Laser-pulse technique for measuring the thermal diffusivity of substrate-supported polymer films

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We describe a technique for measuring the thermal diffusivity of substrate-supported polymer films based on the early-time electrothermal response following a 100 ns pulse from a *Q*-switched ruby laser. Data for a polyimide film spin coated on a *p*-doped Si[111] substrate are used to demonstrate the technique. From the late-time decay of the signal, we also obtain an estimate of the interfacial thermal-transport coefficient of the polymer–semiconductor interface. © *1999 American Institute of Physics.* [S0034-6748(99)04111-8]

INTRODUCTION

The efficiency of thermal transport perpendicular to the plane of thin polymer films and coatings on conducting and semiconducting substrates is an important factor in the design and packaging of microelectronic circuits and devices. Polymer films on the order of 1 μm thick are currently used, for example, as interlevel dielectrics in microelectronics packaging. Because the thermal conductivity of metals and semiconductors is relatively high compared to that of typical polymers, thermal transport across such films will in general be limited by both the thermal diffusivity of the coating material and the thermal boundary resistance of the polymer–metal or polymer–semiconductor interface. From the perspective of synthesizing new polymeric materials and designing new production techniques that optimize the rate at which heat is dissipated in such applications, it is desirable to have an efficient way of measuring one or both of these quantities independently.

For polymer films on the order of 10 μm thick, the thermal transit time is on the order of 1 ms, implying that fast measurement techniques are essential for an accurate determination of thermal-transport coefficients. Techniques such as the mirage method,[1] the pseudoguarded-hot-plate method,[2] the thermal-comparator method,[3] the microstrip technique,[4] and the laser-pulse thermal reflectance technique,[5] have been used to measure thermal transport in thin dielectric films. Here we describe a transient technique based on the thermal-pulse method for measuring charge and polarization distributions in polymer electrets.[6,7] It is an extension of a method used previously to measure the thermal diffusivity of substrate-mounted polymer films.[8] The approach described here, however, extends the usable range of early-time data by an order of magnitude, allowing a measurement of the bulk thermal-transport coefficient without the assumption of ideal heat sinking. From the late-time decay of the signal, we obtain an estimate of the interfacial thermal-transport coefficient of the polymer–semiconductor interface.

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EXPERIMENTAL DETAILS

Details of the thermal-pulse instrumentation and technique are described elsewhere.[9] A *Q*-switched ruby laser produces a 100 ns pulse of 675 nm light with a nominal energy of 0.7 mJ. The light pulse is optically guided into the sample cell, where it is normally incident on a 200 nm thick opaque Al electrode evaporated onto the front surface of a polymer film mounted on a conducting or semiconducting substrate. A bias voltage (either 0 or +27 V in the present work) is applied between the electrode and the substrate, which is maintained at a virtual ground potential and serves as a thermal sink. A charge amplifier connected to the electrode measures the charge response $q(t)$-induced by the thermal pulse via the capacitance change associated with the thermal expansion of the dielectric. A digital storage oscilloscope with a 12 bit, 10 MHz, analog-to-digital (AD) converter stores and averages the signal from 30 consecutive pulses delivered at 10 s intervals. Both a ''slow'' charge amplifier (Kistler model 504E dual mode[10]) and a ''fast'' charge amplifier (EG&G ORTEC Model 142C) are used in the work described here. The former resolves the signal for 10 μs$<t<$1 ms, where $t=0$ is defined by the peak position of the 100 ns pulse. The latter has a faster frequency response and resolves the early-time data (100 ns$<t<$5 μs).

MATERIALS

Polyimide films were prepared from Pyralin precursor solutions (PI-2540) obtained from HD Microsystems.[10] The substrates are *p*-doped [111] silicon wafers obtained from Semiconductor Processing.[10] After the wafers were cleaned and the native oxide layer restored, the Pyralin solution was spin coated onto the silicon wafer and annealed on a hot plate at 100 °C for 30 min. The sample was then annealed under vacuum while the temperature was ramped from 25 to 350 °C at 3 K/min, held at 350 °C for 60 min, and then allowed to cool to ambient temperature overnight. The film thickness d was measured with a model 2010 Metricon prism coupler.[10] For the sample described here, the nominal thickness obtained by averaging measurements at different points on the sample surface is $d=(9.24\pm0.5)$ μm.[11] The cured

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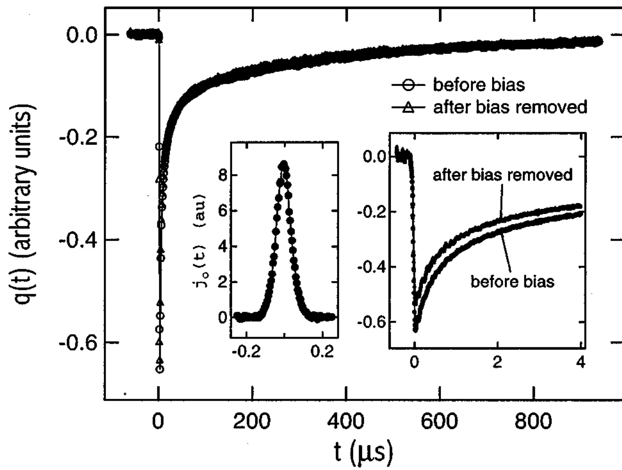

FIG. 1. Thermal-pulse response both before biasing and after a bias of +27 V (applied for roughly 0.25 h) has been removed. The main part is the late-time response measured with the ''slow'' charge amplifier and the inset on the right is the early-time response measured with the ''fast'' charge amplifier. The inset on the left shows the temporal shape of the input pulse.

polyimide coating has a specific heat of $c_p = 1.545$ J/cm^3 K.[12] A 200 nm thick Al electrode with a specific heat of $c_e = 1.408$ J/cm^3 K (Ref. 13) was evaporated onto the polymer film, and conducting silver-filled epoxy was then used to glue the backside of the Si wafer to an aluminum block inside the copper sample cell.

ANALYSIS

For a sample of thickness d, area A, and relative permittivity ε under a bias voltage V, the transient charge $q(t)$ generated by the input thermal pulse is[7,8]

$$q(t) = (\alpha_x - \alpha_\varepsilon)\varepsilon\varepsilon_0 \frac{A}{d} \int E(x,t)\psi(x,t)dx, \tag{1}$$

where $\psi(x,t) = T(x,t) - T_0$ is the deviation from ambient temperature (T_0) inside the dielectric film, α_x is the coefficient of thermal expansion, α_ε is the temperature coefficient of the dielectric permittivity, and ε_0 is the dielectric permittivity of free space. The electric field in Eq. (1) can be written as $E(x,t) = E_\rho(x,t) + V/d$, where E_ρ is the contribution from space charge within the film and V/d is the spatially homogeneous contribution from the external bias. Figure 1 shows the (zero-bias) response both before the bias has been applied and after the bias has been removed, along with the input pulse, which is approximated by a delta function. From these measurements, it is clear that the charge injected into the dielectric over the course of the experiment is small, and the space-charge contribution to Eq. (1) may be subtracted from the total response. Figure 2 shows the signal both with and without a bias of 27 V. The signal $q_b(t)$ due solely to the nonzero bias is calculated by subtracting the zero-bias response from the nonzero-bias response, and is given by

$$q_b(t) \sim \int dx\ \psi(x,t)/d = \bar{\psi}(t). \tag{2}$$

A fit of the early-time data to a model derived in the Appendix [Eq. (A4)] is shown in the inset of Fig. 3, and yields $D = (1.08 \pm 0.08) \times 10^{-7}$ m^2/s for the thermal diffusivity of the polyimide. This is in good agreement with previously reported values for a similar system using a technique that exploits only the late-time data.[8] A fit of the late-time data to the exponential decay (see the Appendix) $q_b(t) \sim \exp(-\Gamma t)$ gives $\Gamma = 2800$ s^{-1}. The assumption of perfect thermal contact at the semiconductor–polymer interface used in a previous study[8] implies $H \rightarrow \infty$, where H is the interfacial thermal-transport coefficient, and yields (see the Appendix) $D = (0.97 \pm 0.10) \times 10^{-7}$ m^2/s for the thermal diffusivity of the polyimide. Although this is in reasonable agreement with

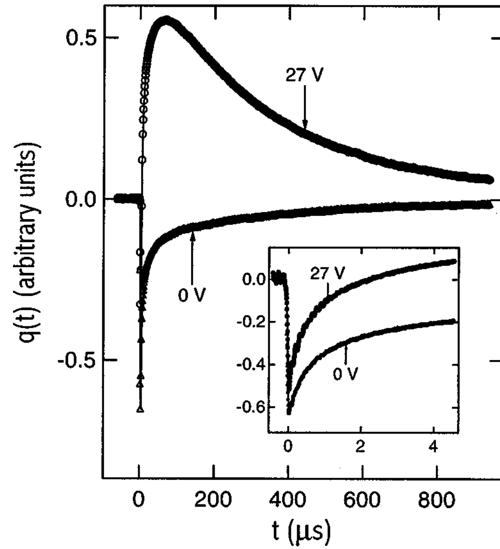

FIG. 2. Thermal-pulse response as a function of time for both a 0 and +27 V bias across the sample, where the main part is the late-time response and the inset is the early-time response. Note that the early-time response shows hysteresis with poling, indicative of weak charge injection in the presence of a nonzero bias.

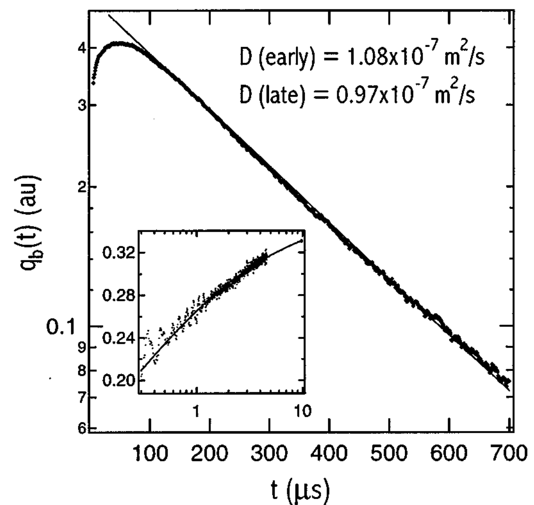

FIG. 3. Thermal-pulse response due solely to the nonzero bias voltage, where the space-charge (zero-bias response, Fig. 2) contribution has been subtracted from the total signal (27 V bias response, Fig. 2). The main part shows the late-time behavior, and the inset shows the early-time behavior. The fits are as described in the text and are used to extract the bulk thermal diffusivity from both the early-time rise of the signal (early) and the late time decay of the signal (late).

the value obtained from the early-time data, it is interesting to wonder if a finite value for H can be deduced from the discrepancy. From the late-time decay rate (Γ), a simple analysis (see the Appendix) yields the *estimate* $H \approx (3.1 \pm 1.0) \times 10^5$ W/m^2 K), and the approach described here thus offers an improvement over the assumption of perfect thermal contact at the polymer–semiconductor interface.

DISCUSSION

We describe a laser-generated thermal-pulse method for measuring the thermal diffusivity of substrate-mounted polymer films. Data for a polyimide (PI-2540) film spin coated on a p-doped Si[111] wafer are used to demonstrate the technique, which has potential applications for studying the distribution of space charge in thin substrate-mounted polymer films. A number of methods for precisely measuring the thermal boundary resistance between two different materials are available,[14–18] and an exact value of H for polyimide spin coated on silicon remains to be determined. The approach does offer an estimate of H, however, which is found to be roughly two orders of magnitude smaller than values previously reported for metal vapor deposited onto a dielectric.[15] This apparent discrepancy might simply reflect relatively imperfect physical contact between the polymer and the wafer.

APPENDIX

The deviation from the background (ambient) temperature inside the polymer film, denoted by $\psi(x,t) = T(x,t) - T_0$, is assumed to satisfy

$$\frac{\partial \psi}{\partial t} = D \frac{\partial^2 \psi}{\partial x^2}, \tag{A1}$$

where D is the thermal diffusivity of the polymeric material. This becomes $D\hat{\psi}''(x,s) = s\hat{\psi}(x,s)$, where $\hat{\psi}(x,s)$ is the Laplace transform of $\psi(x,t)$. For $t \ll d^2/D$, the appropriate boundary conditions are $\psi(x,t) \to 0$ for $x \to \infty$, and

$$\left(-\kappa \frac{\partial \psi}{\partial x} + m_e \frac{\partial \psi}{\partial t} \right)_{x=0} = J_0 \delta(t), \tag{A2}$$

where κ is the thermal conductivity of the polymer, m_e is the thermal mass of the electrode (located at $x=0$), and $J_0 \delta(t)$ models the input thermal pulse from the laser. In Laplace space, Eq. (A2) becomes $(-\kappa \hat{\psi}' + m_e s \hat{\psi})_{x=0} = J_0$, and the mean response is

$$\bar{\psi}(t) = \frac{1}{2\pi i} \int_C ds\, e^{st} \int_0^\infty dx\, \hat{\psi}(x,s)/d$$
$$= \frac{J_0 D}{2\pi i d} \int_C ds^{st}/s(\kappa + m_e \sqrt{Ds}), \tag{A3}$$

where the contour C runs parallel to the Im(s) axis to the right of the singularity at $s=0$. The integral is easily evaluated to give

$$\bar{\psi}(t) = c\{1 - e^{t/a^2}[1 - \mathrm{erf}(\sqrt{t}/a)]\}, \tag{A4}$$

where c is a constant of proportionality and $a = \sqrt{D} m_e/\kappa = (c_e/c_p) l_e/\sqrt{D}$.

For $t \gg d^2/D$, the appropriate boundary conditions are $-\kappa \partial\psi/\partial c = J_0 \delta(t)$ (at $x=0$) and $\kappa \partial\psi/\partial x = -H\psi$ (at $x=d$), where H is the thermal-transport coefficient of the polymer–semiconductor interface. In Laplace space, these are $-\kappa \hat{\psi}' = J_0$ (at $x=0$) and $\kappa \hat{\psi}' = -H\hat{\psi}$ (at $x=d$). Formally, the mean response can be expressed as

$$\bar{\psi}(t) = \frac{1}{2\pi i} \int_C ds\, e^{st} \int_0^d dx\, \hat{\psi}(x,s)/d, \tag{A5}$$

where the pole structure in $\hat{\psi}$ is now considerably more complicated than in the previous limit. Since we are interested in the asymptotic late-t behavior, however, we need only consider the contribution from the singularity closest to the origin, which gives $\bar{\psi}(t) \sim \exp(-\Gamma t)$, with $H = (\kappa/d)\theta_0 \tan\theta_0$ and $\theta_0^2 = \Gamma d^2/D$. In the case of perfect thermal contact between the film and the substrate, $R = 1/H = d \cot\theta_0/\kappa\theta_0 = 0$, which implies $\Gamma = \pi^2 D/4d^2$.

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