**Low Heat Capacity Substrates for Calorimetry Measurements**

**CNF Project # 522-94**

**Principal Investigator: Leslie H. Allen**

**Users: Ravi Kummamuru, Mike Efremov, Eric Olson, Liang Hu**

**Affiliation: Material Science Department, University of Illinois at Urbana-Champaign**

**Primary Funding:**
- NSF DMR (#0108694) Dr. L. Hess;
- NSF (#0304149) Dr. William Nes;
- NSF ECS (#0622117) Dr. Rajinder Khosla;
- NIST (70NANB5H1162) Dr. Martin Green

**Contact:** L-ALLEN9@uiuc.edu

**Web Site:** http://allen.mse.uiuc.edu/index.htm

**Abstract**

Our research focuses on developing calorimetry techniques and instruments for thin film material, nanometer scale particles of metals, polymers and nanoliter volumes of proteins [1]. Development of these devices for such characterization techniques via the nanocalorimetry technique (NanoDSC) makes use of CNF micromachining [2] techniques. Many different sample configurations can be used including vacuum-deposited, spin-cast, or liquid solutions. A variety of materials phenomenon which occurs at the nanometer length scale have been investigated, such as the size-dependence melting point depression or sizes in metal nanoparticles [3], order-disorder transitions of self-assembled monolayers of alkanethiols (SAMS) [4], and thickness dependence of glass transition in polymers [5]. In this report we discuss work on two topics: (1) heat capacity measurements self-assembled monolayers (SAMs) on Ag substrate [6], and (2) preliminary results of a new liquid calorimeter using a model system.

**Summary of Research**

SAMs have tremendous potential in all types of technologies ranging from new type photoresists for microelectronics to surface conditioning for biomaterial applications. One monolayer of a molecule on a surface is a fascinating system to study, especially for long chain alkanes. How do they order themselves? How do they melt? Do they melt? Should they be different than bulk alkanes (alkanethiols)? Should the thermodynamic properties of a 3D SAM differ from a 2D SAM?

One of the most puzzling aspects of SAMs is the contrast of the heat of melting Hm of SAMS. The value of 3-D SAM/Au is only 25% of bulk thiol, where as it is 100% when grown on 3-D SAM/Ag. Confinement of alkanethiols on a Au or Ag surface in the form of a self-assembled monolayer (SAM) generates a material apparently more stable than the bulk alkanethiols having a “melting” temperature 100K greater than the bulk.

The order-disorder transition in this system is unique in that it is done under the ultimate confinement of the length-scale of the molecule (nm). We report here about our recent work on 3-D SAM/Ag. Hexadecanethiol self-assembled monolayers (SAMs) grown on polycrystalline Ag planar surface (2D) and nanoparticles (3D) are studied by measuring heat capacity with NanoDSC. Sharp melting transitions at high temperatures were observed in this system, which indicate the presence of well ordered phases. SAMs on 3D Ag show melting characteristics that are comparable to that of Ag-alkanethiolate layered materials precipitated from solution. The different states of the system can be manipulated by changing the specific heating and cooling schedule.

We have begun developing a liquid-calorimeter which would be used for protein studies. Theoretical models have suggested that protein folding proceeds over an energy landscape described as a “folding funnel”, which has metastable intermediate states with entropic and/or enthalpic kinetic barriers. One limitation to the study of protein folding using conventional calorimetry has been the time scale for measurement. The high rates of the proposed liquid NanoDSC will allow us to observe these fast intermediate steps of protein folding. The design of the NanoDSC will also enable us to develop systems allowing...
combinatorial studies. Furthermore, the small sample sizes is ideal for characterization of new proteins which are usually made in limited quantities. Our preliminary design uses docosane as the test-sample.

This prototype biocalorimeter has a scan rate (10 K/min) which is much smaller than the scan rate (~2,000,000 K/min) of the nanocalorimeter used in the (previously mentioned) SAM work. However, it is much faster than conventional biocalorimeter (1 K/min). It also has a much smaller sample-volume than conventional biocalorimeters (> 100 uL). The plot in Figure 2 shows the Cp(T) data of n-docosane C_{22}H_{46} using a sample volume of 22 uL. The n-docosane enters the sample holder as liquid and then allowed to solidify before the calorimetry measurement. As expected the sample melts near bulk values T_m ~ 44°C and exhibits multiple melting peaks which is expected for this system.

References


