Chem. Mater. **1997,** *9,* 1377−1384

Enhanced Wavelength Selectivity in Molecular Dye Modified High-T_c Superconducting Detectors Using Mirror-Layer Structures

David C. Jurbergs,[†] Steve M. Savoy, Jianai Zhao, Sara J. Eames, and
John T. McDevitt*

*Department of Chemistry and Biochemistry, The University of Texas at Austin,
Austin, Texas 78712*

Received November 19, 1996. Revised Manuscript Received March 6, 1997[⊗]

A new method for enhancing the wavelength selectivity and responsivity of hybrid dye/superconductor optical sensors is described. Here, reflective "mirror layers" deposited atop the high-temperature superconductor, $YBa_2Cu_3O_{7-\delta}$, are used to enhance the optical performance characteristics of such hybrid sensors. Quantification of the wavelength selectivity for such detector structures is detailed for both dye/high-T_c superconductor and dye/mirror-layer/high-T_c superconductor systems. Optical studies suggest that the inclusion of the mirror layer serves to enhance the wavelength selectivity by reducing the amount of off-resonance signal generated by the detector. On the other hand, the on-resonance signals captured by the dye layer are effectively sensed by the superconductor element. Measurement of the wavelength-dependent optical responsivity of the mirror-layer-modified hybrid detectors shows that energy transfer between the dye and superconducting elements is not diminished by the presence of this reflective layer.

Introduction

Molecular dyes previously have been shown to function as light-harvesting antennae in several naturally occurring biological systems such as photosynthesis and human color vision.[1−6] Few man-made examples of molecule-based antennae have been utilized in practical applications. However, recently it has been shown that molecular dyes can be combined with high-T_c superconductor structures to create hybrid optical sensors which display both high sensitivity and good wavelength selectivity properties.[7−10] These recent developments follow the earlier work in the area of high-temperature superconductivity where cuprate superconductor films are utilized as broad-band optical bolometric elements.[11−14] Here, small changes in the temperature of the detector result from the absorption of electromagnetic radiation. These thermal changes cause alterations in the sample resistance which can be sensed readily via electronic means.

In the hybrid dye/superconductor assemblies, the molecular layer has been shown to function as a light-absorbing antenna structure, wherein the response of the dye-coated device is increased relative to that exhibited by an uncoated structure.[8,10,15] Furthermore, the increase in optical responsivity coincides spectrally with the wavelengths of light which are absorbed strongly by the molecular dye layer. That wavelength selectivity has been imparted to these hybrid superconductor detectors can be attributed to the occurrence of efficient light capturing by, and energy transfer through, the molecular-dye antenna structure. The molecular-dye layer is particularly useful in this context because the spectral response characteristics of the hybrid structure can be tailored at the molecular level through judicious choice of the light-absorbing molecule.[16]

Although these hybrid dye/superconductor systems exhibit wavelength selectivity, nonselective response also occurs at wavelengths where the dye antenna layer does not effectively absorb light. The origin of this off-resonance signal is due to broad-band absorption by the underlying high-T_c superconductor. In this regard, light which is not effectively captured by the antenna layer passes through the dye and is then incident upon the superconductor thin film. The transmitted radiation can then be absorbed and detected directly by the superconductor element. Since the dye-coated super-

---

[†] Current address: W. L. Gore & Associates, Inc., P.O. Box 8038, Newark, DE 19714.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1997.

(1) van Grondelle, R.; Dekker, J. P.; Gillbro, T.; Sundstrom, V. *Biochim. Biophys. Acta* **1994**, *1187*, 1−65.

(2) Hall, D. O.; Rao, K. K. *Photosynthesis*; Cambridge University Press: Cambridge, U.K., 1994.

(3) Gregory, R. P. F. *Biochemistry of Photosynthesis*; John Wiley & Sons: Chichester, U.K., 1989.

(4) *Science of Vision*; Leibovic, K. N., Ed.; Springer-Verlag: New York, 1990.

(5) *Colour: Art & Science*; Lamb, T.; Bourriau, J., Eds.; Cambridge University Press: Cambridge, England, 1995.

(6) *Color*; Healey, G. E., Shafer, S. A., Wolff, L. B., Eds.; Jones and Bartlett Publishers: Boston, 1992.

(7) Jurbergs, D.; Haupt, S. G.; Lo, R.-K.; Zhao, J.; McDevitt, J. T. *Mol. Cryst. Liq. Cryst.* **1994**, *256*, 577−582.

(8) Jurbergs, D. C. Dissertation Thesis, The University of Texas at Austin, 1996.

(9) Jurbergs, D.; Zhao, J.; Haupt, S. G.; McDevitt, J. T. In *MRS Symposium Series: Electrical, Optical and Magnetic Properties of Organic Solid State Materials;* Boston, 1993.

(10) Zhao, J.; Jurbergs, D.; Yamazi, B.; McDevitt, J. T. *J. Am. Chem. Soc.* **1992**, *114*, 2737−2738.

(11) Leung, M.; Broussard, P. R.; Claassen, J. H.; Osofsky, M.; Wolf, S. A.; Strom, U. *Appl. Phys. Lett.* **1987**, *51*, 2046−2047.

(12) Forrester, M. G.; Gottlieb, M.; Gavaler, J. R.; Braginski, A. I. *Appl. Phys. Lett.* **1988**, *53*, 1332−1334.

(13) Richards, P. L. *J. Appl. Phys.* **1994**, *76*, 1−24.

(14) Brasunas, J. C.; Lakew, B. *Appl. Phys. Lett.* **1994**, *64*, 777−778.

(15) Jurbergs, D. C.; Zhao, J.; McDevitt, J. T. *Appl. Phys. Lett.* **1996**, *69*, 688−690.

(16) McDevitt, J. T. *Chem. Br.* **1994**, 292−295.

S0897-4756(96)00594-7 CCC: $14.00

conductor exhibits enhanced responsivity relative to the uncoated superconductor at wavelengths which the dye absorbs, the device displays overall wavelength selectivity. However, improved selectivity might be achieved if the influence of the nonselective, transmissive component of the signal could be diminished. Improvement of the wavelength selectivity is desirable for future optical applications where wavelength discrimination and, therefore, color discrimination is sought (e.g., imaging and remote sensor applications).

Here, we report the concept, fabrication, and operation of hybrid detector structures in which a "mirror-layer" is used to increase the wavelength selectivity and sensitivity of dye/high-T_c superconductor detectors. The inclusion of this reflective layer serves to reject off-resonance optical signals without disturbing the on-resonance response. Important materials-related considerations concerning the preparation of the hybrid structures are also described in some detail.

Experimental Section

Thin films (typically ~1500 Å thick) of the high-temperature superconductor, $YBa_2Cu_3O_{7-\delta}$, were deposited onto MgO (100) single-crystal substrates by the laser ablation method.[17,18] These films were patterned into microbridge geometries (~6 mm long × 150 μm wide) using a laser-etching method which has been described previously.[19] Dielectric thin films of ZnS were deposited using an Edwards AUTO 306 Cryo thermal evaporator (background pressure $< 1 \times 10^{-6}$ Torr). Thin MgO films were deposited by laser ablation using a Mg target. Typical parameters for MgO deposition were 550 °C deposition temperature, 1×10^{-6} Torr background pressure with 5 mTorr oxygen partial pressure added during film preparation, a 4 J cm^{-2} laser power density, 10 Hz pulse rate, and 0.2 Å/pulse deposition rate. Metallic contacts and "mirror layers" of Ag or Al were deposited by thermal evaporation using the above-described thermal evaporator. The dye materials, rhodamine 6G and acridine orange base, were deposited using a glass vacuum sublimator (with a background pressure $<1 \times 10^{-5}$ Torr). These dye films were deposited onto a liquid nitrogen cooled substrate from a source operating at 180 °C for rhodamine 6G and 100 °C for acridine orange base. Deposition rates of approximately 400 Å/min were achieved for the dye thin films used in this work. The substrates were cooled during thermal evaporation of the dye layer in order to minimize damage of the superconductor thin film. Previous work has shown that superconductor thin films can degrade at elevated temperatures.[8,10,15] Localization of the dye layers on the superconductor films was accomplished through the use of poly(tetrafluoroethylene) tape which was applied to the film assembly prior to dye sublimation. The sequence of deposition steps and structures formed using these deposition techniques are described in greater detail in the Results. After deposition of the appropriate dye overlayer, the electrical properties of the superconductor microbridge were characterized using a four-point van der Pauw geometry in which Ag contacts pads were positioned at the corners of the device.[20] Characterization of the structures before and after thin-film deposition was carried out in a closed-cycle helium cryostat which was equipped with quartz optical windows. Optical measurements were completed using a mechanically chopped monochromatic light beam which originated from a 300-W xenon arc lamp (Oriel Corp.) prior to its passage through a monochromator (HR250, ISA Jobin Yvon). Using a dc bias current of 1×10^{-2}–1×10^{-4} A, the in-phase voltage which developed across the junction was measured with a lock-in amplifier (SR510, Stanford Research Systems).

Wavelength Selectivity

To evaluate the effectiveness of modifications to the dye/superconductor detector structure, performance criteria must be established which are capable of quantifying the changes in the device response characteristics. Previously, researchers studying optical detectors have developed several figures of merit to gauge detector performance. These parameters include the sensitivity, responsivity, detectivity, speed, spectral range, field of view, and several other important variables.[21,22]

Most prior studies of optical sensors have focused on the development of structures which exhibit large sensitivities over broad wavelength ranges. In some cases, broad-band sensors are combined with filtering agents for applications which require color recognition capabilities.[23] Although quantification of wavelength discrimination capabilities has not been applied to optical detectors, the determination of frequency selectivity has been common in the area of radio frequency (rf) detection.[24,25] The concept of tuned circuits to selectively amplify specific frequencies of radio waves has been used for nearly 100 years. Since many simple tuned circuits possess Gaussian or near-Gaussian frequency-dependent response about the tuned center frequency, the frequency selectivity of a tuned circuit has been quantified in terms of the −3 dB bandwidth relative to the center frequency. The quality-factor Q of the rf tuned circuit that quantifies the frequency-selectivity is expressed as follows:

$$Q = f_0/\Delta f \qquad (1)$$

where f_0 is the center frequency and Δf is the −3 dB bandwidth of the tuned circuit (i.e., full width at half-maximum of the output power). Therefore, rf tuned circuits which display a very small bandwidth relative to their center frequency possess high Q values, and therefore, a high level of frequency selectivity.

In many ways, the RF antenna/tuned circuit is similar to the above-described dye-coated superconductor detector system. Both entities possess an absorbing element, a wavelength-selective element, and an electromagnetic radiation-to-electrical signal transducer structure. In the rf system, the antenna acts as both the absorbing and transducing element, while the tuner circuit affords selectivity. On the other hand, in the hybrid dye/superconductor detector, the superconductor structure serves as the transducing element, while the dye layer functions as the absorbing and selective element. The dye structure, therefore, performs a role analogous to that of a tuned circuit element in a rf detection system. Although the dye layer may exhibit several resonance

---

(17) Dijkkamp, D.; Venkatesan, T.; Wu, X. D.; Shaheen, S. A.; Jisrawi, N.; Min-Lee, Y. H.; McLean, W. L.; Croft, M. *Appl. Phys. Lett.* **1987**, *51*, 619.

(18) Char, K.; Fork, D. K.; Geballe, T. H.; Laderman, S. S.; Taber, R. C.; Jacowitz, R. D.; Bridges, F.; Connell, G. A. N.; Boyce, J. B. *Appl. Phys. Lett.* **1990**, *56*, 785–787.

(19) Vase, P.; Yueqiang, S.; Freltoft, T. *Appl. Surf. Sci.* **1990**, *46*, 61–66.

(20) van der Pauw, L. J. *Philips Res. Rep.* **1958**, *13*, R334–339.

(21) Dereniak, E. L.; Crowe, D. G. *Optical Radiation Detectors*; John Wiley & Sons: New York, 1984.

(22) Budde, W. *Optical Radiation Measurements: Physical Detectors of Optical Radiation*; Academic Press: New York, 1983; Vol. 4.

(23) Böttcher, H.; Fritz, T.; Wright, J. D. *J. Mater. Chem.* **1993**, *3*, 1187–1197.

(24) Schoenbeck, R. J. *Electronic Communications: Modulation and Transmission*; Merrill Publishing Co.: Columbus, OH, 1988.

(25) Tomasi, W. *Fundamentals of Electronic Communications Systems*; Prentice Hall: Englewood Cliffs, NJ, 1988.

frequencies (i.e., absorption peaks), the spectral characteristics for a single absorption peak are nearly Gaussian in shape. Therefore, the selectivity of the detector structure in spectral regions where the dye possesses a single absorption band can be estimated using the above-described quality-factor equation. However, for the wavelength selectivity of systems which exhibit non-Gaussian behavior, the ratio of the on-resonance response to the off-resonance response can also be used as a figure of merit. Thus, a relevant figure of merit is the wavelength-selective amplification (or gain), *A*, (expressed in terms of decibels) which is given by

$$A = 20 \times \log(R_{\mathrm{on}}/R_{\mathrm{off}}) \qquad (2)$$

where R_{on} represents the on-resonance response and R_{off} details the off-resonance response.

Results

Prior work with the dye/superconductor composite systems has shown that these structures operate via a bolometric detection mechanism in which light energy absorbed by the dye layer is transferred to the superconducting element as a thermal wave.[12,26-28] Thus, it is expected that the inclusion of a thin film of a thermally conductive material between the dye layer and the high-T_c superconductor structure should not substantially impact the operation of the optical device. Likewise, materials which reflect the light that is transmitted through the dye antenna-layer might be expected to increase the amplification factor of the device. The inclusion of this reflective layer should serve to reject off-resonance optical signals without disturbing the on-resonance response. These phenomena form the basis for the concept of the "mirror-layer" structure.

In Figure 1, the structure of a hybrid dye/mirror/superconductor device is illustrated schematically as are the functions of the various components. The optical sensor is comprised of a wavelength-selective absorbing dye layer, a metallic mirror-layer and a high-T_c superconductor microbridge junction. According to the mirror-layer concept, if the wavelength of light matches a resonance peak of the dye, there is a high probability that the light will be absorbed by the antenna layer and the energy therein converted into thermal energy (Figure 1A). The thermal energy can propagate down through the device structure until it reaches the high-T_c superconductor element where it can be sensed electrically. If the light is not absorbed by the dye, then it can pass through the dye layer where it may be reflected from the surface of the metallic mirror layer (Figure 1 B,D). If the off-resonance light is rejected from the sensor structure, then a decrease in sensitivity will result for such wavelengths (Figure 1C). On the other hand, the on-resonance photons not absorbed on the initial pass through the dye are reflected back through the dye layer, increasing their probability of absorption (Figure 1D). Therefore, the mirror-layer-modified, hybrid bolometer is expected to exhibit increased wavelength selectivity due to two distinct benefits. First, the wavelengths of light which do not match the resonance absorption of the dye layer are likely to be rejected. Second, the on-resonance photons possess a higher probability of being absorbed. Thus, the inclusion of the mirror layer serves to increase the "effective" thickness of the dye layer.

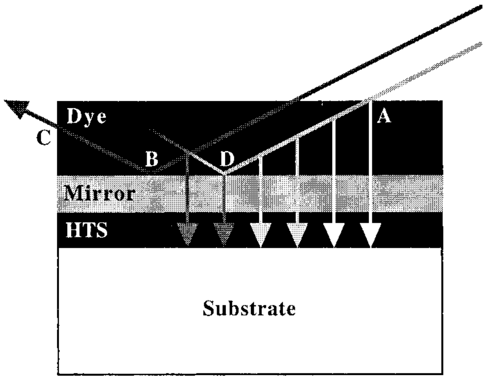

Figure 1. Schematic representation which details the important light absorption, light rejection, and energy-transfer events which occur in dye/mirror layer/high-temperature superconductor structures. Two parallel rays of incident light are shown which differ in wavelength. The dark gray line represents light that cannot be effectively absorbed by the dye, and the light gray line represent light of an appropriate wavelength for absorption. Downward arrows detail conductive transport of thermal energy to the superconductor temperature-sensing element.

To create the mirror-layer modified dye/superconductor detector, several deposition and patterning steps must be completed. Since the high-T_c superconductor material is susceptible to degradation by water, acids, and reducing agents, it is important to choose compatible materials and processing methods. One procedure effective for the preparation of dye/mirror/high-T_c superconductor detector structures is outlined in Figure 2. Initially, a single-crystal substrate of MgO (100) is cleaned. Then, the substrate is loaded into a laser-ablation vacuum chamber, where a ~1500 Å thick film of $YBa_2Cu_3O_{7-\delta}$ is deposited thereon using the laser deposition method. At this juncture, the thin film is characterized by four-point resistivity versus temperature measurements in order to verify that the sample maintains good superconducting properties following all of the processing steps. The film is then patterned via a laser etching method utilizing a very narrow metal mask to produce superconducting microbridge structure. This etching technique has been described elsewhere.[19] Electric transport measurements are typically conducted after etching of the microbridge in order to verify that no significant damage has occurred to the film and that connectivity is maintained through the microbridge structure.

To create the mirrored detector structure, it is important to isolate the metallic layer from the superconductor element to prevent electrical shorting of the microbridge structure. Here, a thin insulating layer of dielectric material such as MgO or ZnS is utilized for the electrical isolation of these two conductors. Detector structures lacking the insulator layer or those created wherein electrical shorting between the mirror and superconductor layers has occurred were found to be

---

(26) Brocklesby, W. S.; Monroe, D.; Levi, A. F. J.; Hong, M.; Liou, S. H.; Kwo, J.; Rice, C. E.; Mankiewich, P. M.; Howard, R. E. *Appl. Phys. Lett.* **1989**, *54*, 1175–1177.

(27) Nahum, M.; Verghese, S.; Richards, P. L.; Char, K. *Appl. Phys. Lett.* **1991**, *59*, 2034.

(28) Phelan, P. E.; Hijikata, K. *J. Electrochem. Soc.* **1994**, *141*, 810–815.

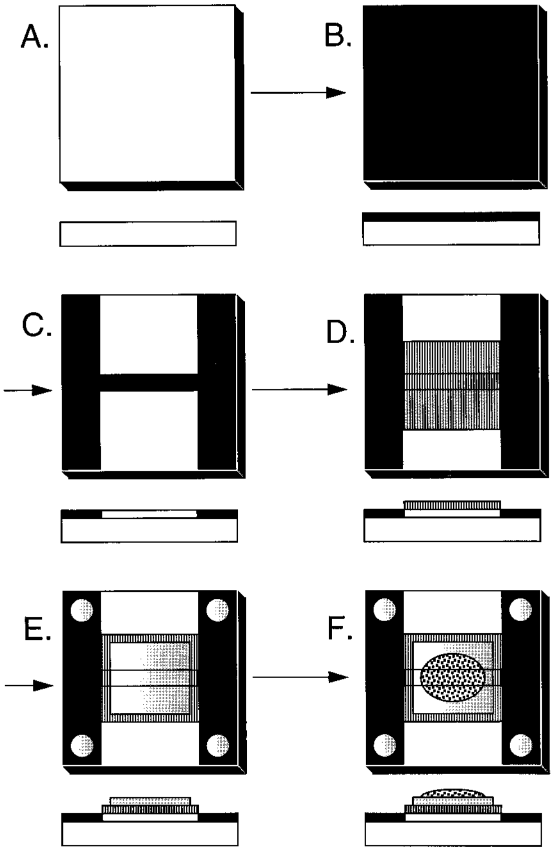

Figure 2. Schematic illustration showing the basic steps that are required to prepare hybrid dye/mirror/superconductor detectors: (A) In the initial step, a MgO (100) substrate is cleaned. (B) Second, ~1500 Å of $YBa_2Cu_3O_{7-\delta}$ is deposited by pulsed laser deposition. (C) Third, a microbridge pattern is created in the central portion of the film, typically by laser ablation etching. (D) Next, a thin insulating layer (400−4000 Å thick) of MgO or ZnS is deposited by pulsed laser deposition or thermal evaporation. (E) After the insulating thin film has been deposited over the microbridge region, a thin metallic mirror-layer ~2000 Å thick of Al or Ag is deposited on top of the insulator. Then, Ag or Au contact pads are also added to the corners of the device to foster the formation of good electrical contact. (F) In the final step, the molecular dye layer is deposited over the mirror region of the microbridge junction via thermal evaporation.

unsuitable for optical detection. Avoidance of electrical shorting between the two conductors can be achieved with MgO layers in the 400−1000 Å thickness range and for ZnS layers with thicknesses in excess of 3000 Å.

After the insulating material is deposited over the microbridge structure, a mirrorlike film of an appropriate metal such as Ag or Al is deposited. Suitable reflective layers are obtained through the evaporation of ~2000 Å of Ag or 1500−2000 Å of Al. Careful studies of the device-processing steps reveal a number of advantages for using Al as the reflective layer relative to Ag. First, although Al is oxidized on the surface immediately upon exposure to atmosphere, the Al_2O_3 layer which forms over the metallic Al is transparent and acts as an passivation layer to prevent further oxidation of the underlying metal. In contrast, Ag slowly and continuously tarnishes in air, causing the surface to display a lower reflectance over time. Second, Al exhibits a lower rate of surface diffusion during deposition than does Ag. Thus, Al layers can be deposited without electrical shorts more readily than can Ag layers. Finally, thin Ag films display a transmission peak in the near-UV to blue-visible region of the electromagnetic spectrum which depends on film thickness and surface morphology.[29−31] Layers of Al exhibit a much more uniform reflectance due to the absence of an absorption band in or near the visible region. Electrical contact pads are then deposited at the corners of the sensor structure to foster the formation of good electrical contacts. In the final processing step, molecular dye layers of rhodamine 6G (Rh6G) or acridine orange base (AOB) are deposited by sublimation with thickness values ranging from 400 to 4000 Å onto selected regions of the bridge.

With the complex deposition and patterning process outlined above, it is important that checks be made to verify that damage is not occurring to the device structure. In addition to described electrical measurements, scanning electron micrograph (SEM) studies were completed for several device structures in order to understand the role of each processing step on the morphology of the final device. Scanning electron micrographs of a typical detector structure are illustrated in Figure 3.

Crucial to the development of quality sensing elements is the ability of the molecular antenna layer to efficiently channel energy into the superconductor layer. Smooth, nongranular films are ideal candidates as heat flow is optimized by minimizing intergranular voids and defects. Rough interfaces are expected to exhibit smaller contact areas between grains than smooth, regular interfaces, thus diminishing thermal conductance through the antenna layer and into the superconducting element. Figure 3 shows electron micrographs of different regions of a $YBa_2Cu_3O_{7-\delta}$ microbridge which was patterned by laser ablation etching. The morphological features of the molecular antenna layer vary with the device substrate layer upon which the dye is deposited and play an important role in good thermal coupling to the superconductor.

The uncoated region of the microbridge displays structural features with dimensions on the order of microns, even in the smooth center portion of the bridge (Figure 3A,D). These large particles decorate ~1−5% of the surface of the high-T_c film and have been attributed to debris caused by the laser ablation etching process. Dye layers deposited directly on the surface of the superconductor (Figure 3B,E) possess relatively large crystallites which protrude from the high-T_c surface. However, the region where dye is deposited directly onto the surface of the ZnS insulating layer shows minimal roughness (not shown). This behavior suggests that the ZnS is deposited as a smooth, continuous film. Furthermore, the ZnS films do not appear to foster the nucleation and crystal growth of the vapor-deposited dye layers. The smoothest region of the film is found where the dye material is deposited on the Al mirror layer (Figure 3C,F). The Al exhibits a nearly featureless layer which provides an ideal surface for dye film formation. From these studies, it can be seen that the Rh6G, ZnS, and Al layers form relatively smooth

---

(29) Roark, S. E.; Rowlen, K. L. *Appl. Spectrosc.* **1992**, *46*, 1759−1761.

(30) Dudek, J. C.; Sabary, F. *Vacuum* **1990**, *41*, 1469−1471.

(31) Davis, C. A.; McKenzie, D. R.; McPhedran, R. C. *Opt. Commun.* **1991**, *85*, 70−82.

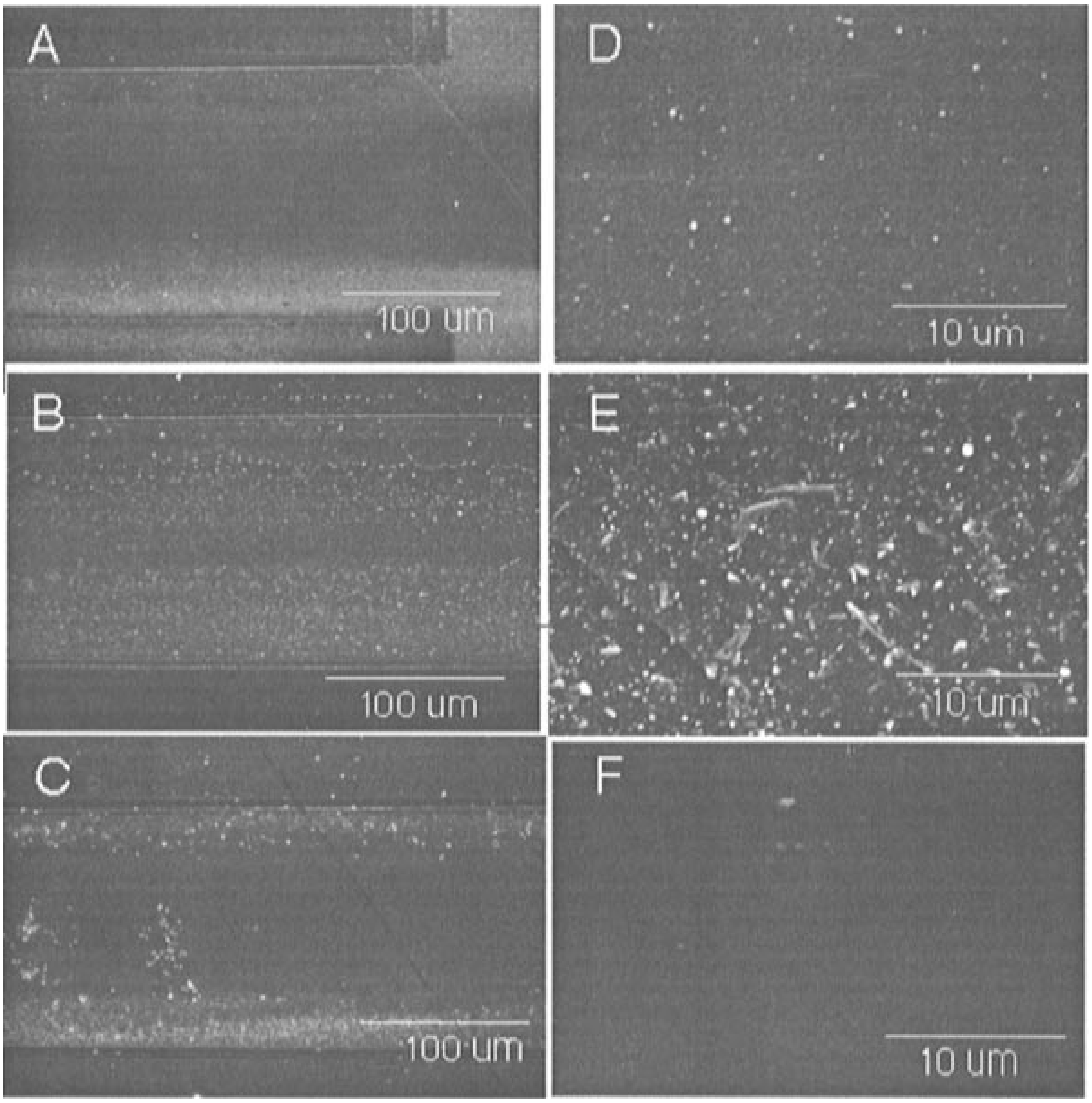

Figure 3. Images recorded with a scanning electron microscope for the following cases: (A, D) uncoated $YBa_2Cu_3O_{7-\delta}$; (B, E) rhodamine 6G (1000 Å) on $YBa_2Cu_3O_{7-\delta}$; (C, F) rhodamine 6G (1000 Å) on Al (1500 Å), ZnS (4000 Å), $YBa_2Cu_3O_{7-\delta}$ (1500 Å). Images (A-C) are low magnification views, and (D−F) are high magnification images of the respective regions, the latter taken near the center of the $YBa_2Cu_3O_{7-\delta}$ microbridge.

thin films which might be expected to promote effective heat transfer within the device structure.

After fully characterizing the morphological and electrical properties of the hybrid sensors, the structures were loaded into a cryostat to evaluate their optical properties. Optical characteristics were measured with the device held at a temperature near the midpoint of the transition temperature (T_c(mid)), which ranged between 84 and 88 K for the devices used in this study. The output voltage of the detector due to incident light was measured with a lock-in amplifier. Here, a constant dc bias current was applied across the $YBa_2Cu_3O_{7-\delta}$ microbridge element while a focused beam of monochromatic light was used to probe various regions of the microbridge. In addition, wavelength-dependent spectra were obtained for the specified device regions. These spectral characteristics were compared with those obtained from the UV/visible/NIR absorbance spectra of the same dye films which were deposited on glass substrates. Although there exists a possibility that the dye films may undergo a phase change upon cooling to ~86 K, we have not seen substantial differences between the spectra obtained on the dye films at room temperature and the action spectra evoked by the dye-coated devices at low temperatures.

To evaluate the effectiveness of the mirror layer, first the optical response properties of the microbridge device were interrogated and found to be uniform within ±3% over the entire length. Portions of the bridge were then prepared so that the optical response of uncoated $YBa_2Cu_3O_{7-\delta}$, dye/$YBa_2Cu_3O_{7-\delta}$, mirror/$YBa_2Cu_3O_{7-\delta}$, and dye/mirror/$YBa_2Cu_3O_{7-\delta}$ cases could be evaluated under identical conditions. Comparison of the different superconductor regions shows a dramatic reduction in signal for the mirror-only case. The effectiveness of the reflective layer is thus noted. Although the signal is reduced relative to the bare microbridge, the spectral features follow that recorded for the uncoated region. Thus, no wavelength discrimination is noted for the mirror-only case.

Once the dye is deposited over the mirror layer, two interesting and important features become apparent.

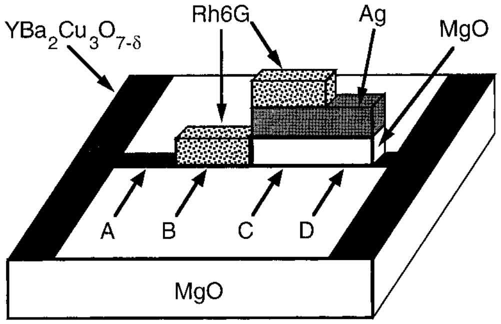

Figure 4. Schematic illustration detailing the various regions which are evaluated in the associated data which is provided in Table 1. Here, the optical responsivity values are recorded for a series of regions which exist on a 1500 Å $YBa_2Cu_3O_{7-\delta}$ thin film microbridge: (A) uncoated $YBa_2Cu_3O_{7-\delta}$; (B) $YBa_2Cu_3O_{7-\delta}$ coated with ~2000 Å of rhodamine 6G; (C) $YBa_2Cu_3O_{7-\delta}$ coated with ~500 Å of MgO, ~1500 Å of Ag and ~2000 Å of rhodamine 6G; (D) the $YBa_2Cu_3O_{7-\delta}$ coated with ~500 Å of MgO and ~1500 Å of Ag.

Table 1. Relative Responsivity and Wavelength Selectivity of a $YBa_2Cu_3O_{7-\delta}$ Microbridge Coated with Dye and Mirror Layers[a]

		relative optical responsivity			
		prior to	after coating		A^c
region[b]	coating layers	processing	$\lambda = 633$ nm	$\lambda = 580$ nm	(dB)
A	none	1.00	1.00	1.00	0
B	rhodamine 6G	0.97	0.99	1.80	5.24
C	rhodamine 6G/ Ag/MgO	0.99	0.83	1.95	7.42
D	Ag/MgO	0.99	0.23	0.23	0

[a] Responsivity values are given in dimensionless units relative to the uncoated $YBa_2Cu_3O_{7-\delta}$ region prior to deposition of the mirror and dye layers. The wavelength-selective amplification of the detector region was determined for each region according to Expression [2], using the responsivity at 580 nm for the on-resonance response and the responsivity at 633 nm for the off-resonance response. [b] See Figure 4 for a schematic illustration which details the various regions. [c] Wavelength-selective amplification *A* (in decibels) calculated using expression 2 is given for the various device regions.

First, an increase in responsivity at the wavelengths in which Rh6G absorbs light is seen for both the Rh6G/$YBa_2Cu_3O_{7-\delta}$ and Rh6G/mirror/$YBa_2Cu_3O_{7-\delta}$ regions. This behavior suggests that dye-to-superconductor energy transfer can occur even through the mirror layer. Second, the wavelength-dependent responsivity of the dye/mirror/superconductor structure is enhanced relative to the dye/superconductor structure due to a slight increase in the on-resonance response and a decrease in the off-resonance response. Since the only substantial difference between the two regions is the presence of the mirror-layer structure, these changes in responsivity can be attributed to its effect on the dye/superconductor detector assembly.

To quantify the color discrimination characteristics of the described structures, different regions of a microbridge were evaluated as detailed in Figure 4. The response of these various regions of the microbridge, recorded under identical conditions, are summarized in Table 1 both before and after deposition of the mirror and dye layers. The wavelength dependence of the device prior to the addition of the mirror or dye layers was found to be constant (independent of wavelength) for the entire microbridge. Since the response of each region of the microbridge did not vary with the wavelength of light exposed upon it, the wavelength-dependent response characteristics of the microbridge prior to processing can be effectively summarized in one column. However, after deposition of the mirror and dye layers, regions of the device which were coated with rhodamine 6G displayed wavelength-selective response. Consequently, the postdeposition responsivity values are given in Table 1 at two different wavelengths: 580 nm, which matches the absorption peak of the Rh6G layer and 633 nm, at which the dye layer does not absorb light effectively. The solid-state absorption coefficient of R6G thin films is approximately 1×10^4 cm^{-1} at 580 nm (on-resonance) and is approximately 1×10^3 cm^{-1} at 633 nm (off-resonance).

From an evaluation of region D before and after addition of the MgO and Ag layers, it is readily apparent that the optical responsivity of the mirrored region is substantially diminished. The optical response of the mirrored region is reduced by about 80% with the inclusion of the reflective layer. Since the response of the uncoated region (region A) remains unchanged after deposition and processing, it is unlikely that the addition of the MgO and Ag layers substantially degraded the superconducting detector element. This statement is further supported by the fact that after several deposition and patterning steps, the room-temperature resistance of the microbridge increases by only about 7% relative to that of the device prior to its handling.

If the decrease in responsivity cannot be explained by degradation of the superconducting bolometer element, then the most probable explanation is given by reflection of incident light from the surface of the modified device structure. We have found that thin films of Ag which are deposited in a similar fashion onto smooth glass substrates reflect ~85% of the incident visible light. Therefore, it is not unreasonable to believe that the MgO/Ag mirror layer is effective in reflecting ~80% of the light from the superconductor surface. Increases in superconductor surface roughness relative to glass are probably responsible for the subtle decrease in reflectivity relative to the control. Although $YBa_2Cu_3O_{7-\delta}$ itself reflects some visible light, the monolithic material does not function well as a mirror. Accordingly, the reflectance of a 1000- to 2000-Å-thick film of $YBa_2Cu_3O_{7-\delta}$ in the visible region is on the order of 0.3. On the other hand, Al thin films of similar thicknesses display reflectivity values above 0.95. Therefore, at wavelengths which are not absorbed strongly by the dye, the response of the detector structure should be reduced by at least 90% if smooth, highly reflective films of Al are positioned over the patterned high-T_c surface. Although the Al films exploited here did not display optimum reflectivity, the advantage of the Al "mirror-layer" over the monolithic $YBa_2Cu_3O_{7-\delta}$ structure is apparent from the data shown in Table 1 when the 633 nm responses of regions B and C are compared.

As expected, the addition of a mirror layer by itself does not provide utility to the superconducting device. However, when the mirror layer is used in conjunction with a dye layer, high responsivity and color recognition properties are afforded to the composite detector. The color selectivity properties are readily quantified through a comparison of the data values compiled in Table 1. Most relevant in this regard are the values in the fourth and fifth columns. The relative optical responsivity of the dye-coated regions is substantially higher at wavelengths where the Rh6G dye layer absorbs light effectively (i.e., at 580 nm) when compared to regions where the dye absorbs very little light (i.e., at 633 nm). Furthermore, both dye-coated regions of the device display substantially higher responsivity at wavelengths where the dye absorbs light effectively. This behavior indicates that efficient energy transfer occurs between the dye and the superconductor elements. Interestingly, addition of the insulator/mirror layers beneath the dye-coated regions does not hamper this energy transfer. Furthermore, the addition of the mirror-layer structure increases the responsivity of the dye-coated microbridge at wavelengths where the dye absorbs light effectively. An effective increase in the optical path length caused by the inclusion of the reflective layer is likely responsible for this effect.

The key role of the mirror layer which makes this work significant is that it substantially affects the wavelength-dependent response characteristics of the detector structure. Although gains in responsivity by reflection of on-resonance light back through the dye may increase the on-resonance responsivity of the device, this dual-pass responsivity cannot be expected to be any larger than twice the responsivity evoked by a single pass of light through the dye layer. Rather, the main function of the mirror layer is to increase the wavelength selectivity of the device. Therefore, it is the wavelength-selective amplification of the device that is truly of interest. This ratio between the on-resonance response and the off-resonance response can be maximized either by greatly increasing the on-resonance responsivity or by substantially decreasing the off-resonance responsivity. At best, the mirror layer can, in theory, approach 100% rejection of off-resonance light from being absorbed and detected by the superconductor-based detector. In this case, the wavelength-dependent amplification will approach infinity. In actuality, simple thin-film metallic mirrors can reflect up to 95% of visible light.

As a further quantification of the wavelength selectivity of the different device regions, the wavelength-selective amplification, *A*, was determined for each region using its wavelength-dependent responsivity (see expression 2). The relative responsivity of each region as determined at 580 nm (on-resonance) and at 633 nm (off-resonance) was utilized to calculate this value (last column in Table 1). As is evident from these data, both the uncoated and mirror-coated microbridge regions display nonselective responsivity; the responsivity of the two regions are comparable at both wavelengths. However, the dye-coated regions display selective response. Contrary to many other color-discriminating detector systems, these dye-coated devices display wavelength-selective gain (instead of attenuation) at the dye resonance wavelength.[23] Furthermore, the wavelength-selective gain is higher for the dye-coated region in which a mirror-layer structure is incorporated. This behavior suggests that the mirror layer is capable of effectively rejecting the off-resonance light while maintaining good sensitivity toward the on-resonance light. Similar structures incorporating ZnS/Al mirror-layer structures and the organic dye, acridine orange base, yield analogous results.

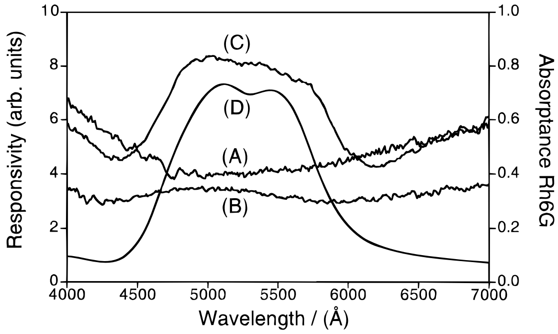

Figure 5. Relative optical responsivity as a function of wavelength for various regions of a 1500 Å $YBa_2Cu_3O_{7-\delta}$ microbridge structure. (A) Uncoated region of $YBa_2Cu_3O_{7-\delta}$; (B) Al mirror layer ~1500 Å on $YBa_2Cu_3O_{7-\delta}$; (C) $YBa_2Cu_3O_{7-\delta}$ microbridge coated with rhodamine 6G ~2000 Å on an Al mirror layer ~1500 Å. (D) For comparison purposes, an absorptance spectrum of rhodamine 6G ~2000 Å on a glass slide is provided.

When attempting to optimize the thickness of the dye-layer antenna, an important tradeoff between responsivity and wavelength selectivity must be made as demostrated in the following examples. For a 400 Å thick film of Rh6G, 8.4% of the light is absorbed at 580 nm, while only 1% of the light is absorbed at 633 nm for a single pass through the dye film. For two passes through the same dye film, 16.8% of the light is absorb at 580 nm and 2% is absorbed at 633 nm. For a 4000 Å thick film of Rh6G, 58% of the light is absorbed at 580 nm and 9.6% is absorbed at 633 nm for a single pass through the dye layer. For a dual pass through the thick film, 82.6% of the light is absorbed at 580 nm while 18.3% is absorbed at 633 nm. This simplified analysis is based on transmission measurements and, therefore, does not account for reflectance or scattering losses. However, it is important to note that there will always be an increase in off-resonance absorption as the on-resonance absorption is also increased. Moreover, the value of the wavelength-selective amplification (580 nm/633 nm) approaches its maxima as the thickness approaches zero.

Further confirmation for the wavelength discrimination capabilities of the composite sensors is provided with the detector spectral response curves provided in Figure 5. Here, data are included for (a) bare superconductor, (b) superconductor coated with a mirror layer, and (c) a structure which possesses both Rh6G dye and a mirror layer. Also, included (d) for comparison purposes is the absorptance spectrum of a Rh6G layer which was deposited onto a glass slide. From these data it is clear that the inclusion of the dye layer serves to alter radically the spectral response properties of the hybrid structure. Increases in response are noted at wavelengths where the dye absorbs strongly. Furthermore, the enhancement caused by the dye layer agrees remarkably well with the dye absorptance spectrum. Here the absorptance spectrum of a dye film is the fraction of light absorbed by the dye versus wavelength. In contrast to the more familiar absorbance units, absorptance is linearly proportional to the amount of light absorbed by the material. Since the responsivity of the detector structures is expected to be linear with respect to the amount of light energy captured, absorptance is a better measurement of the absorption properties of the dye antenna since it can be compared directly to the wavelength-dependent action spectrum of the device.

Summary

In conclusion, it has been shown that both ZnS and MgO can be deposited over high-T_c superconductor thin films in order to provide an insulating barrier that is receptive to further overcoating with reflective layers. Metals such as Ag and Al can be deposited over these insulators in order to obtain electrically isolated metallic reflecting layers. These mirror-layer/high-T_c structures, when utilized without an absorbing antenna element, effectively reject a substantial amount of the light which is incident upon the surface of the device structure, thereby greatly diminishing the responsivity of the bolometric detector. However, by incorporating a molecular dye layer as an antenna structure, enhanced responsivity of the dye/mirror/high-T_c superconductor detector is obtained at wavelengths where the dye effectively absorbs light. These new structures also exhibit better rejection of off-resonance light than comparable dye/high-T_c superconductor bolometers. Furthermore, it has been demonstrated that efficient energy transfer between the molecular dye species and the superconductor element can occur in these multilayer systems. This behavior suggests that thermal conduction plays a substantial role in the transfer of energy from the dye layer to the superconductor.

Acknowledgment. This work was supported by the National Science Foundation (Grant DMR-9631394) and the Texas Advanced Research Program.

CM960594Y