Giant voltages upon surface heating in normal $YBa_2Cu_3O_{7-\delta}$ films suggesting an atomic layer thermopile

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Experiments are reported which show that temperature gradients perpendicular to the surface of epitaxial normal conducting $YBa_2Cu_3O_{7-\delta}$ films give rise to large transversal voltages between contacts on the film surface. The temperature gradients have been produced by pulsed laser irradiation and by continuous heating of the films by heater wires. To explain the large lateral voltages, an atomic layer thermopile is proposed, which may be formed by the layered structure of the material.

In recent experiments, transient voltaic signals have been observed at room temperature in $YBa_2Cu_3O_{7-\delta}$ films in response to pulsed laser irradiation.[1,2] An explanation of the signals suggested by the observed signal polarity reversal upon irradiating the films through the substrate based on a transverse thermoelectric effect[2] was questioned by the authors because of the diagonality of the Seebeck tensor in the orthorhombic point group D_{2h}. A photogalvanic mechanism due to an assumed noncentrosymmetric local symmetry of $YBa_2Cu_3O_{7-\delta}$ was suggested by Scott.[3] Transient voltaic signals were also observed in $YBa_2Cu_3O_{7-\delta}$ single crystals upon applying heat pulses and stress.[4] These results were attributed to pyro- and piezoelectricity.

In this letter, we report on the observation of voltaic signals in epitaxial $YBa_2Cu_3O_{7-\delta}$ films induced by pulsed laser heating, and also by continuous heating with heater wires. The signals picked up by lateral point contacts on top of the film are proven to be due to a temperature gradient normal to the film surface. Effects due to lateral gradients should show a polarity reversal if the focus of the laser beam is moved from one contact point to the other, reversing the lateral temperature gradient thereby. Even more surprising is the magnitude of the observed effect. In a typical laser pulse heating experiment, temperature differences of $\Delta T \sim 50$–100 K between film surface and substrate are obtained, giving rise to signal voltages of ~ 1 V. Using a Seebeck coefficient measured in $YBa_2Cu_3O_{7-\delta}$ single crystals,[5,6] signal voltages of only $\leqslant 10^{-3}$ V should be observed. Both the occurrence of lateral voltages and the strength of the signal contradict the usual Seebeck effect in a homogeneous material. Detailed investigations of the distribution of the electric potential in the film surface with respect to the location of the laser heated spot suggest a simple model which is still based on thermoelectricity. Conducting CuO_2 layers and less conducting material separating the layers may form a series of thermocouples. A high T_c film oriented with a small angle between c-axis and substrate normal may then be regarded as an atomic layer thermopile. Finally, we give an estimation of signal voltages on the basis of this model and obtain values consistent with the magnitude of the experimentally observed effect.

$YBa_2Cu_3O_{7-\delta}$ films of about 500-nm thickness epitaxially grown on $SrTiO_3$ and MgO substrates were used for the measurements. Electrical point contacts were made with silver epoxy paint on the film surfaces. The film area was 10×10 mm^2 and the distance between contact points on the film surface was typically 6 mm. A Nd:YAG laser ($\lambda = 1.06$ μm) with pulse duration ~ 100 ns and pulse energies 1–10 mJ was used for film heating. The irradiated film area was limited to a spot of about 2-mm diameter by a diaphragm. Signals obtained at room temperature are shown in Fig. 1 together with the orientation of the laser beam with respect to the sample. The central area of the film was irradiated with a pulse energy of 10 mJ/cm^2. Heating the film directly with the laser beam [Fig. 1(a)] leads to a signal pulse of nearly 1 V and of constant polarity. From bolometric measurements,[7] a heat propagation model,[8] and investigations of the Nernst effect in high T_c films,[9] we estimate a maximum temperature difference between film surface and substrate during laser heating of $\Delta T \sim 50$–100 K for the described conditions. The temporal behavior of the observed voltaic signal is consistent with decay of the temperature gradient due to heat diffusion. The temporal evolution of ΔT was also calculated numerically. The detailed time dependence of the laser output (with overall pulse duration 100 ns) was used to model a time dependent surface heat source. $\Delta T(t)$ was then calculated [dashed line in Fig. 1(a)] using a modified Schmidt method[8,10] and values 5000 Å and 0.02 cm^2/s for the film thickness, and thermal diffusion constant, respectively. The experiment demonstrates that the observed voltages are of thermal origin, but are very large with respect to values of $\Delta T \sim 50$–100 K produced by the laser heating. The time dependence of a signal pulse obtained by irradiating the film through the substrate is shown in Fig. 1(b). At first during laser heating, the temperature gradient and thus, the signal voltage, is reversed with respect to the arrangement of Fig. 1(a). After completion of the laser pulse, when heating of the film is terminated, the polarity of the signal changes. The sign of the signal is now the same, like irradiating the free surface of the film. This observation again proves the interpretation of the voltage signal being caused by a temperature gradient normal to the film. As the heat flow from the film to the substrate is larger than from the free film surface to the ambient air, the temperature gradient in the freely cooling film gets reversed and, therefore, the induced voltage changes sign. A calculation of the time dependence of the temperature gradient

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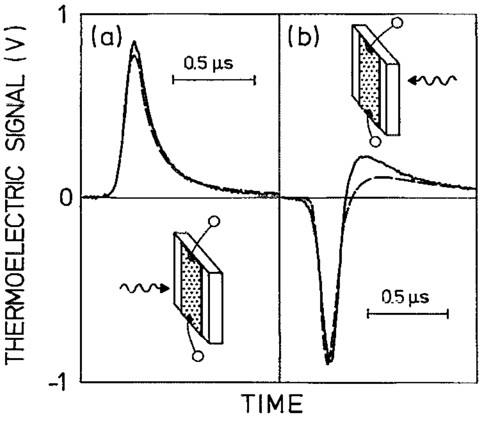
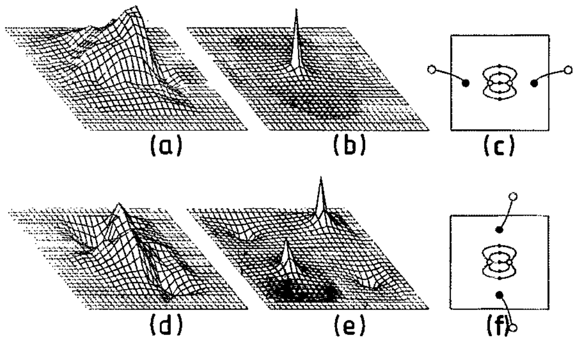


FIG. 1. Thermoelectric signal of $YBa_2Cu_3O_{7-\delta}$-film in response to pulsed laser heating, for different geometries. Dashed lines: Calculated temperature gradient, normalized to the signal maximum. Irradiating the film through the transparent substrate (b) leads to a reversed gradient during laser heating, with respect to the arrangement of (a).

[dashed line in Fig. 1(b)] again gives agreement with the experiment.

The spatial distribution of the electric potential in the plane of the film due to heating a small spot on the film surface was determined by a series of point contacts on the circumference of a circle of about 4-mm radius. The center of the circle was heated by the focused laser beam and the voltage signal of diametrically facing contacts was recorded. The signal height showed a sinusoidal dependence on the angle around the circle with maximum values, zeroes, and polarity reversals. This result demonstrates that at the heated spot a dipolar electric source is generated with a component in the plane of the film. The orientation of the dipole is fixed with respect to the geometry of the sample.

For a more detailed investigation of signal dependence on the heating spot position, the focus of the laser was scanned over the film surface and the signal height was recorded for several different contact pairs. Two examples are given in Fig. 2. In Fig. 2(a), a contact pair is investigated along the induced dipole [schematic representation Fig. 2(c)]. The vertical axis of Fig. 2(a) gives the height of the thermoelectric signal. Maximum signal is obtained for film heating half way between the contacts. Reversed signal polarity is observed if the heated spot is moved beyond the contacts. Figure 2(d) shows a similar experiment. However, contacts at ~90° with respect to the arrangement of Fig. 2(a) have been used. Relatively small signals are observed in this case, with extended regions of reversed signal polarity. The signal shows a symmetry characterized by a reflection in a plane normal to the diagonals of the film.


(a) (b) (c)

(d) (e) (f)

FIG. 2. (a),(d) Height of the thermoelectric signal (vertical figure axis) in dependence of heating spot position, for two pairs of contacts (black dots). (b),(e) Results of a computer model simulating the signal by a plane dipole source located at the heated spot. Maximum signal (a),(b),(c) or zero signal (d),(e),(f) is obtained, depending on contact pair.

In a simple heuristic model, we assume the creation a macroscopic electric dipolar source within the plane of the film due to the laser heating, with a dipole length corresponding to the diameter of the heated spot, and an orientation of the dipole "built in" in the film. In a computer simulation, we scan this source across the plane of the film and calculate the electrical potential at the contact points. Results are shown in Figs. 2(b) and 2(e). For the geometry of Fig. 2(a), we find, as may be expected, a maximum signal if the dipolar source is placed between the contacts. Signal reversal is obtained if the dipole is moved beyond the contacts. For the geometry shown in Fig. 2(d), no signal is found for heating the center of the film. Placing the dipole into one of the film corners, the signal polarity is due to the sign of the charge nearest to a contact, and a signal pattern with diagonal symmetry is obtained, as observed in the experiment. The model could be improved by use of a distributed dipolar source instead of a point source to give a better description of the relatively smooth dependence of the thermoelectric signal on location.

Instead of laser heating, the film surface was also heated with heater wires. Taking into account the small temperature gradients, the magnitude of the observed signals is consistent with the voltages obtained by laser irradiation. Again, reversal of temperature gradients results in a polarity reversal.

From the experiments, we find that the observed voltaic signal is due to temperature gradients in the film, the dynamical behavior of the signal is consistent with heat transport by heat diffusion. On the other hand, the magnitude of the signal is by several orders too large to be explained by Seebeck coefficients.[5,6] Therefore, we suggest an explanation of the large thermoelectric voltages based on a model of a series connection of thermocouples, which may be formed by the high T_c materials in a natural way. In Fig. 3(a), a plane thermopile is shown, consisting of a series connection of thermocouples. The thermopile is heated from above, leading to a temperature difference $\Delta T = T_1 - T_2$ between upper and lower contacts. A voltage $U = N(S_A - S_B) \times \Delta T$ should be obtained, where N is the number of elements, and $S_A - S_B$ is the difference of Seebeck coefficients of the two involved materials.

A similar thermopile may be formed by conducting layers of different materials (with Seebeck coefficients S_A and S_B), inclined with respect to the substrate [Fig. 3(b)]. Such a structure may be given by the high T_c materials. With film thickness $D = 5000$ Å, period $c \simeq 11$ Å in direction of c axis for $YBa_2Cu_3O_{7-\delta}$, we obtain with

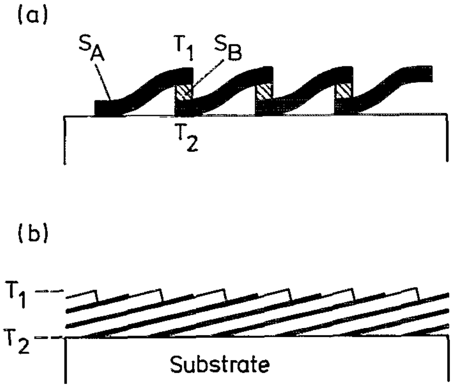


FIG. 3. (a) Plane thermopile made from materials with Seebeck coefficients S_A and S_B. Temperature of upper contacts, T_1, of lower contacts, T_2. (b) Plane thermopile formed by layers inclined with respect to the substrate. For $YBa_2Cu_3O_{7-\delta}$, the layer period is $c\simeq 11$ Å.

$\delta T\simeq[(T_1-T_2)c]/D$ for the temperature difference between layers and the number $N=(d\sin\alpha)/c$ of elements within a heated spot of diameter d, and an assumed inclination α of the c axis with respect to the surface normal,

$$U=\frac{d\sin\alpha}{c}\frac{(T_1-T_2)c}{D}(S_A-S_B)\simeq\frac{d\alpha}{D}\Delta T\Delta S.$$

For the Seebeck coefficient, a value $\sim 15\ \mu$V/K (at 300 K) has been found[6] perpendicular to the c axis, smaller values 5 μV/K along the c axis. We take $\Delta S=10\ \mu$V/K in our estimation. With a heating spot diameter $d\sim 2$ mm, $\alpha=10°$, and $\Delta T=100$ K we obtain $U=0.7$ V, which is of the same order of magnitude as the voltages found in the experiment.

The exact value of the angle α has not been investigated by us. However, small angles between surface normal and c-axis have been reported by several groups.[11] Small angles α may be due to not precisely cut substrates, or may depend on details of the film deposition process. Finally, we qualitatively have observed a correlation between film quality and the height of the thermoelectric signal. Granular films did not show a thermoelectric signal; largest signals were obtained for smooth metallic mirrorlike films.

The symmetry of the assumed layer film structure may be reduced compared to the bulk by finite size effects. Thus, lateral thermoelectric voltages, pryolectricity, and the photogalvanic mechanism proposed by Scott[3] could become effective leading to voltage signals. However, the mere strength of the voltage response observed in the present measurements, the long decay time after pulsed irradiation, and the dependence of the sign of the signal on the orientation of the temperature gradient are strong evidences that the signals are dominantly generated by the suggested atomic layer thermopile. Additionally, the fact that corresponding voltages can be produced by hot wire heating indicates a thermoelectric origin. Our model, admittedly somewhat speculative, reproduces almost quantitatively the observed phenomena. Finally we note that $YBa_2Cu_3O_{7-\delta}$ films at room temperature represent simple photovoltaic energy monitors for pulsed laser radiation.

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