N unknowns are produced. This resulting system of equations was solved by the point-successive-over-relaxation method (SOR).¹⁵

Instantaneous heating by the laser source was assumed for a penetration depth of 2100 \AA into the dye. Through measurements of the absorption of a solution prepared from a sublimed film of Rh6G, the density of the dye was found to be 1.24 g/cm^3 . The thermal parameters of heat conductivity and specific heat were used to fit the theoretical temperature curves to that obtained experimentally through transient voltage and resistivity curves. The thermophysical constants for MgO and YBCO at 80 K were obtained from Phelan and Hijikata and references therein.¹⁶ The thermal boundary resistance between YBCO/Rh6G and YBCO/MgO was not treated in this initial study.¹⁷ The diffusivity that produces the best fit (within $0.02 \times 10^{-3} \text{ cm}^2/\text{s}$) of experimental and modeled temperatures for 7000 \AA and other thicknesses was $\alpha_{\text{Rh6G}} = 1.4 \times 10^{-3} \text{ cm}^2/\text{s}$. The best fit for diffusivity was determined by comparing the theoretical rise time with the experimental rise time. The diffusivity value of $1.4 \times 10^{-3} \text{ cm}^2/\text{s}$ agrees nicely with that obtained by the above

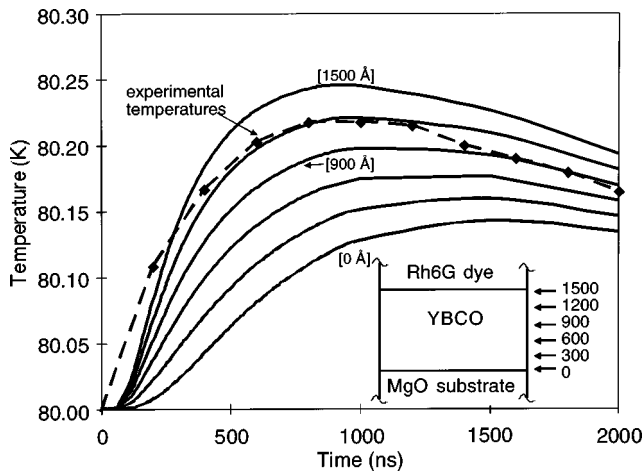


FIG. 3. The typical modeled structure and selected nodal locations are shown in the inset schematic. The theoretical transient temperature response obtained from finite difference modeling for a series of nodal planes through the superconductor of a 7000 Å layer of Rh6G coated on YBCO is shown as solid lines. The experimental transient observed for 7000 Å of Rh6G on YBCO is shown as dashed lines for comparison.

described one-dimensional heat flow estimation. A comparison of the theoretical and experimental transient temperatures at different nodes through the superconductor film is shown in Fig. 3. The peak temperatures in the superconductor are reached at about 900 ns; the temperature distributions through the structure for this and other selected times are shown in Fig. 4. Because the heat disperses throughout the dye film, a thicker dye film leads to a smaller absolute temperature change within the superconductor relative to the

heat sink. This feature is important for future design of sensitive, wavelength-selective bolometers.

In summary, a method for the determination of the thermal diffusivity of a highly absorbing thin organic layer on the surface of a very sensitive and fast, high temperature superconducting bolometer has been demonstrated. These studies were enabled because the chromophore layer had a solid-state extinction coefficient that was large enough to prevent nonuniform heating effects through the thickness of the organic layer [e.g., $\beta_s(532 \text{ nm})_{\text{Rh6G}} = 4.7 \times 10^4 \text{ cm}^{-1}$ which corresponds to 36.8% transmittance through one penetration depth, 2100 Å]. Finite difference modeling was used to determine the diffusivity of the laser dye, rhodamine 6G. This study was designed to compliment previous studies on steady-state optical devices made from this type of structure.⁷⁻⁹ Knowledge of the thermophysical parameters of the absorbing layer is crucial for a complete understanding of the performance capabilities of these assemblies to function as wavelength-selective optical sensors. Future work will include investigation of the thermal properties of a range of highly absorbing chromophore layers which can be used for wavelength discrimination. Additionally, finite difference modeling will be exploited to design more responsive devices.

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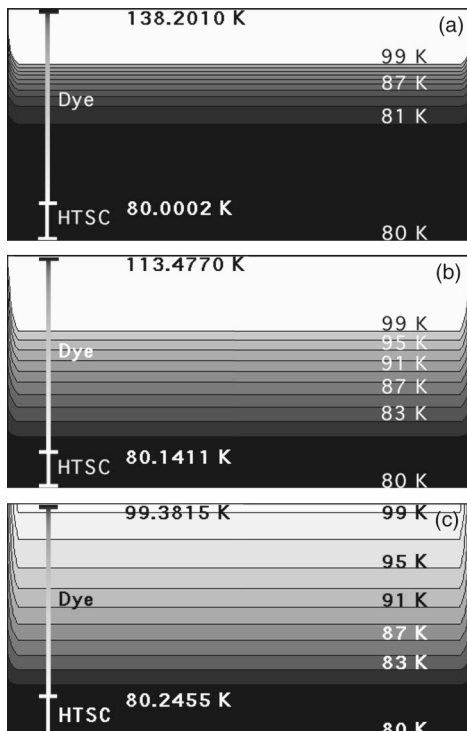


FIG. 4. Temperature distributions through the dye and superconductor in the illuminated region are shown in (a-c). For all structures, the temperatures shown on the right are the temperatures corresponding to the contour line directly beneath those numbers. Temperatures shown at the left are those of the dye and superconductor surfaces. The temperature distributions at 50, 300, and 900 ns are shown in (a-c), respectively.

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