MEMBRANE-BASED NANOCALORIMETERS TO MEASURE ULTRATHIN FILMS AND NANOSCOPIC SAMPLES AT HIGH TEMPERATURES

A.F.Lopeandia[1], E.León-Gutierrez[1], G.Garcia[1], F. J. Muñoz[2], J.Rodríguez-Viejo[1].
[1] Grup de Nanomaterials i Microsistemes. Departament de Física, Universitat Autònoma de Barcelona. Campus UAB, 08193 Bellaterra, (Spain).
[2] Instituto de Microelectrónica de Barcelona-Centro Nacional de Microelectrónica. Campus UAB, 08193 Bellaterra, (Spain).

aitor@vega.uab.es, javirod@vega.uab.es

Many materials of current fundamental or technological interest are mainly made in thin film form or as nanostructured systems. The fabrication of ultrathin films, multilayers, nanoislands or quantum dots with high surface to volume ratios introduces the need for a deep knowledge of new physical phenomena. In most uses of thin films, the promotion or inhibition of reactions, such as nucleation, grain growth, interdiffusion, crystallization or melting play a central role in the ultimate performance of the system. Basic studies of these processes are contributing significantly to our comprehension of materials' behavior and create stimulating new opportunities for scientific investigation. A critical step towards understanding thin film reaction is to characterize their thermodynamic and kinetic parameters. Up to now, differential scanning calorimetry (DSC) has primarily being used on bulk or multilayered samples [1], since in typical individual thin films, the amount of energy released by a given reaction is too small to be measured and analyzed with accuracy. The development of micromachining techniques associated to the Silicon technology enables the scaling down of several types of devices [2]. We have recently developed a SiN_x membrane-based calorimeter for thin films, with a heat capacity of 100 nJ/K at room temperature, that consist on a 180 nm thick freestanding silicon-rich nitride membrane, on which thin film heaters and sensors are deposited [3]. An schematic of the microfabrication process is detailed in Figura 1. These MEMS can also work as high sensitive calorimeters in power compensation mode [4]. Under high vacuum, the Platinum elements of the calorimetric cells can be heated with a constant current pulse, to rates near 10^6 K/s. At heating rates faster than $4x10^4$ K/s the nanocalorimeter works in adiabatic mode [5] and measures transitions occurring to the sample directly located underneath the heater. The heater material, its specific design and the SiN_x membrane shape have been optimized to span the operation range to higher temperatures while preserving a good mechanical and electrical stability. These new nanocalorimeters offer the possibility to carry out reproducible measurements from 30 to 1300 K.

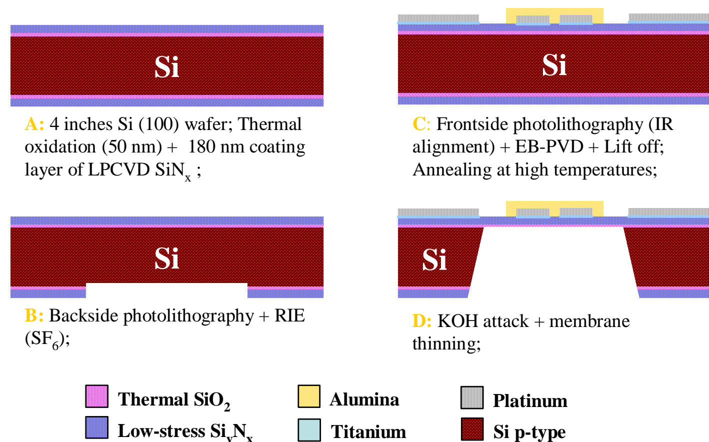
The nanocalorimeters are mounted on an electrical contact socket inside an UHV e-beam evaporator, see Figure 1. Measurements in-situ during the deposition process of nanometer thin films demonstrates the high sensitivity of the nanocalorimeters. Figure 3(a) shows the heat capacity curves as a function of temperature for different In films, ranging from 0.8 to 8 nm, deposited on top of the SiN_x membrane. At these thicknesses the layers are formed by isolated islands. The endothermic peak is related with the solid-liquid melting transition, and its temperature depression with the size of the nanoparticles. The data shown in figure 3(a) is obtained after averaging 500 consecutive scans providing a resolution below 50pJ/K [3]. Measurements on a 3nm Ge layer sandwiched between 10nm SiO_2 films have also been performed to show the applicability of these nanocalorimeters in the high temperature domain. Figure 3(b), shows the melting transition peak of crystalline Ge. The temperature decrease with respect to the bulk value, T_m=938°C, is again related to a size depression effect. In summary, we show nanocalorimetry is useful to analyze phase

transitions in ultrathin films revealing new phenomena produced by the finite size of the samples.

References:

[1] F. Spaepen et al., Appl. Surf. Sci., **38** (1) (1989) 1-12.
[2] R.Srinivasan et al., AIChE J., **43** (1997) 3059.
[3] A.F. Lopeandía et al., JMMS., in press (2006).
[4] A.F. Lopeandía et al., Rev. Sci. Instrum, **76** (2005) 065104.
[5] M.Y. Efremov et al. Phys. Rev. Lett. **85** (2000) 3560.

Figures:



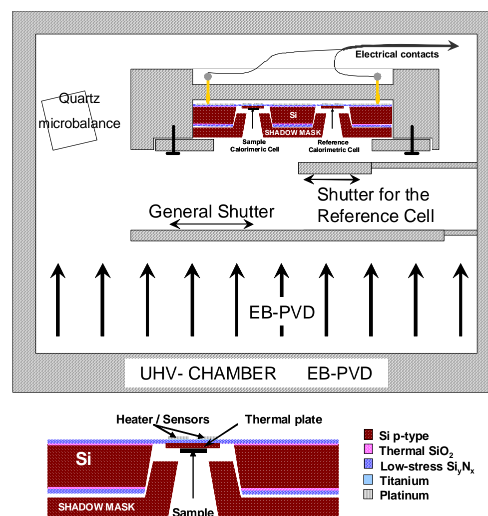


Figura 1. Microfabrication process

Figura 2. Experimental Setup

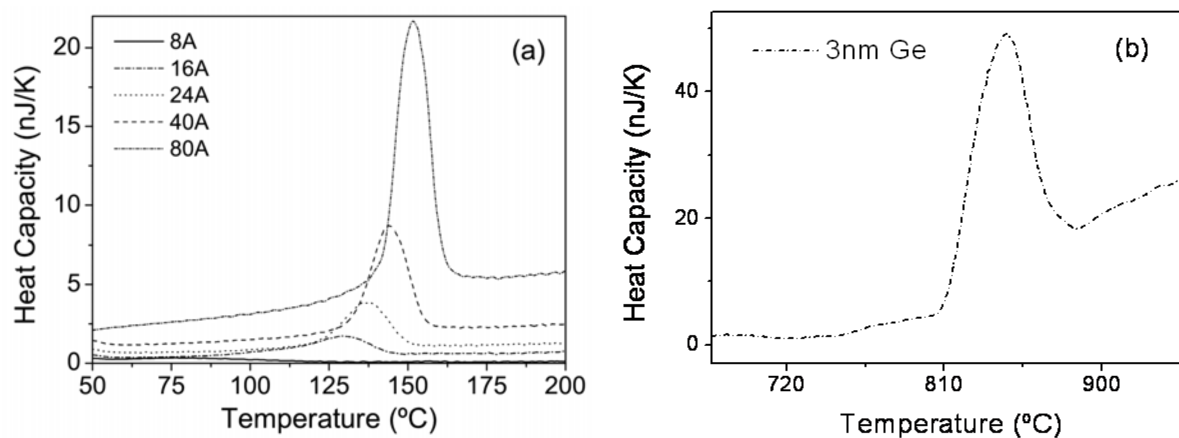


Figure 3. Heat capacity .vs. temperature for (a) In thin films and (b) 3 nm c-Ge.