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Nanocalorimetry study of the evolution of melting characteristics of single layer silver alkanethiolate lamella: Fast heating/cooling and electrical annealing

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ABSTRACT

Nanocalorimetry (NanoDSC) is applied to measure the melting characteristics of single layer silver pentadecanethiolate (AgSC15) crystals. Its attribute of high sensitivity enables the characterization of single layer species. The fast heating (~50,000 K/s) and cooling (~10^4 K/s) rates employed allow an *in situ* study of lamella layer evolution. By controlling the maximum temperature (T_{max}) achieved during heating/cooling cycles, the samples can be either melted or annealed. If T_{max} is larger than sample melting point (T_m), the first NanoDSC pulse shows the melting behavior of the as-synthesized crystal. The following rapid cooling (quenching) causes crystallinity loss. If T_{max} is smaller than T_m, electrical annealing takes place and partially recovers the quenched layered structure, but the melting enthalpy never reaches that of the first pulse.

1. Introduction

Nanocalorimetry (NanoDSC) [1–3] is a unique technique due to its ultra-fast heating rate (5000–200,000 K/s) and high sensitivity of specific heat (0.1 nJ/K) and enthalpy (1 nJ). This enables measurement of thermodynamic properties of very small amount (~50 ng)of materials, which is much less than the minimum mass (~mg) needed for conventional differential scanning calorimetry (DSC). The central part of NanoDSC is a chip-based calorimetry sensor (Fig.1a) fabricated on silicon wafer with a metal patterned silicon nitride membrane as the calorimetric cell. Nanocalorimetry was introduced in the 1990s and is now used worldwide [4–16]. Currently, NanoDSC has been applied to measure the thermodynamic properties of magic number metal clusters [17–21], glass transition (T_g) in polymer films [22], self-assembled monolayers (SAM) [23], metal silicides [24,25] and two-dimensional (2D) alkanethiolate layered crystals [26].

The rise of research in graphene [27] spawned the recent growing interest in other 2D layered materials with low aspect ratio [28,29]. These materials exhibit extraordinary size effect properties as the change of atomic/molecular layers. An interesting perspective of size effect phenomena in 2D layered systems lies in their melting behavior. Size-dependent melting finds its historical root in the 19th century with the pioneering theory of Gibbs–Thomson law [30]. This phenomenon has been observed in metal nanoparticles such as In [19,20], Sn [17] and Bi [21], as well as polymeric thin films [22]. Our recent work [26] on silver alkanethiolate (AgSCn, n = 7–18) lamellar crystals systematically extends this size effect melting to 2D layered systems, with single layer lamellae (~2–5 nm) as the thinnest species investigated. This is realized by the coupling of NanoDSC and a layer-control synthesis method [31,32].

AgSCn lamellar crystal was first synthesized by Dance et al. through a solution based chemical reaction [33]. Each single layer AgSCn has a bi-layer ribbon-like structure composed of a central plane of Ag-S network with alkanethiol chains extending on both sides [33–37]. Adjacent layers are bonded *via* van der Waals interaction, forming stacked AgSCn. The melting process of AgSCn involves an order-disorder phase transition due to the change of alkanethiol chain conformation from all-trans to partial gauche whereas the central plane structure is unaffected [26,38,39]. Currently, this organometallic lamellar crystal finds applications in the field of electronics [40], nanolithography [41] as well as biophysics [42].

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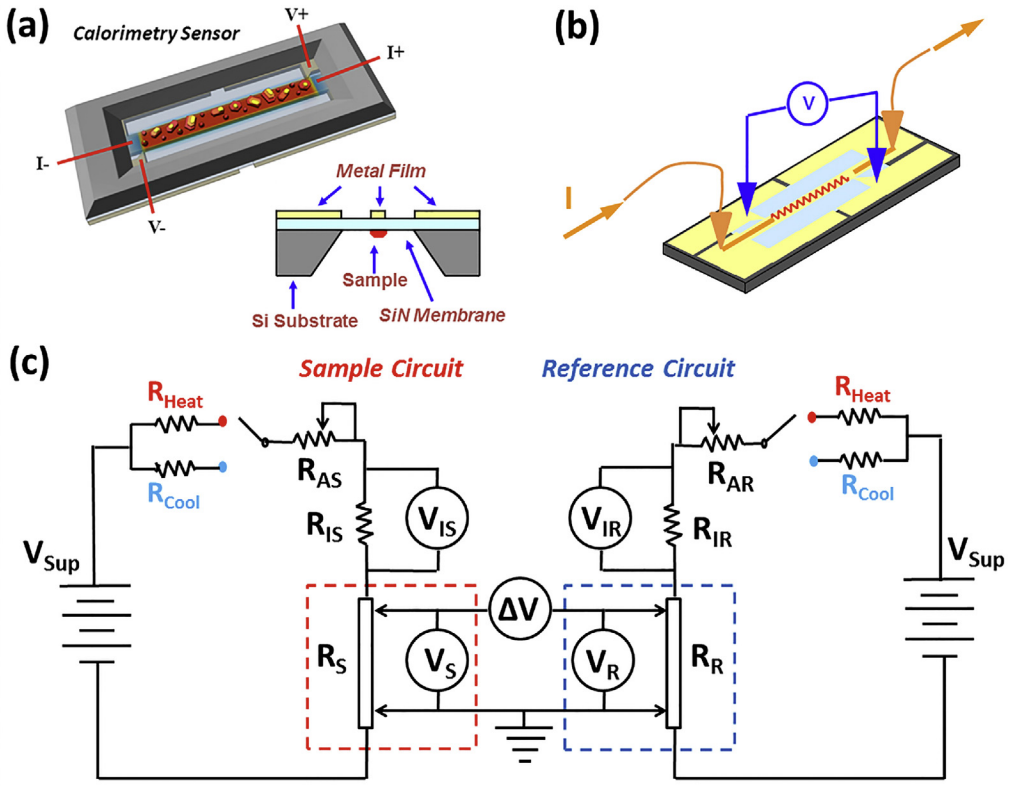

Fig. 1. (a) Bottom-view and cross-section schematic of the nanocalorimetry sensor. Si substrate: 500 μm thick; silicon nitride membrane: 100 nm thick; platinum metal film: 50 nm thick; platinum strip directly above sample: 0.5 mm wide [1]; (b) schematic of NanoDSC pulsing (front-side-view): C_p *vs.* T curve for every sensor is obtained *via* four-point probe measurement; (c) circuit diagram of differential mode NanoDSC. The region inside the red dashed box refers to Sample Sensor while the region inside the blue dashed box refers to Reference Sensor. R_{IS} and R_{IR} are the current determination resistance in the sample circuit and reference circuit, respectively. Heating rate is precisely controlled by adjusting R_{AS} and R_{AR} values. The switches shown can be changed between regular pulsing mode and cooling mode. (For interpretation of the references to color in this figure legend and text, the reader is referred to the web version of this article.)

In our prior work [26], size effect melting of AgSCn layered crystals is observed from two degrees of freedom. Single layer AgSCn shows a discrete increase of melting point T_m (total $\Delta T \approx 20\,^{\circ}C$) as the integer increments of alkanethiol chain length ($n = 7$–18). Stacked AgSCn layers exhibit an odd/even melting effect as well as a layer-number-dependent collective melting in which crystals with larger number of layers melt at higher T_m. This is the first time that chip-based calorimetry is employed to investigate 2D layered materials. The successful measurement of single layer melting highlights the possibility of studying extremely thin materials *via* NanoDSC, which is unique in that conventional DSC is only designed for bulk materials where size effect is negligible.

In this paper, *in situ* multiple NanoDSC pulses are carried out on single layer silver pentadecanethiolate (AgSC15) crystals. The first pulse represents the melting behavior of the original crystals. The second and subsequent multiple pulses show irreversible loss of crystallinity under such fast heating (~50,000 K/s) and cooling (~10^4 K/s [25]) rates. Electrical annealing technique is introduced and is able to recover the value of T_m but the heat of fusion (H_m) of quenched samples never reaches that of the first pulse. As a comparison, conventional DSC is employed to analyze bulk multilayer AgSC15 samples. Unlike NanoDSC, reversible melting of bulk AgSC15 is revealed because of the relatively low heating/cooling rate (~10 K/min) used. As a consequence, NanoDSC proves itself to be a unique technique in the thermodynamic analysis of 2D layered materials in terms of three aspects: (1) melting characteristics of single layer species can be easily resolved; (2) its ultra-fast nature enables *in situ* investigations of layer evolution during heating/cooling cycles; (3) electrical annealing is a potential tool for crystallinity recovery.

2. Experimental

2.1. Synthesis

2.1.1. Materials

Silver pellets (99.99%) obtained from Kurt J. Lesker Co., are used as silver source for physical vapor deposition. Silver nitrite powder ($AgNO_3$, ≥99.0%), acetonitrile (99.8%), triethylamine (≥99.0%), 1-pentadecanethiol (1-$C_{15}H_{31}SH$, ≥98%) and 1-hexadecanethiol (1-$C_{16}H_{33}SH$, ≥99%) used in this study are purchased from Sigma–Aldrich Co., and used without further purification. Toluene (≥99.5%) is used as received from Macron Fine Chemicals Co.

2.1.2. Synthesis of single layer AgSC15

Single layer AgSC15 crystals are prepared from a layer-control synthesis method on NanoDSC sensors (SiN_x surface). The detailed procedures are described in our previous publications for both single-layer [32] and stacked-layer samples [31]. Fig. 2 briefly illustrates the synthesis procedure of single layer AgSCn. The final product is precisely determined by the amount of silver deposited at the first synthesis stage and the furnace annealing temperature in the last step.

The deposition of silver (step 1 in Fig. 2) is carried out in a thermal evaporator at a base pressure of 5×10^{-8} Torr. The exact amount of silver deposited is estimated by a quartz crystal

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