



Short communication

Temperature calibration procedure for thin film substrates for thermo-ellipsometric analysis using melting point standards



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ABSTRACT

Precise and accurate temperature control is pertinent to studying thermally activated processes in thin films. Here, we present a calibration method for the substrate–film interface temperature using spectroscopic ellipsometry. The method is adapted from temperature calibration methods that are well developed for thermogravimetric analysis and differential scanning calorimetry instruments, and is based on probing a transition temperature. Indium, lead, and zinc could be spread on a substrate, and the phase transition of these metals could be detected by a change in the Ψ signal of the ellipsometer. For water, the phase transition could be detected by a loss of signal intensity as a result of light scattering by the ice crystals. The combined approach allowed for construction of a linear calibration curve with an accuracy of 1.3 °C or lower over the full temperature range.

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1. Introduction

Precise control of the sample temperature is essential for studying thermally activated processes [1,2]. Even minor errors in the recorded sample temperature potentially lead to large errors, if derivative calculations on the data are performed [3]. The behavior of thin films may be systematically different from that of bulk materials [4–7]. For the thermal analysis of thin films it is imperative to know the temperature at the substrate–film interface. In such experiments, the properties of the thin film are typically probed by optical techniques, and heating is performed substrate-sided to leave the film open to the light beam. As a result, heat losses may occur from the topside of the sample, or a time-lag may be introduced in the sample heating. The extent of the heat losses can strongly depend on the thickness and thermal conductivity of the substrate. Contrary to the analysis of (semi)bulk samples by, e.g., thermogravimetry or calorimetry [3,8,9], no standardized temperature calibration strategies exist for these type of measurements. In this paper, we will shortly review the existing techniques for probing the temperature of a substrate–film interface. Subsequently, we will demonstrate a simple method to calibrate the substrate–film interface temperature using melting

point standards. This simple method is applicable for different types of substrates.

The state-of-the-art temperature calibrations for flat substrates are found in the rapid thermal processing (RTP)-environments in the semiconductor industry, where accurate control over the temperature of silicon wafers is achieved. For these systems, pyrometry is the commonly employed technique. The drawback of this technique is the fact that below ~600 °C lightly-doped wafers are partially transparent at the pyrometer's wavelength [10].

Plainly placing a thermocouple on top of the sample suffers from imperfect thermal bonding [10]. Embedding of a thermocouple or optical sensor into a wafer would circumvent this problem, but is not straightforward [11,12]; moreover, this technique is not generically available for different substrates. Other techniques such as ellipsometry, Raman spectroscopy, or ultrasonic measurements, require knowledge on the change in the (optical) properties of the substrate as function of temperature [10]. Measurement of the thermal changes and matching it to reference data requires extensive knowledge on the technique and the substrate studied.

Precise temperature calibration is a problem that has been extensively addressed in the thermal analysis community. For standard thermal analysis methods, such as thermogravimetric analysis (TG/TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA), several temperature calibration methods are available. Typically, calibration involves measuring a transition temperature of a standard, and comparing it with the known value of this transition temperature. The melting point

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of metals is typically used for DSC and DTA-capable instruments [1]. This method is also recorded in the current ASTM-standard for DSC calibration [8]. For TG-apparatuses, the state-of-the-art technique involves the placement of a magnet above or under the apparatus, and recording the apparent mass change in a ferromagnetic material when it loses its magnetic properties, as it passes through the Curie temperature [9]. An alternative method involves the use of a dropping weight that hangs from a fusible link made from a melting point temperature standard [13]. Other options include recording the decomposition point of a material [14] or the difference between sample and set temperature that occurs as a result of sample self-heating or cooling (this technique is named calculated DTA and is the technique behind Netzsch's c-DTA[®]).

The use of melting point standards is an attractive technique for the calibration of wafer temperatures. In the past, this technique has been performed by visual observation of the phase transition [15]. In our experience, visual observations of the phase transition of a thin film are inaccurate because of the small changes in the film properties. Moreover, if a calibration needs to be performed in a closed chamber, visual observation will not be possible.

Here, we report the use of metal melting point standards for simple and fast temperature calibration of thermo-ellipsometric analysis. Because of the light absorbance by the thin metal films, the layers are optically semi-infinite when thicker than ~ 100 nm, and the substrate can be considered optically invisible. The method relies on the change in the amplitude ratio of the polarized light, Ψ , that takes place upon melting of a thin metal film. Upon heating without a phase change Ψ is relatively constant [16]. Melting induces a step change in Ψ that is a result of an abrupt change in the roughness, the material's density, the films alignment angle or light intensity. The melting temperature of the film is a good indication for the substrate–film interface temperature, because of the large thermal conductivity of the thin metal films. The versatility of the presented method is demonstrated by determining the temperature on silicon wafers and porous alumina substrates.

2. Experimental

In, Sn, Bi, and Zn melting standards (>99.99% purity) were obtained from Netsch. Pb melting standard (99.999% purity) was obtained from Chempur. Silicon wafers ((100)-oriented *p*-type, thickness = 508 μm , front side polished, abbreviated by Si) were obtained from Silchem. Porous α -alumina disks (thickness = 2 mm, $d_{\text{pore}} \approx 80$ nm, porosity $\approx 40\%$) were obtained from Pervatech.

DTA and TGA measurements were carried out on a STA 449 F3 Jupiter (Netsch) fitted with a TGA-DTA-holder (DTA measurement) or a TG-only holder (TGA experiments). Experiments were carried out with ~ 20 mg of metal, at heating rates of $5\text{--}20^\circ\text{C min}^{-1}$, under nitrogen. For the TGA measurement, the melting onset was determined using the calculated DTA signal ($T_{\text{set}} - T_{\text{exp}}$).

Spectroscopic ellipsometry measurements were recorded on an M2000X spectroscopic ellipsometer (J.A. Woollam) equipped with a heating stage with quartz windows at 70° incident angle (HCS622, INSTEC) and focusing probes. Ψ was measured at an interval of 5 s over the full wavelength range of 210–1000 nm. The measurements were performed under a blanket of nitrogen with negligible flow rate.

To obtain a measurable signal without scattering, a small piece of metal was placed on top of the substrate. Then, the temperature was increased to above the melting point of the metal, and the metal was spread over the surface using a flat spatula. Next, the sample and/or the light beam were aligned to achieve maximum light intensity. The wavelength that displayed the best

signal-to-noise ratio was selected for the evaluation of the phase transition. Typically, multiple wavelengths could be selected with identical results. The melting and solidification steps were subsequently studied at different heating rates.

3. Results and discussion

Fig. 1 shows the melting curves of zinc using three different methods. The figure displays a clear difference between the instantaneous melting of the thin film in the ellipsometry, and the time-dependent melting of the metal in the DTA and calculated DTA measurements. Because heating and cooling are both initiated from the wafer–film interface, the absence of hysteresis between the heating and cooling cycle indicates the homogeneous temperature distribution throughout the thin film. The (extrapolated) onset of the curve is the indication for the melting point, as the shape and maximum are heating-rate and sample-mass dependent [1]. As can be expected for a dedicated thermal analysis device, the DTA and TGA measurements displayed the least deviation from the true melting point, with a difference between experimental and known melting temperature of only 0.4°C for DTA, and a difference of 1.8°C for TGA (where melting was determined via calculated DTA). For the hot stage of the ellipsometer, a temperature difference of 12.8°C was determined.

During the ellipsometry measurements, the phase transition fully occurs between two temperature values. The melting points can be determined as the average of these two temperature values, the accuracy of the ellipsometry temperature calibration depends on the data spacing. Shorter measurements intervals therefore lead to a more accurate determination of the melting point; however, at the expense of increased noise in the data, making the transition less pronounced. A measurement time of 5 s was heuristically determined to give optimal results. For the DTA and TGA, the accuracy depends on the precision of the extrapolated onset. Although the onset is theoretically not dependent on heating rate, the extrapolated onset in practice is, and the accuracy can be different for different heating rates.

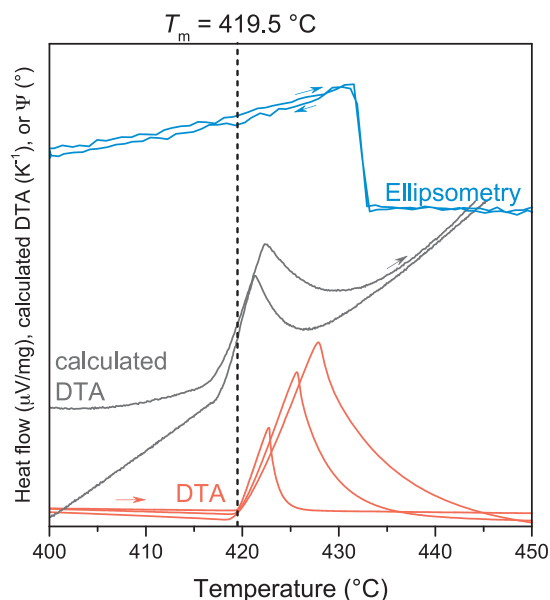


Fig. 1. Melting curves of zinc obtained by DTA, TGA (via calculated DTA), and ellipsometry. For DTA and calculated DTA, the onset of the melting step indicates the melting point. The difference between the known melting point of zinc (419.5°C) and the recorded melting point indicates the temperature offset that needs to be corrected for.

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