Thermochimica Acta 640 (2016) 42–51

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Heat conduction in ultrafast thin-film nanocalorimetry

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ARTICLE INFO

Article history:
Received 30 May 2016
Received in revised form 19 July 2016
Accepted 29 July 2016
Available online 1 August 2016

Keywords:
Thin-film nanocalorimetry
Thermal contact resistance
Non-Fourier heat conduction
Temperature-modulated calorimetry
Ultra-Fast calorimetry

ABSTRACT

Ultrafast nanocalorimetry on the basis of thin-film gauges was developed and utilized for studying phase-transition kinetics in thin-film samples. Ultrafast measurements at increasing rates of temperature change require a comprehensive analysis of the heat conduction processes. In this paper the analysis of the fast thermal response in thin-film samples at the boundary conditions corresponding to ultrafast calorimetric gauges is performed. The effects of interfacial thermal contact resistance and non-Fourier heat conduction are calculated analytically. The limits of validity of the classical diffusive heat conduction theory at high-frequency temperature-modulation measurements are studied. The alternatives of Fourier and non-Fourier heat conduction are considered. The conditions optimal for detection of the effect of non-Fourier heat conduction are defined.

1. Introduction

Thin-film ultrafast calorimetry was intensively developed in the last two decades [1–16]. It provides opportunities to generate nonequilibrium states and to study phase-transition kinetics at sub-millisecond timescales. The capabilities of thin-film calorimetry have been greatly enhanced with introduction of the low-stress amorphous silicon nitride membrane technology [9]. The scheme of such a thin-film calorimeter gauge from Xensor Integration, Nl, which can be utilized for ultrafast thin-film nanocalorimetry [8,10,11] is shown in Fig. 1. The technical details for the gauges are available on the website of Xensor Integration [12]. Calorimeters based on such thin-film (silicon-nitride membrane) gauges were recently constructed [6,7] and they were also utilized for investigation of thermodynamic processes in thin-film samples at high-frequency temperature-modulation [13–15]. Small thermal inertia and high resolution ca. nJ/K of thin-film calorimeters are possible due to the very small addenda heat capacity (ca. 10 nJ/K) of the silicon-nitride membrane gauges. The controlled ultrafast cooling and heating is possible up to 10^7 K/s [8,16] with the gauges similar to that available from Xensor Integration. Temperature-modulated calorimetry at frequencies up to 10^6 Hz was also realized [15]. However, the potential capability of thin-film calorimetric gauges is still not attained. As a realistic goal it is considered to achieve at least 10^7 Hz for thin-film samples in Helium gas as the cooling medium.

Increasing of the rate of the temperature change in calorimetric experiments is essential for research of irreversible processes in glass forming and nanoscale materials. However, a comprehensive analysis of heat conduction processes is required for correct measurements. In fact, the interfacial thermal contact conductance is a very significant parameter for ultrafast thermal measurements. Besides, the limits of validity of the classical diffusive Fourier heat conduction theory at ultrafast measurements should be determined. The possibility of the effect of nonequilibrium (non-Fourier) heat conduction at ultrafast thermal experiments should be taken into account. Actually, the effect of non-Fourier heat conduction can be essential, when the sample parameters are sharply varying in space and time. Relaxation effects in heat conduction were considered primarily by Maxwell [17], Cattaneo [18], and Vernotte [19]. Hyperbolic heat conduction equations (see below) were proposed for fast thermal processes as an alternative to the classical parabolic Fourier's law.

Recent trends in nanoscale devices and manufacturing processes promotes rapidly growing interest in non-Fourier heat conduction. Non-Fourier heat-conduction effects were found in dynamic thermal response of Graphene [20], single-walled carbon nanotube [21], and metal-dielectric core-shell nanoparticles [22]. The short-time heat conduction phenomena are of interest for the thermal design of micro- or nanosystems. Non-Fourier heat-transfer equations were utilized for designing of metal-oxide-semiconductor field-effect transistors [23]. Several studies were performed to solve non-equilibrium thermophysical problems aris-

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http://dx.doi.org/10.1016/j.tca.2016.07.023
0040-6031/

Nomenclature

Latin Symbols

$\hat{A}$, $\hat{B}$	Complex-valued amplitudes, K
c	Specific heat capacity, J kg^{-1} K^{-1}
D	Thermal diffusivity, m^2 s^{-1}
d	Sample thickness, m
f	Frequency, Hz
h	Thermal contact conductance, W m^{-2} K^{-1}
$\hat{k}$	Complex wave number, m^{-1}
l_q	Thermal-diffusion length, m
l_{ph}	Phonon mean-free-path, m
l_T	Thermal-wave length, m
N	Number of phonon collisions
n	Integer number
P	Volumetric heat power, W m^{-3}
$\mathbf{q}$	Heat flux vector, W m^{-2}
q	Heat flux modulus, W m^{-2}
$\mathbf{r}$	Space variable vector, m
t	Time variable, s
T	Temperature, K
ΔT	Interfacial temperature step, K
$D\hat{T}_h$	Normalized differential amplitude, K m s^{-1-1}
V	Speed of sound, m s^{-1}
x	Space variable, m

Greek Symbols

$\hat{\beta}$	Complex-valued coefficient, dim. less
γ	Coefficient, W^{-1} m^2 K
η	Damping coefficient, m^{-1}
κ	Wave number, m^{-1}
λ	Thermal conductivity, W K^{-1} m^{-1}
μ_n	Coefficient, s^{-1}
ξ_n	Eigenvalue, m^{-1}
ρ	Density, kg m^{-3}
τ	Time constant, s
Φ	Normalized heat power, K s^{-1}
φ	Phase shift, rad.
ω	Angular frequency, rad. s^{-1}

Subscripts

A	Amplitude
D	Dual-phase-lagging
H	Hyperbolic
h	Heater
n	Number of fourier component
m	Membrane
P	Parabolic
S	Sample
T	Temperature

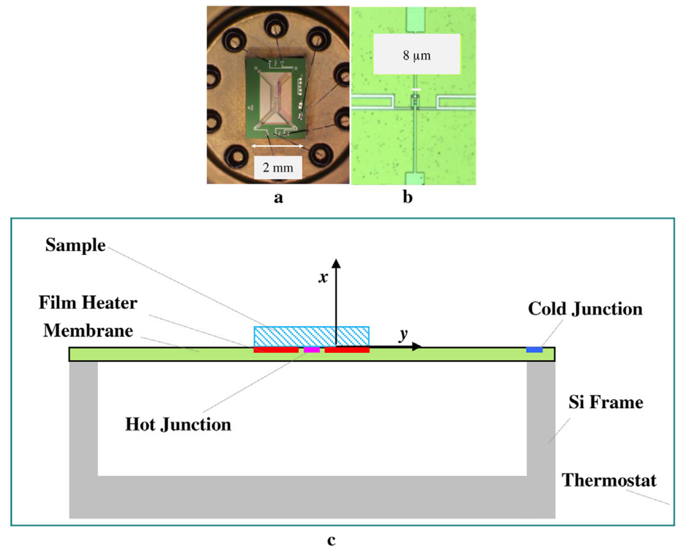

Fig. 1. Photograph of the gauge XEN-39394 utilized as a calorimetric measuring cell. The rectangular 2×3 mm^2 silicon frame supporting the submicron silicon-nitride membrane is bonded on a standard chip holder (a). Zoomed photograph of the central part of the membrane with $8 \times 10\,\mu$m^2 region heated by two parallel heater stripes and the hot junction of the thermocouple located in between the heater stripes (b). Schematic cross-sectional view of the gauge with the sample is shown in (c).

ing in materials processing [24,25]. Non-Fourier heat conduction theory was applied for explanation of physical properties of non-homogeneous [26], functionally graded [27,28], porous [29,30], and composite materials [31,32] designed for specific functions. Numerous studies were performed to solve non-Fourier heat conduction equations at different conditions [33–37]. An analytical solution of a transient thermal response in a slab sample under a periodic surface heating was obtained [33]. The thermal resonance in a slab sample at periodic heating was investigated; the conditions of under- and overdamped thermal oscillations were established [34]. Standing wave behavior at non-Fourier heat conduction was analytically studied in a porous material [35]. Stationary temperature oscillations in a slab sample in contact with a semi-infinite layer at periodic heating were investigated analytically for a broad frequency range [36]. The transient thermal response in thin-film samples was analyzed analytically in reference [37].

Comprehensive reviews of non-Fourier heat-conduction problems are available in the literature [38–42]. The concepts of local entropy-production and local temperature were reconsidered. Thus the extended irreversible thermodynamics was developed as a background for the non-Fourier heat-conduction theory [43–46]. It is worth mentioning that the numerical simulation for a one-dimensional chain of particles demonstrates a crossover from diffusive parabolic long-wave heat conduction to hyperbolic heat conduction in the short-wave range [47]. Such behavior requires application of the parabolic Fourier equation and demonstrates the necessity of a hyperbolic heat conduction theory. However, this study reveals that the characteristic relaxation time in an oscillatory hyperbolic regime depends on the wavelength of the temperature perturbations. Furthermore, a ballistic-diffusive equation is required to describe heat-conduction in very thin samples, when the phonon mean-free-path is comparable with the sample thickness [48]. Without doubt the classical diffusive Fourier heat-conduction theory is adequate for most applications; nevertheless, it may be insufficient for ultrafast processes in nanoscale systems.

The aim of this paper is to study heat conduction processes at ultrafast calorimetric experiments and to answer the question: what are the limits of validity of the classical diffusive heat conduction at high-frequency temperature-modulation measurements? What is expected in ultrafast experiments at considerable non-Fourier heat conduction? The goal is to compare the alternatives of Fourier and non-Fourier heat conduction in thin-film samples at high-frequency temperature modulation. The analysis is performed for boundary conditions corresponding to thin-film nanocalorimetry; the interfacial thermal contact resistances are taken into account. The origins of the factors, which suppress the effect of non-Fourier heat conduction at temperature-modulation experiments, are analyzed.