Pyroelectric effect in Y–Ba–Cu–O thin films under laser illumination

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The thermoelectric response of amorphous, semiconducting Y–Ba–Cu–O thin films was investigated by illumination with 150 ps optical pulses at 1064 nm and with a continuous wave at 493 nm (argon laser). The measured unbiased voltage response was consistent with pyroelectricity. At high pulse energies, the voltage response saturated due to the saturation of the spontaneous polarization. The pulsed responsivity was limited by the short pulse duration compared to the thermal time constant of the structure. The electrical time constant for the change in the spontaneous polarization was estimated to be 50 ns. © 1999 American Institute of Physics.

I. INTRODUCTION

The thermoelectric behavior of crystalline metallic (x \( \sim \)1) and semiconducting (oxygen deficient, x \( \ll \)0.5) YBa\(_2\)Cu\(_3\)O\(_{6+\delta}\) (YBCO) and similar compounds in the normal state\(^{1,11}\) has been studied extensively in recent years. Very recently, thermoelectric behavior has been investigated in amorphous, semiconducting YBCO thin films\(^{12-14}\). The latter studies were motivated by the application of YBCO as an uncooled thermal detector for infrared and other radiation or solar cells. Thermoelectric behavior was first observed by Chang \textit{et al.}\(^{1}\) who reported an induced potential difference up to a few volts in unbiased, normal state YBa\(_2\)Cu\(_3\)O\(_{6+\delta}\) c axis oriented thin films on (100) SrTiO\(_3\) substrates, illuminated by laser pulses with energies up to 30 mJ/cm\(^2\). The authors were uncertain as to the origin of the observed voltages, however, did not believe them to be thermal in origin. Scott\(^{15}\) presented an argument that the voltage pulses were likely photovoltaic in origin. Shortly afterwards, Mihailovic and Heeger\(^2\) observed induced voltages along the c axis in single-crystal YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) in response to a heat pulse. Mihailovic and Heeger attributed the behavior to pyroelectricity. Piezoelectricity was also observed in these samples. Although, these effects should be forbidden due to the centrosymmetric crystal structure, the symmetry was postulated to be broken by the coupling of the hole to the apex oxygen of a CuO\(_2\) plane.\(^{16}\) Lengfellner \textit{et al.}\(^3\) measured voltages in YBCO thin films in response to both laser illumination and heating with heater wires, with polarity reversal when illuminated through the substrate. To explain the observed behavior, a model, based on the Seebeck effect, of atomic layer thermopiles formed by the layered structure of YBCO was proposed. In this work, granular films did not show thermoelectric behavior. More recently, amorphous YBCO thin films have been investigated with illumination by broad band infrared light and by substrate temperature ramping.\(^{13,14,17}\) In this work, the pyroelectric coefficient, \(p\), of as-deposited, amorphous YBCO films was measured to range from 50 nC/cm\(^2\)K to 20 \(\mu\)C/cm\(^2\)K. Poling the YBCO thin films that exhibited weak pyroelectric behavior with the application and subsequent removal of the electric field increased the pyroelectric coefficient to 20 \(\mu\)C/cm\(^2\)K. This compares favorably with other thin film ferroelectrics such as lithium tantalate (LiTaO\(_3\)) \(p\) = 20 nC/cm\(^2\)K, lead zirconium titanate (PbZrTiO\(_3\)) \(p\) = 70 nC/cm\(^2\)K, lead scandium tantalate [Pb(Sc\(_{1-x}\)Ta\(_x\))\(_2\)O\(_6\)] \(p\) = 500 nC/cm\(^2\)K and lead titanate (PbTiO\(_3\)) \(p\) = 95 nC/cm\(^2\)K.\(^{18}\) The pyroelectric figure of merit \(F_d\) = \(p/\rho C_p (\varepsilon, \varepsilon_0\tan\delta)^{1/2}\) provides a more useful comparison between materials. Here, \(\rho\) is the density, \(C_p\) is the specific heat, \(\varepsilon, \varepsilon_0\) is the permittivity, and tan \(\delta\) is the dielectric loss tangent. The pyroelectric figure of merit for amorphous YBCO films has been measured to be 0.032–0.065 (cm\(^3\)/J\(^{1/2}\))\(^{12,14,17}\). This compares favorably with LiTaO\(_3\) \(F_d\) = 0.048 (cm\(^3\)/J\(^{1/2}\)), PbZrTiO\(_3\) \(F_d\) = 0.019 (cm\(^3\)/J\(^{1/2}\)), Pb(Sc\(_{1-x}\)Ta\(_x\))\(_2\)O\(_6\) \(F_d\) = 0.069 (cm\(^3\)/J\(^{1/2}\)) and PbTiO\(_3\) \(F_d\) = 0.056 (cm\(^3\)/J\(^{1/2}\)).\(^{18}\) In this case, the behavior was determined to be a strong pyroelectric effect, with the ability to pole the thin film demonstrated. Therefore, based on current literature findings, one can expect that voltage pulses from unbiased YBCO under optical illumination might be due to the photovoltaic effect, Seebeck effect, or pyroelectric effect.

In this work, the laser response of amorphous YBaCuO thin films is investigated. The amorphous YBaCuO thin films lack the long-range order that would allow the atomic layer Seebeck effect or Scott’s\(^{15}\) photovoltaic response to occur.

II. BACKGROUND

The pyroelectric effect refers to the temperature dependence of the spontaneous electric polarization.\(^{18,19}\) The change in the polarization varies the surface charge, resulting in the flow of a pyroelectric current. A voltage is observed

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when the pyroelectric current flows through the combination of the resistance of the material and amplifier recording the signal. The equivalent circuit is shown in Fig. 1. The voltage $V$ measured across the pyroelectric detector by the preamplifier is given by

$$C \frac{dV}{dt} + \frac{V}{R} = pA \frac{dT}{dt} = I_p,$$

where $C$ is the equivalent capacitance ($C_A + C_d$) and $R$ is the equivalent resistance [$R_pR_A/(R_p+R_A)$] of the preamplifier ($C_A,R_A$) and pyroelectric detector ($C_d,R_d$). $p$ is the pyroelectric coefficient of the detector material, $A$ is the area of the detector sampling the change in the surface charge, $T$ is the detector temperature, $t$ is time and $I_p$ is the induced pyroelectric current. The time constant, $\tau_e$ ($=RC$), is the electrical time constant of the equivalent circuit including the detector and preamplifier.

Since the pyroelectric response is thermal in nature, the heat balance equation for the detector (material) with thermal mass $C_{th}$ and thermal conductance $G_{th}$ to the substrate must be satisfied along with the electrical response. The heat balance equation determines the temperature of the detector being heated by the incident optical power $\Phi(t)$ and is given by

$$C_{th} \frac{dT}{dt} + G_{th}(T-T_0) = \eta \Phi(t),$$

where $T_0$ is the temperature of the substrate or thermal reservoir and $\eta$ is the fraction of incident optical power absorbed by the detector or its absorptivity.

The voltage response of a pyroelectric detector is obtained by simultaneous solution of Eq. (1) and Eq. (2). In the case of chopped or a sinusoidal optical intensity, the voltage responsivity $R_v$ to be given by

$$R_v = \frac{\eta pA}{C_{th} C} \frac{\omega \tau_e}{\sqrt{1+\omega^2 \tau_e^2}} \frac{\tau_{th}}{\sqrt{1+\omega^2 \tau_{th}^2}},$$

where $\omega$ is the modulation frequency of the light, and $\tau_{th}$ is the thermal time constant of the detector ($\tau_{th}=C_{th}/G_{th}$). Under pulsed laser illumination, the transient voltage behavior of the detector is still determined by the simultaneous solution of Eq. (1) and Eq. (2). The two time constants $\tau_{th}$ and $\tau_e$ are present in the transient voltage response, which is the form of an exponential rise and fall with the rise and fall time constants determined by $\tau_e$ and $\tau_{th}$, respectively. In this experiment, the optical pulse duration is much less than both the electrical and thermal time constant and can be approximated as an impulse. Solution of Eq. (1) and Eq. (2) yields the measured impulse voltage response to be given by

$$V_A(t) = K \frac{\tau_e}{\tau_{th} - \tau_e} \left[ \exp \left( \frac{-t}{\tau_e} \right) - \exp \left( \frac{-t}{\tau_{th}} \right) \right],$$

where $K = pA \eta \Phi/C_{th} C$.

### III. EXPERIMENTAL DETAILS

The amorphous, semiconducting, YBCO thin film used in this investigation was fabricated by rf magnetron sputtering. A 7.5 cm diameter, superconducting, orthorhombic YBCO sputter target was used to deposit the films onto 10-cm-diam Si (100) wafers. The sputtering was performed at room temperature using a CVC601 sputtering system in 10 mTorr of Ar. The substrate to target distance was approximately 12 cm. The Si wafers were prepared by thermally wet growing a 200-nm-thick SiO$_2$ layer at 1200 °C. A 35-nm-thick MgO buffer layer was then deposited on top of the SiO$_2$ by rf magnetron sputtering from a 20-cm-diam MgO target in an 90% Ar:10% O$_2$ atmosphere with the substrate at ambient temperature. The MgO layer prevents Si diffusion into the YBCO film and Cu diffusion out of the YBCO film. The SiO$_2$ layer is used to electrically isolate the YBCO film from the substrate and it could serve as a supporting membrane if Si micromachining was used to fabricate thermal isolation structures for uncooled infrared pyroelectric detectors. X-ray diffraction and Raman microprobe investigation of YBCO thin films fabricated in a similar manner yielded broad peaks, consistent with an amorphous thin film. The grain size in the YBCO thin films is estimated to be less than 10 nm from the X-ray diffraction data by using Scherrer’s Formula, indicating the absence of long range structural order. To allow for the propagation of high frequency electrical signals, silver (Ag) microstrips were fabricated on top of the YBCO, with a 20-μm-wide gap to allow for the optical illumination of the YBCO film. The Ag microstrips were fabricated to be 100 μm wide and 300 nm thick by thermal evaporation at room temperature and lift-off patterning. The substrate holder provided a conducting ground plane for the microstrip transmission lines. Aluminum (Al) wires were ultrasonically bonded to the ends of the silver microstrips to provide electrical contact.

The experimental setup for the study is shown in Fig. 2. A YAG laser was used to excite a fast, transient photoreponse in our samples. The laser had a repetition rate of 80 kHz, pulse duration of 150 ps, wavelength of 1064 nm, and beam spot diameter of less than 50 μm at the sample surface. The pulse energy, measured approximately 2 cm from the sample, was varied from 0.125 to 25 μJ with neutral density filters. The sample formed a photoconductive switch-type structure as the laser radiation illuminated the YBCO in the 20 μm gap between the two Ag microstrips (see inset in Fig. 2). The structure was illuminated through a microscope objective and positioned with the help of an X-Y-Z stage and visible light from the doubling crystal. The microstrip was connected to a high-speed semirigid coaxial cable. The volt-
The voltage response of the sample was recorded directly by a 400 MHz bandwidth, 2 gigasamples/s Tektronix digital oscilloscope.

The continuous-wave (cw) excitation experiments were conducted in the same setup as presented in Fig. 2, but with an Ar-ion laser beam at 493 nm and the frequency-doubling crystal removed. The beam was focused to a 20-μm-diam spot. The laser fluence varied from 1 to 100 W/cm². The voltage response was measured with a voltmeter.

IV. RESULTS AND DISCUSSION

Typical voltage transients of an amorphous, unbiased YBCO thin film to pulsed laser illumination are presented in Fig. 3. The voltage signal corresponds to the change in the voltage across the gap in the microstrip. In this geometry, the microstrips sampled the change in the surface charge underneath the strips due to the temperature dependence of the spontaneous polarization. The amorphous YBCO thin film was likely strain poled during the fabrication process. Figure 3(a) displays the voltage response signals for the sample illuminated with different laser energies, while the inset shows a sequence of pulses on a time scale much larger than the laser pulse width. We note that the response is composed of a two-step microsecond risetime of the pulse and much slower, millisecond decay.

The rise time detail is presented in Fig. 3(b). We see clearly that the voltage signal consists of an initial fast rise time component of approximately 50 ns, followed by the slow risetime component of approximately 20 μs. The amplitudes of each component are shown in the inset. In both cases, they exhibit a rapid increase for laser pulse energies up to \( E / E_{\text{max}} = 0.2 \) and subsequent saturation for higher energies. The fast rise time observed in our samples is most likely due to the initial heating of the film by the laser pulse. In this case, a rapid reorientation of the polarization is believed to occur. Since, the intrinsic rise time of the oscilloscope is much shorter than the rise time measured, the electrical time constant \( \tau_e \) is attributed to the rate of change of the spontaneous polarization in the YBCO thin film. The situation may be complicated by a relatively fast thermal conduction mechanism along the Ag microstrips, carrying the heat to other areas of the film, thereby increasing area over which the microstrips sample the changing surface charge. Previous work on thermally isolated microbolometers has shown that metal leads are the dominant paths of thermal conduction. In this case, the microstrips, which are used to carry the electrical signal, also carry heat away from the gap region illuminated by the laser pulse, heating the underlying YBCO thin film over a larger area. The slow rise time component is not predicted by Eq. (4), but is most likely due to the redistribution of heat as discussed above. The combination of the electrical and thermal time constants of our system would thereby determine this slow rise time behavior. The prediction of Eq. (4) is compared to the measured pulse data \( (E = 0.005 E_{\text{max}}) \) in Fig. 4 using the electrical and thermal time constants and amplitude factor as fitting parameters. By least-squares fitting, the electrical and thermal time constants were determined to be \( \tau_e = 5 \) μs and \( \tau_{\text{th}} = 0.16 \) ms, respectively. In this case, the fitted electrical time constant determines the rise of the voltage from Eq. (4) and
would possess a significant thermal component due to the redistribution of the heat in the system. The fast rise time component is therefore a better measure of the actual electrical time constant of the YBCO film.

The thermal conduction to the Si substrate has been observed to proceed much more slowly, at least for the combination of YBCO on MgO/SlO/Si. This slow thermal relaxation due to thermal conduction to the substrate dominates the fall time of the voltage response \( (\tau_{th} \approx 0.16 \text{ ms}) \). The discrepancy between the prediction of Eq. (4) and the experimental data shown in Fig. 4 is likely due to an additional, even slower, thermal relaxation [see inset in Fig. 3(a)].

The saturation of the voltage response with increasing pulse energy [see inset in Fig. 3(b)] occurs due to the saturation of the spontaneous polarization with temperature. The overall voltage responsivity is estimated to be \( 30 \mu \text{V/W} \). This relatively low voltage responsivity is due to the long thermal time constant of the structure. Although the laser deposits a large amount of energy, the structure does not have the time to heat up significantly before the laser pulse has ended. This value is comparable to the \( 0.5-20 \mu \text{V/W} \) measured in Ref. 6 for ‘‘off-c axis’’ epitaxial YBa\(_2\)Cu\(_3\)O\(_y\) films illuminated with nanosecond-width pulses. In Refs. 13 and 17, responsivities as high as \( 10^4 \mu \text{V/W} \) were measured in similar films incorporated into thermal isolation structures and illuminated with chopped broadband infrared radiation. The relatively high thermal conductance to the substrate and the combination of long thermal time constant for the structure and very short optical pulse width are responsible for the drastically reduced responsivity observed in this work.

The voltage response was also measured when the structure was illuminated by a cw Ar-ion laser. The magnitude of the dc voltage with respect to optical power is plotted in Fig. 5. In this case, the voltage responsivity is measured to be as high as \( 40 \mu \text{V/W} \). At first, the observation of a dc voltage under cw illumination may not seem to be consistent with pyroelectricity since the temperature of the structure should reach equilibrium within a few milliseconds. However, the large input resistance of the multimeter used to measure the dc voltage does not allow the accumulated surface charge to decay other than through the high resistivity, semiconducting YBCO. The result is an extremely long electrical time constant and the appearance of a dc voltage. Therefore, the observed voltage would be determined by the temperature-dependent polarization, rather than its rate of change. Again, the responsivity is lower than previously observed\(^{13,17}\) because of the high thermal conductance to the substrate, but it is significantly higher than in the pulsed case since the temperature of the film has time to respond to the optical illumination.

**V. CONCLUSIONS**

We have investigated the unbiased, transient voltage response of amorphous YBCO thin films under pulsed and cw laser illumination. The transient behavior was found consistent with pyroelectricity with the transients being determined by the electrical time and thermal time constants of the material and the structure. The electrical time constant for the reorientation of the polarization is estimated to be \( 50 \text{ ns} \). The voltage responsivity of the thin films was measured to be \( 30 \mu \text{V/W} \) for 150-ns-duration laser pulse at low energies. At high pulse energies, the voltage response saturated due to the saturation of the spontaneous polarization. In our case, the pulsed response was limited by the short pulse duration compared to the thermal time constant of our structure. Under cw illumination, the voltage responsivity as high as \( 40 \mu \text{V/W} \) was observed, demonstrating that amorphous YBCO thin films are attractive for uncooled infrared detection. Higher responsivities are possible if the thermal conductance to the substrate is reduced by micromachining or by depositing the YBCO on a low thermal conductance substrate. In addition, it has been shown before that these detectors are compatible with Si technology and very easy to fabricate.

The photovoltaic effect has been ruled out for the following reasons. The amorphous YBCO thin films lack long-range crystalline order. There was also no evidence of photocconductivity in these samples under optical illumination over the range of 0.6–12 \( \mu \text{m} \) wavelength. Investigations of photoluminescence under 0.6 \( \mu \text{m} \) laser illumination were also negative. The random orientation of the small grains in the YBCO films would also seem to rule out the atomic layer thermopile effect observed in tilted crystalline YBCO thin...
films. Finally, it has been demonstrated that an unbiased voltage response can be induced in similar amorphous YBCO thin films by electric poling,\textsuperscript{14} which is again strong evidence of pyroelectricity.

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