Laser-induced transverse thermoelectric potential in bismuth films: Evidence for optical pumping to a metastable band

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A model is developed to explain the temporal evolution of the laser-induced transverse thermoelectrical response in bismuth films. The effect is studied with a 1.064-μm laser and with a 10.6-μm laser. The qualitative difference of the film response to each wavelength is evidence of the existence of a metastable band in bismuth. Its energy is $\approx$0.58 eV and its recombination rate is lower than 2×10^7 s^{-1}.

I. INTRODUCTION

It is well known that pulsed laser irradiation in metallic films generates transverse thermoelectric potentials.[1–5] The origin of these potentials is believed to be the ingrown tensions produced by controlled or uncontrolled asymmetries in the deposition process.[4,5]

The heat-diffusion equation has been often used to calculate the thermal distribution produced by laser pulses in surfaces[6] and in thin films.[7] In several works indirect evidence exists that this equation gives rise to correct predictions. Some authors point out limitations to its applicability in pulses of very high intensity, $I > 10^{10}$ W/m^2.[8] In the case of ultrashort pulses (in a time scale of hundreds of picoseconds) it seems necessary to consider the electrons that are unthermalized with the lattice.[9] However, when the pulse's temporal width is in the nanosecond time scale and the radiation intensity is moderate, it has been experimentally shown that the heat-diffusion equation predicts the temporal evolution of the induced temperature in a silver surface.[10]

In a previous paper[11] we have studied the electric response to a Nd-YAG (neodymium-doped yttrium aluminum garnet) (1.064-μm) laser pulse in 5.5-μm bismuth films when a magnetic field was applied parallel to the film surface and perpendicular to the measurement direction. The anomalous temporal evolution of the thermomagnetic response then observed was well explained by supposing that electrons were optically pumped to a metastable band. This model fitted reasonably well the film response. The present work studies the thermoelectrical response to two different wavelength laser pulses in 5.5-μm Bi films. As other metallic films, those of bismuth generate a transverse thermoelectric voltage when they are irradiated with laser pulses. If the laser photon's energy is below the energy of the lowest state of the metastable band, the dominant energy absorption is by free carriers and the laser-induced thermoelectric pulse will follow the prediction of the heat-diffusion equation. On the contrary, if the laser photon's energy is enough to produce optical pumping, the temporal profile of the thermoelectric response will not follow the expected temporal evolution as in the already observed case of the thermomagnetic voltage.[11]

In bismuth, the edge of the lowest absorption band is 0.3 eV above the Fermi level.[12–14] To study the thermoelectric response with and without a possible optical pumping, two different laser wavelengths were used. Photons with 1.17 eV (1.064-μm wavelength) will pump electrons into the metastable band, which will modify the thermoelectric response, and photons with 0.12 eV (10.6-μm wavelength) will produce the thermoelectric effect without such an optical pumping. These predictions are well proved by fitting both experimental responses with the heat diffusion equation. In the case of 1.17-eV photons the fit is only possible if an additional source term is included: the delayed heat generated by the recombination of those carriers optically pumped.

The experimental results provide enough evidence about the existence of a metastable band in bismuth and the influence of such a band in the generation of transport effects by laser pulses of wavelengths shorter than $\approx$ 3.5 μm.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation and characterization

Films were grown on glass substrates by vacuum evaporation (10^{-6} Torr) of 99.9999% pure Bi. Before evaporation the substrates underwent a standard process of ultrasound cleaning. The film thickness was controlled by a quartz-crystal monitor during evaporation and later confirmed by a surface-profile analyzer. 5.5-μm samples were evaporated at room temperature (300 K). The estimated deposition rate was 23 nm/sec. Electrical connections were made with silver paste. The films' configuration on the glass substrate, as well as the design of the support connections to extract the electrical signal, are shown in Fig. 1. The films were circular, having a diameter of 3.5 mm. The dc electrical resistance of the samples was about 1.2 Ω.

Films grown with a deposition rate between 5 and 10 nm/sec under identical conditions, having thicknesses

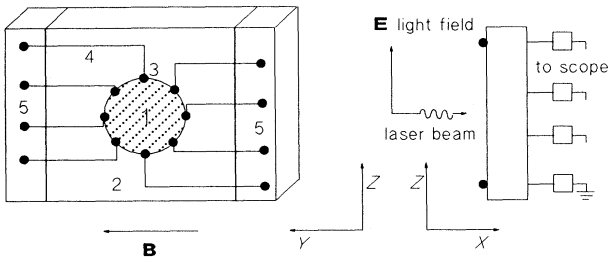

FIG. 1. 1, Bi film; 2, glass substrate; 3, Ag paste; 4, Cu electrical contacts; 5, isolator.

between 80 and 90 nm, were analyzed by electron-transmission microscopy. The films had a microcrystalline structure, the trigonal axis being perpendicular to the substrate and the binary axis being randomly oriented. The grain size was of the same order of magnitude as the film thickness.

The films were optically characterized by means of a spectroscopic ellipsometer in the 300–900-nm wavelength range. From these measurements we obtained extrapolated values at 1.064 μm for the absorption coefficient $A \approx 0.65$ and for the attenuation distance $x_L \approx 50$ nm.

B. Measurement system

Two different lasers were used to irradiate the films at room temperature. The first set of measurements was obtained irradiating the films with a Q-switched and polarized Nd-YAG laser. A typical impinging laser pulse had a temporal width of $\approx$ 6 nsec and an energy of $\approx$ 0.39 mJ evenly distributed on a $\approx$12-mm^2 section where the sample was placed. Thus the radiation intensity was below the limit 10^{10} W/m^2.

A beam splitter was used to divide the laser beam. The first of these beams was detected by a <1 nsec rise time photodiode to be used as a monitoring signal. This first beam was also used to synchronize a transient programmable digitizer. The second beam fell on the surface of the film. The electrical potentials generated in the film were registered in the transient programmable digitizer, its 3-dB bandwidth being 600 MHz. The sample was directly linked with the oscilloscope through a BNC connector. All electrical lines were impedance matched at 50 Ω.

A second set of measurements was taken using an experimental CO_2 transversely excited atmospheric (TEA) pressure laser[15] to irradiate the films. In this case, the typical laser pulse temporal width was about 60 nsec and the laser pulse energy was about 0.35 mJ homogeneously distributed on a $\approx$12-mm^2 section where the sample was placed. The laser energy was measured with a photon drag detector having a rise time <1 nsec. The pulses were recorded by a transient digitizer with a real time bandwidth of 600 MHz. In order to avoid the stray field produced by radio frequency, the entire measurement system was placed inside a Faraday cage. All electrical lines were impedance matched at 50 Ω.

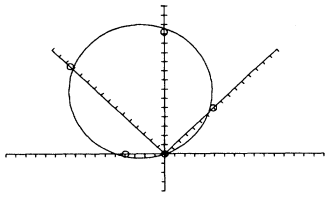

FIG. 2. Polar diagram of the thermoelectric potential.

C. Results

The contact's design of the sample (see Fig. 1) allowed us to measure the thermoelectric response of the film in four different directions. The sample was irradiated with the Nd-YAG laser at the same energy density of $w_r \approx$ 39 J/m^2 for all the directions. Figure 2 shows the results of these measurements. Each point is an average of five values. These values are the ratio V_{TE}/V_L, V_{TE} being the maximum of the thermoelectric pulse and V_L the maximum of the laser pulse. The polar diagram shows a clear Lambertian dependence of the thermoelectric response. The direction of highest thermoelectric response was selected to perform the experiments.

A typical Nd-YAG laser pulse and the corresponding generated transverse thermoelectric potential are shown in Fig. 3. The thermoelectric signal of this figure corresponds to an average of ten registers. Figure 4 shows a typical CO_2 laser pulse and the film thermoelectric response. In this case, the thermoelectric signal corresponds to an average of five registers. The CO_2 laser pulses are very repetitive.[15] It can be noted that in the case of the Nd-YAG laser, the transverse thermoelectric response has a longer fall time (in the time scale of the laser pulse width) than in the case of CO_2 laser irradiation.

III. THEORETICAL APPROACH

The transverse thermoelectric potential studied in this work is produced by the absorption of a laser pulse in a

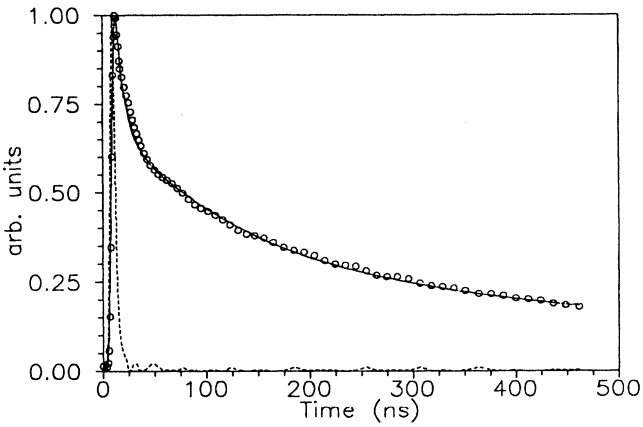

FIG. 3. Experimental and theoretical curves in the case of irradiation with the Nd-YAG laser. Dashed line, Nd-YAG laser pulse; circles, thermoelectrical response of the Bi film; solid line, theoretical result.

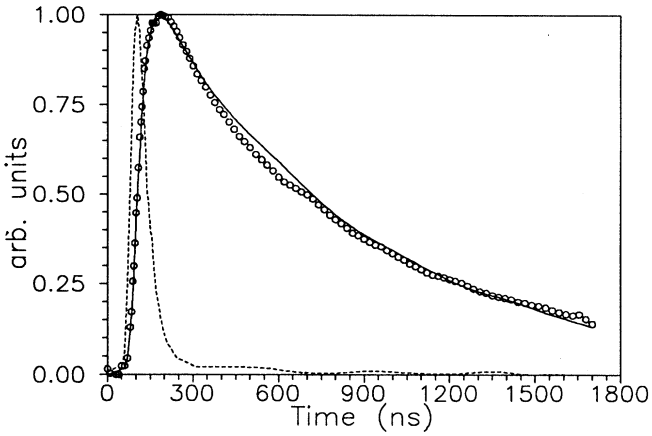

FIG. 4. Experimental and theoretical curves in the case of irradiation with the CO_2 laser. Dashed line, CO_2 laser pulse; circles, thermoelectrical response of the Bi film; solid line, theoretical result.

bismuth film. If we take the X axis parallel to the laser beam direction and orthogonal to the film surface, and the Z axis parallel to the transverse thermoelectric field, then the transverse thermoelectric potential will be

$$V_t = l\beta_{zx}\frac{\partial T}{\partial x}\,, \tag{1}$$

where l is the distance between electrodes, β_{zx} the transverse thermopower coefficient, and $\partial T/\partial x$ the thermal gradient.

The thermal gradient could be inhomogeneously distributed in the film thickness. In order to find an expression for the measured thermoelectric potential V_t we must find the Thèvenin equivalent of the film. We divide the film in slices of thickness Δx_i [see Fig. 5(a)]. The generated potential in one slice is

$$\Delta V_i = l\beta_{zx}(x_i)\frac{T_i - T_{i+1}}{\Delta x_i}\,. \tag{2}$$

The resistance of this slice in the transverse direction is

$$\Delta R_i = \frac{c}{\sigma(x_i)\Delta x_i}\,, \tag{3}$$

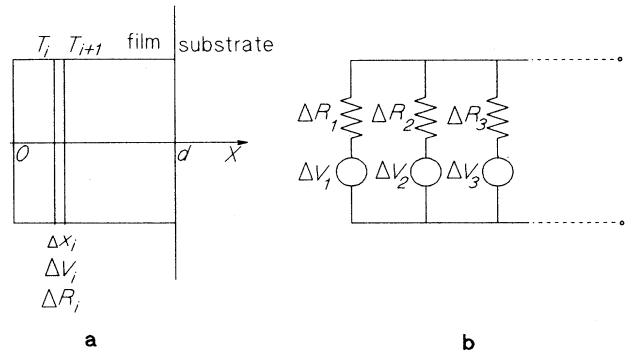

FIG. 5. (a) Cross section of the film showing a generic slice. (b) Equivalent circuit of the film.

where $\sigma(x_i)$ is the electrical conductivity and c is an adimensional geometrical factor.

Each slice is equivalent to a generator of electromotive force ΔV_i and internal resistance ΔR_i [see Fig. 5(b)]. When Δx_i tends to zero, the Thèvenin equivalent of all these generators associated in parallel will be

$$V_t = \frac{\int_0^d l\beta_{zx}(x)\frac{\partial T}{\partial x}\sigma(x)dx}{\int_o^d \sigma(x)dx} \tag{4}$$

and

$$R_t = \left(\int_0^d \frac{\sigma(x)}{c}dx\right)^{-1}\,, \tag{5}$$

d being the film thickness.

In principle, the temperature increase in each slice must be taken into account, and so then, the dependence of $\sigma(x)$ and $\beta_{zx}(x)$ with x. For bismuth the heat capacity is $c_p = 125.4$ J/kgK, the mass density $\rho = 9747$ kg/m^3,[10] and the thermal conductivity along the trigonal axis is $K_t = 6$ W/mK (Ref. 16) at 300 K. Under the CO_2 laser irradiation conditions, the energy density is $w_r \approx 30$ J/m^2. At 10.4 μm, the absorption coefficient is $A \approx 0.4$.[10,17,18] Assuming that the laser energy is absorbed in a thickness equal to the thermal diffusion distance, then the maximum temperature increase will be reached in this slice. This increase is about 12 K. In a semimetal in thermal equilibrium, this local temperature increase would result in a change in the electrical conductivity σ and perhaps in the transverse thermoelectric coefficient β_{zx}. In a compensated semimetal at room temperature, the main contribution to transport phenomena is given by thermally excited carriers. But the transition from the valence band to the conduction band is an indirect transition. The phonons' density, with the necessary energy and crystalline momentum to induce this indirect transition, is very low at room temperature. Then, the probability of such a thermal process is very low and the conduction-band population is not affected by the lattice temperature increase in the time scale of our measurements. So then we deal with a nonequilibrium phenomenon. When enough time has passed to consider this kind of indirect transition, the thermal gradient is much lower, the averaged temperature increase of the film being about 2 K.

We can apply the same argument for the thermal transitions when we irradiate with the Nd-YAG laser. The effect of electrons optically pumped to the metastable band will be modeled by a modified recombination rate for this band.

Consequently, we take the transport parameters $\sigma(x)$ and $\beta_{zx}(x)$ as constants along the X direction. Then it can be written as

$$V_t = l\beta_{zx}\frac{T(d) - T(0)}{d}\,, \tag{6}$$

$$R_t = \frac{c}{\sigma d}\,. \tag{7}$$

Thus, the measured transverse thermoelectric potential

is independent of the thermal distribution across the film and only the temperatures in both surfaces are needed.

If the laser energy is mainly absorbed by free carriers and instantaneous energy transfer to the lattice is supposed, the thermal power per unit of volume entering the film is the source term in the heat-diffusion equation and it can be written as

$$\phi = \phi_0 e^{-\delta x/d} f(\tau) , \tag{8}$$

$$\phi_0 = \frac{A w_r}{\Delta t \int_0^d e^{-\delta x/d} dx \int_0^\infty f(\tau) d\tau} , \tag{9}$$

where $\delta = d/x_L$ and $\tau = t/\Delta t$; Δt is the pulse temporal width, x_L is the attenuation distance of the laser radiation in the material, $f(\tau)$ is the temporal profile of the laser pulse, A is the absorption coefficient, and w_r is the ratio E_r/s, E_r being the laser pulse energy and s the beam cross section.

If an optical pumping takes place between the valence band and one excited band, the laser power is absorbed mainly through interband transitions. These excited electrons will transmit a part of their energy to the lattice in a quick nonradiative relaxation process occupying the levels that are closest to the band edge. The rest of the energy will be liberated in a recombination process that would presumably take a time of about some tens of nanoseconds.

We also may assume that during the recombination time at least the slowest kinds of carriers do not spread excessively. The recombination processes that take place near the irradiated surface are the only ones that contribute to the thermal gradient. The diffusion length of carriers during the laser pulse width Δt is $\Delta x = \sqrt{2D\Delta t}$, D being the carrier's diffusivity. Taking D from the current literature[19] and having $\Delta t \approx 6$ ns, this length is $\Delta x \approx 8$ μm for holes. This distance is comparable to the film thickness. For electrons, the diffusion distance is much longer. Then, the studied phenomenon is clearly dependent of the carrier's diffusion from the irradiated surface neighboring the innerside of the film. The effect of this spread is formally included in the model as an additional relaxation rate, so we take the thermal energy produced during the recombination as entering with the same spatial distribution of the incident radiation.

With this model the thermal power per unit of volume entering the film would have the same form of Eq. (8),

$$\phi' = \phi_0 e^{-\delta x/d} f'(\tau) , \tag{10}$$

with $f'(\tau)$ expressed by

$$f'(\tau) = \left(1 - \frac{E_m}{h\nu_L}\right) f(\tau) + \frac{E_m}{h\nu_L} S_m \Delta t \int_0^\tau f(\tau') e^{-S_m(\tau-\tau')\Delta t} d\tau' , \tag{11}$$

where $h\nu_L$ is the photon energy, S_m is the total rate due to recombination and spread processes of carriers, and E_m the average recombination energy.

The temperature distribution is the solution of the heat diffusion equation

$$\rho c_p \frac{\partial T}{\partial t} = \phi_s + K_t \frac{\partial^2 T}{\partial x^2} , \tag{12}$$

where ϕ_s is the source term that will be given by Eq. (8) or (10), as we have discussed.

Since the film thermal conductivity is much higher than that of the substrate, the boundary conditions in the film surfaces are

$$\left(\frac{\partial T}{\partial x}\right)_{x=0} = \left(\frac{\partial T}{\partial x}\right)_{x=d} = 0 . \tag{13}$$

The integration of Eq. (12) is carried out by a standard Fourier-series expansion procedure arriving at

$$T(0) - T(d) = \frac{-4d\phi_0(1 - e^{-\delta})}{K_t F^2 \delta} \times \sum_{n=0}^{\infty} \frac{e^{-\gamma_{2n+1}^2 \tau}}{1 + \chi_{2n+1}^2} \int_0^\tau f_s(\tau') e^{\gamma_{2n+1}^2 \tau'} d\tau' , \tag{14}$$

where

$$\gamma_n = n\pi/F , \quad \chi_n = n\pi/\delta , \qquad F = d/\sqrt{a\Delta t} , \quad a = K_t/(\rho c_p) . \tag{15}$$

The function $f_s(\tau)$ must be replaced by the temporal profile of the laser pulse $f(\tau)$ (in the case of absorption by free carriers) or by $f'(\tau)$ given in Eq. (14) (in the case of optical pumping).

IV. FIT TO THE EXPERIMENTAL RESULTS

The expression (14) has been used to fit the temporal evolution of the measured transverse thermoelectric response to the laser pulses in the bismuth films. Since we are interested in the temporal profile of the phenomenon, the theoretical curves have been normalized to the maximum of the experimental curves.

Under the hypothesis of an interband absorption, we have fitted the response to 10.6-μm TEA CO_2 laser pulses. Figure 4 shows the best fit. The bismuth physical constants $c_p = 125.4$ J/kg K and $\rho = 9747$ kg/m^3 were taken from current literature. The magnitudes K_t and x_L were taken as free parameters. The fit shown in Fig. 4 was obtained with $K_t = 6.0$ W/mK and $x_L = 1.2$ μm, which are in good agreement with those values reported in the literature.[16–18]

The thermoelectric response to 1.064-μm Nd-YAG laser pulses cannot be fitted by the intraband absorption model. We need a K_t value one order of magnitude lower than in the previous case to fit the experimental results with this model. Nevertheless we get a good fit to the 1.064-μm laser-induced transverse thermoelectric profile using the source term given by Eqs. (10) and (11), which includes the optical pumping (Fig. 3). The same K_t value is used here. The values of E_m and S_m that fit the experimental transverse thermoelectric profile are $E_m = 0.58$ eV and $S_m^{-1} = 57$ nsec.

The value of E_m is nearly the same as that obtained in the 1.064-μm laser-induced Nernst-Ettingshausen ef-

fect and the value of S_m is lower.[11] This result is not surprising since that fit was made to the very beginning of the thermomagnetic response profile and the value of the radiation penetration depth $x_L = 20$ nm was taken from the literature. This value is quite lower than the one measured in the present work. Both reasons justify the discrepancy in the S_m value.

V. DISCUSSION AND CONCLUSIONS

In a previous paper, the existence of a metastable band in bismuth was assumed to explain the temporal evolution of the thermomagnetic potential induced in Bi films by 1.064-μm laser pulses. The present work describes a different kind of experiment consisting in the study of the temporal evolution of the thermoelectrical potential generated in the films when they are irradiated with 1.064-μm and 10.6-μm laser pulses. The experiment gives additional proof about the existence of the mentioned band in bismuth.

The results are completely consistent with the metastable band hypothesis. Nonoptical pumping of carriers can be produced for this metastable band by the low energetic TEA CO_2 laser photons ($h\nu_L \approx 0.12$ eV), the absorption being mainly due to free carriers. The free carriers transfer their energy to the lattice in a fast scattering process that, in the time scale of our experiments, is practically instantaneous. The heat-diffusion equation explains perfectly well the phenomenon, considering only the laser absorption source term. Nevertheless, the more energetic Nd-YAG laser photons ($h\nu_L \approx 1.17$ eV) are able to pump electrons from lower bands to the metastable band. About half the energy ($h\nu_L - E_m$) of the excited carriers is quickly released into the lattice in a nearly instantaneous scattering process. This energy generates a source term similar to the one produced by the intraband absorption. The remaining energy is released through recombination processes at a slower rate. This energy is transferred to the lattice by scattering by phonons and gives rise to the additional source term given in expressions (10) and (11). Integrating the heat-diffusion equation with this source term, we have fitted the response to the Nd-YAG laser pulses using the same thermal parameters that fitted the response to the CO_2 laser pulses. The fit is almost perfect in this case also. It is completely impossible to get a good fit with reasonable values of thermal and optical constants without supposing that optical pumping occurs.

Then we must conclude, in agreement with the results of Ref. 11, that a metastable band exists in bismuth and can be populated by optical pumping in this kind of experiment. The mean energy of the populated states of this band is $E_m \approx 0.58$ eV. The recombination rate of this band is lower than the S_m value obtained, which takes into account the influence of carrier diffusion processes.

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