Thermochimica Acta 505 (2010) 1–13

Contents lists available at ScienceDirect

Thermochimica Acta

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

Fast scanning power compensated differential scanning nano-calorimeter: 1. The device

E. Zhuravlev, C. Schick*

University of Rostock, Institute of Physics, Wismarsche Str. 43-45, 18051 Rostock, Germany

ARTICLE INFO

Article history:
Received 18 January 2010
Received in revised form 18 March 2010
Accepted 22 March 2010
Available online 30 March 2010

Keywords:
Fast scanning nano-calorimetry
Differential power compensation
Temperature calibration
Crystallization
Metals

ABSTRACT

Fast scanning calorimetry becomes more and more important because an increasing number of materials are created or used far from thermodynamic equilibrium. Fast scanning, especially on cooling, allows for the in situ investigation of structure formation, which is of particular interest in a wide range of materials like polymers, metals, and pharmaceuticals to name a few. Freestanding silicon nitride membranes are commonly used as low addenda heat capacity fast scanning calorimetric sensors. A differential setup based on commercially available sensors is described. To enhance performance of the device a new asymmetric power compensation scheme was developed. The hardware realization of the scheme and calculation of differential power are presented in the first part of this paper. The fast analog amplifiers allow calorimetric measurements up to 100,000 K/s. The lower limit is defined by the sensitivity of the device and is 1 K/s for sharp melting or crystallization events in metals and ca. 100 K/s for broad transitions in polymers. Another limiting factor is accuracy of sample temperature measurement. A strong dependency of temperature on sample placement on the sensor is observed; even reproducibility is within ±1 K. For finite sample thicknesses the commonly observed thermal lag must be considered too. Uncertainty of the temperature measurement based on previous thermopile calibration is in the order of ±10 K. A significant improvement is possible by adding a small particle of a temperature calibration standard, e.g. indium or tin, on top of the sample under investigation. Then uncertainty is about ±3 K. The second part of the paper describes sample heat capacity determination and an example to demonstrate the performance of the device.

1. Introduction—fast scanning calorimetric techniques

Conventional differential scanning calorimetry (DSC) is one of the few techniques that have a relatively large dynamic range of scanning rates. It allows (quasi) isothermal measurements and scanning rates up to 10 K/s for power compensated DSCs [1,2]. Several approaches are known how to increase scanning rate. Most of them are based on thin film techniques. Quasi-adiabatic scanning calorimetry at high heating rates, ca. 500 K/s, was developed by Hager [3] and even for rates up to 10^7 K/s, by Allen et al. [4,5]. Similar approaches were used to study the behavior of metastable materials like vapor deposited films [6–8]. But investigation of metastable phase formation is possible only if the same high controlled cooling rates are available too. Fastest cooling of a calorimetric cell is obtained if no heat is applied to the cell (electrical power $P_0(T) = 0$ in the heat balance Eq. (1.1)). The maximum possible cooling rate is therefore defined by the ratio between the heat flow rate away from the measuring cell ($P_{loss}(T)$) and the heat capacities of measuring cell (addenda) ($C_0(T)$) and sample ($C(T)$).

$$(C_0(T) + C(T))\frac{dT}{dt} = P_0(T) - P_{\text{loss}}(T) \tag{1.1}$$

At a given temperature $P_{loss}(T)$ is in first approximation, assuming conductive and convection losses only, proportional to the temperature difference to the heat sink. Linear cooling is realized by keeping the right hand side of Eq. (1.1) at a constant negative value by controlling heater power $P_0(T)$. This idea was realized for fast scanning non-adiabatic nano-calorimeters based on thin film sensors (Fig. 1) [9] with extremely small addenda and sample heat capacity. It was shown that a gas is the optimum cooling agent to achieve largest cooling rates [10–12]. Furthermore, thermopiles are better suited compared to resistive thermometers because they do not need an electrical current, which always generates some unwanted power. The technique described in [9,11] is based on a single thin film chip sensor and is capable of applying both controlled heating and controlled cooling at rates up to 10^6 K/s.

This single sensor ultra-fast scanning device [11] was successfully applied for the investigation of polymer melting and crystallization. The reorganization kinetics in PET and iPS was studied in combination with conventional DSC at scanning rates

---

* Corresponding author. Tel.: +49 381 498 6880; fax: +49 381 498 6882.
E-mail address: christoph.schick@uni-rostock.de (C. Schick).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.03.019

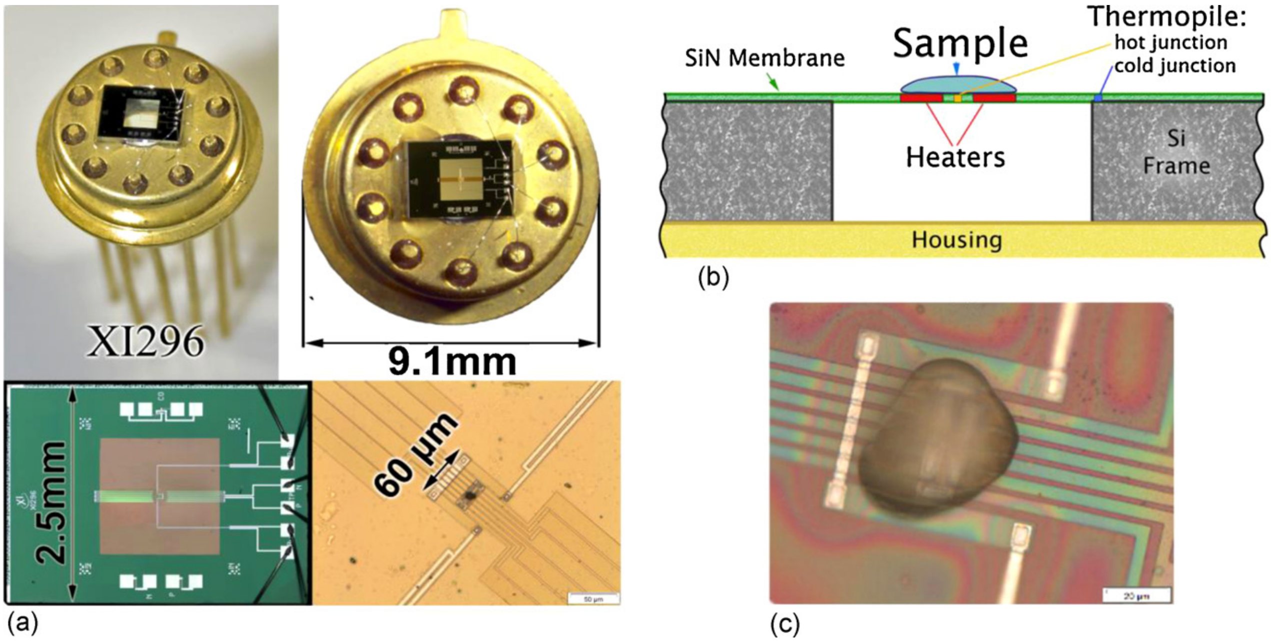

Fig. 1. Thin film chip sensor based on a thin free standing SiN_x film on a silicon frame and measuring area of 60 μm × 80 μm in the center of the film. (a) Different photographs of the sensor. (b) Schematic cross-section of the sensor with sample (not to scale). (c) Photomicrograph of a sample loaded sensor XI-296 [13].

covering 8 orders of magnitude [14–16]. Isothermal and non-isothermal crystallization and the formation of different crystal polymorphs were studied in a wide range of temperatures and scanning rates applying DSC and the fast scanning setup in PE, iPP and PVDF [9,17–24]. The complex behavior in the temperature range between glass transition and melting temperature was investigated in PBT [25]. The crystallization and cold crystallization suppression in PA6 confined to droplets and in the bulk was studied using such fast scanning calorimeter [26]. The dynamic range of scanning rates of the device allowed the investigation of superheating in linear polymers like iPS, PET, PBT and iPP [12,27].

The examples given above have shown that the effective range of controlled heating and cooling rates using different sensors [13] is 100–10^6 K/s. Unfortunately, at low rates signal to noise ratio and therefore sensitivity is reduced. Usually the device is limited to rates above 100 K/s for polymers. Nevertheless, the scanning rate range between conventional DSC and this technique – the range 10–100 K/s – is of high interest because several material processing steps are applying cooling rates just in this range [28,29].

In order to improve fast scanning nano-calorimetry the very successfully applied single sensor device as described in [9–11,30,31] was therefore first analyzed and the week points were identified.

- The first problem is the non-interactive temperature control, which is based on a predefined voltage–time profile yielding an essentially linear temperature increase of the sensor. But the needed voltage is only known for the empty sensor and not for the sample loaded one. Therefore the voltage profile should be corrected for each experiment by making at least one test scan with the sample under investigation [9]. This excludes the application to “first scans”, which are often needed if the influence of the sample history is of particular interest.
- Another problem is the sample temperature discontinuity at phase transitions. Even if a preliminary scan was performed to adjust the voltage profile for linear heating and cooling, the scanning rate during sharp transitions may significantly deviate from the programmed value due to large heat absorption or release by the sample. This results in smearing and inaccuracy of heat capacity and enthalpy determination. Similar problems exist for the adiabatic fast scanning devices [32].
- The main problem for heat capacity determination for the non-adiabatic single sensor device is the subtraction of the heat loss function. It is realized as a subtraction of a 3rd to 5th order polynomial function [9] providing C_p values symmetric around zero. But as soon as we have several sharp events in the sample, the error in determination of the loss polynomial increases dramatically. A solution to this problem is given in the second part of this paper [33].

To overcome these problems a differential scheme of two such sensors [9,11,34] with power compensation was constructed. The presence of an empty reference sensor reduces the influence of heat losses and addenda heat capacity on the obtained data dramatically. For a better sample temperature control, particularly in the transition regions, power compensation was introduced, this way following the work by Rodríguez-Viejo and co-workers [35,36] and Merzlyakov [37]. To improve signal to noise ratio and resolution of the device even under fast scanning conditions an analog power compensation technique was implemented. A differential power compensation scheme provides, under conditions of ideal symmetry of both sensors, directly the heat flow rate into the sample, which simplifies heat capacity calculation. Furthermore, user-friendly experiment management software and a software package for data evaluation were developed. The device including control and data treatment algorithms and measurements of metal samples on melting and solidification are presented finally to demonstrate the benefits of the instrument.

2. The device

The developed instrument is intended to measure heat flow rate into the sample as the power difference between an empty and a sample loaded sensor during fast temperature scans on heating and cooling at controlled rate. Finally, the obtained heat flow rate should be recalculated into heat capacity [33].

A very successful version of a power compensation differential scanning calorimeter was realized by PerkinElmer [38–41]. It