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Multi-environment Nanocalorimeter with Electrical Contacts for Use in the Scanning Electron Microscope

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Abstract

We have developed a versatile nanocalorimeter sensor which allows imaging and electrical measurements of samples under different gaseous environments using the scanning electron microscope (SEM) and can simultaneously measure the sample temperature and associated heat of reaction. This new sensor consists of four independent heating/sensing elements for nanocalorimetry and eight electrodes for electrical measurements, all mounted on a 50 nm thick, 250 $\mu\text{m} \times 250 \mu\text{m}$ suspended silicon nitride membrane. This membrane is highly electron transparent and mechanically robust enabling *in situ* SEM observation under realistic temperatures, environmental conditions and pressures up to one atmosphere. To demonstrate this new capability, we report here on 1) *in situ* SEM-nanocalorimetry study of melting and solidification of polyethylene oxide, 2) the temperature dependence of conductivity of a nanowire; 3) the electron beam induced current measurements (EBIC) of a nanowire in vacuum and air. Furthermore, the sensor is easily adaptable to operate in liquid environment and is compatible with most existing SEM. This versatile platform couples nanocalorimetry with *in situ* SEM imaging under various gaseous and liquid environments and is applicable to materials research, nanotechnology, energy, catalysis and biomedical applications.

Introduction

Nanocalorimeters are small scale thermal analysis sensors designed to exploit the small sensor size and mass possible with modern micro- and nano-fabrication and can measure heat capacity, enthalpies, associated heats of chemical reactions and physical processes for small samples with high sensitivity and high heating rate^{1–3}. The extraordinary sensitivity is achieved by fabricating the thermal sensor on a very thin silicon nitride membrane to minimize its heat capacity and heat losses. Due to its small size, it can be integrated in other instruments. Recently, we have integrated a nanocalorimeter in the dynamic transmission electron microscope (DTEM)^{4, 5} for *in situ* microstructural characterization and have used a nanocalorimeter sensor in the time of flight mass spectrometer^{6, 7} to capture the evolved species associated with thermal events.

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To extend this measurement capability to adsorption and/or redox-reactions⁸, calorimetry under realistic conditions and couple it with electron microscopy, the sensor redesign is necessary. The challenge is that a conventional SEM operates under high vacuum and direct observation of samples in different environments is not possible. The environmental scanning electron microscope (ESEM) does not completely solve the measurement challenge due to the limited number of gases acceptable and the limited pressure range.^{9–12} Recently, with developments of thin film technology and microfabrication, extensive efforts have been made to develop a suitable observation window capable of withstanding atmosphere pressure for electron microscope, such as polymer membrane¹³, carbon foil¹⁴, graphene membrane¹⁵, silicon nitride (SiN) membrane¹⁶. Of them, few tens nanometer thick SiN membrane supported on silicon frame is the most widely adopted due to their high electron transparency for few keV electrons, facile fabrication, homogeneous composition and thickness. Numerous demonstrations have been reported on SEM imaging of samples using microfabricated SiN windows under realistic conditions relevant to material science and biological science^{10, 13, 16–19}. However, to our knowledge, those devices were not used to collect thermal and thermodynamic information on the sample.

Here we report on SiN membrane based device that enables combination of the *in situ* SEM observation with calorimetric measurements of melting and solidification of a polymer film during heating cooling cycles; In addition the device can be used for *in situ* conductometric measurements of nanostructures. The comparative electron beam induced current measurements of a metal oxide nanowire have been demonstrated in vacuum and air (at 10^5 Pa); The combined SEM and calorimetry measurements therefore can be conducted in a wide range of pressures, temperatures and different environments.

Experimental Methods

A. Nanocalorimeter sensor

Figure 1A shows the schematic cross-section of the nanocalorimeter sensor; it is based on a 50 nm thick SiN_x membrane for thermal isolation, an adhesion layer of 10 nm of Ta²⁰ and 150 nm thick Pt meander heaters and electrodes fabricated on a silicon wafer. The silicon is back etched leaving an unsupported membrane in the center of the die. The low-stress SiN_x membrane was deposited by low pressure chemical vapor deposition (LPCVD) to achieve slight residual tensile stress. The metal layer was patterned by lift-off photolithography and e-beam evaporation. The SiN_x window is created by backside patterning, reactive-ion etching (RIE) through the SiN_x membrane followed by a KOH deep etch to release the 250 $\mu\text{m} \times 250 \mu\text{m}$ membrane window. To protect the front Pt layer and provide electrical isolation, 30 nm of aluminum oxide is selectively deposited by e-beam evaporation and patterned by lift-off photolithography. We calculated and experimentally confirmed that the SiN_x membrane window can withstand a pressure difference of more than 10^5 Pa (≈ 1 atm), and is highly transparent for electrons with energies above 5 keV.

Figure 1B shows the top view of the sensor. There are two pairs of meander heaters for nanocalorimetry measurements or sample heating and they can be addressed individually. Four sets of electrodes for electrical measurements (including the choice of four probe Van der Pauw method) are in the center and were designed to accommodate thin films, powders,

or 10 μm to 100 μm long nanowires. The heaters are deposited in a pattern such that the net electromagnetic field is self-canceled by configuring the current flow in the four heaters. To reduce the electromagnetic noise affecting both current-voltage and electron beam induced current measurements, two guard electrodes are incorporated to further isolate the electrical measurements from the heaters.

B. Sensor holder and SEM environmental cell

The sensor chip was mounted and wire bonded on to a commercial ceramic multipin chip carrier. Figure 1C shows the ceramic chip carrier attached to gas flow environmental cell via vacuum tight gasket. The interior of the sensor with the sample can be exposed to atmosphere pressures or different gas/liquid environments, while the outer side of the assembly is under high vacuum of the standard SEM. A custom-made gas/liquid gas flow control system enables the controlled gas delivery and rapid change of the sample environment from vacuum to atmospheric pressure.

C. Nanocalorimetry measurements

The sensor was first annealed in a quartz tube furnace at 600 $^{\circ}\text{C}$ in air for 30 min to stabilize its microstructure²⁰. The Pt heaters are used to heat the sample and simultaneously serve as the temperature sensor based on the temperature coefficient of resistance. The latter calibration was obtained in advance by placing the sensor in to an oven with preset temperatures and measuring the corresponding resistances. The detailed measurement circuit can be found in our previous work^{4, 21}. Briefly, the sample is heated by ramping a current through the heaters. The voltages drop across the heaters and a precision reference resistor as a current sensor are measured and the instantaneous current, power, resistance and temperature is determined. Finally, the heat capacity, enthalpy and reaction energies are calculated^{2, 4}.

D. SEM observation

Depending on the sample and research task SEM imaging was conducted either in vacuum or under atmospheric conditions. The choice of the electron beam energy was dictated by the required probing depth. During the imaging of the dynamic processes the SEM video was recorded with frame rate of 1 Hz. An Everhart-Thornley type detector was used for SEM image acquisition.

Results and Discussion

To demonstrate the versatility of applications of the nanocalorimeter sensor integrated with SEM, three example experiments were performed: 1) *in situ* melting and solidification of polyethylene oxide (PEO) coupled with nanocalorimetry measurements, 2) evaluation of the electron transport properties of n-type metal oxide nanowire and 3) *in situ* measurement of electron beam induced effects on reactivity and transport properties of an individual single crystal SnO_2 nanowire in vacuum and in air.

***In situ* observation of phase transition**

Nanocalorimetry performed under different ambient conditions can be used to investigate environmental effects on phase transitions. An example is seen in some of our recent work on rapid measurements of lipid phase transition kinetics with different humidity levels²². Incorporating imaging modality like SEM to corresponding thermal analysis would provide insights to various reaction dynamics, such as gas-solid reactions or liquid phase reactions. To demonstrate the feasibility of such measurements we selected.

PEO (molecular weight: 35 000 g/mol) for *in situ* SEM observation of its melting and solidification during the nanocalorimetry measurement. PEO was dissolved in water at a concentration of 20 mg/mL and was deposited on the sensor by a droplet generator. Nanocalorimetry data, shown in Figure 2(d), illustrated the melting with a measured peak of 62 °C which is in agreement with the literature²³. The associated melting enthalpy is 33.9 μJ. A 3D deconvolution of an image stack of the sample captured using a Zeiss LSM 800 confocal system on a AxioImager Z2m microscope was used to calculate the sample volume as $3.1 \times 10^{-7} \text{ cm}^3$, which along with the manufacturers nominal density of 1.2 g/cm³, provides a sample mass of 370 ng and specific enthalpy of 92 J/g. Comparing this to bulk values is done for general information as this sample is not expected to be in the same condition as bulk; the crystallinity and density of the sample as deposited is not known. The specific enthalpy of 100 % crystalline PEO has a reported range of 166 J/g to 265 J/g²⁴. Comparing the two shows that the measured enthalpy is in the range of 34 % to 57 % of the value reported for PEO (noting again that this value is based on the confocal measurement of volume, the nominal density, and the assumption of 100 % crystallinity). This comparison shows the initial device design is producing specific enthalpy results within a factor of two, and may benefit from further improvement.

An alternative analysis approach is to use the measured heat capacity and compare that to the bulk heat capacity to estimate the sample mass²⁵. After subtracting the baseline from the data, as shown in Figure 2, the measured heat capacity at room temperature is 0.4 μJ/K. The nominal bulk heat capacity is 2.1 J/g/K, which provides an estimate of sample mass of 190 ng. When 190 ng is used in calculations of the enthalpy, the specific enthalpy is 178 J/g, which is within the reported range for PEO. Using either approach requires assuming some bulk value (density or heat capacity), which is not ideal. This comparison highlights the need and importance of methods to quantify sample mass on chip based nanocalorimeters, which is an ongoing effort.

The SEM images in Figure 2 show as-deposited PEO (Figure 2(a)), the sample during melting (Figure 2(b)) and again after solidification (Figure 2(c)). In the latter case the domain boundaries can be seen. The as-deposited PEO film covers most of the heater and the fine features visible in insets in Figure 2a and Figure 2c imply that PEO crystallized as spherulites with fibrillar crystals grown in predominantly radial directions. However, it is relatively difficult to get crystalline films as shown here. On many measurements, an amorphous film is obtained and the melting transition is not evident in the thermal data. This phenomenon may be related to the environmental humidity or the unavailability of nucleation sites. The temperature ramp takes 1 s from 22 °C (room temperature) to 200 °C with an average heating rate of $\approx 180 \text{ °C/s}$. Observations in the SEM at 2 keV show the PEO

melting as the temperature is increased and the fibrillar morphology of the as-deposited film disappears. After solidification, a SEM image shows PEO is re-crystallized with fine crystal structures visible again.

Electron beam induced cross-linking in polymers is a basis of electron lithography. Our technique can shed a light on thermodynamics of this process. While in situ SEM and calorimetric measurements with 2 keV of electron beam were reversible with respect to melting-solidification cycles (data not shown), the increase of primary electron energy to 15 keV, resulted in irreversible chemical changes in the PEO film. Figures 3(a) and (b) show crystalline PEO films before heating under 15 keV beam and after the solidification. As can be seen the PEO surface morphology is significantly changed exhibiting multiple wrinkles upon cooling. In addition, the characteristic 62 °C melting peak was absent in nanocalorimeter results and the film was insoluble in water. The material apparently becomes crosslinked through the entire volume in the second experiment. Monte Carlo electron energy trajectories simulations (Figure 3 c) support these conclusions. As can be seen, electron penetration depth of 2 keV electrons in PEO is limited to the ≈ 100 nm thick near surface region and the bulk of the film remains unaffected by radiation. However, 15 keV electrons penetrate through the entire 2 μm thick film inducing cross-linking throughout. The alteration of the film structure resulted in the formation of the wrinkles²⁶.

Electrical measurements

In addition to calorimetric studies, an array of Pt electrodes enable measurements of the electron transport properties on the samples during heat treatment. A single crystal SnO_2 nanowire was used as a model sample in this work. The nanowire was placed on the chip to bridge two electrodes and electrical contacts between the nanowire and electrodes were defined by additional electron beam induced Pt deposition. Figure 4 (blue curve) shows the changes in conductivity of SnO_2 nanowire upon annealing in vacuum. The temperature of the heaters was increased in steps (red staircase curve) from room temperature to 950 K. The nanowire remained poorly conducting and shows no change in resistance up to ≈ 580 K. This is a typical behavior observed in metal oxide conductometric sensors which require activation at these temperatures²⁷. The activation process is related to thermal desorption of hydroxyl and preabsorbed water molecules from the surface of the sensor. At higher temperatures (580 K to 770 K), the nanowire conductivity increases at onset of the temperature increase and then exponentially decays with time. We believe the onset in conductivity increase is the temperature induced conductivity change which immediately follows a decay as the chemical status of the SnO_2 nanowire surface changes due to dissociation of water and formation of electron acceptor OH groups. The OH groups can trap thermally activated free electrons from conduction band resulting in a lower conductivity of the nanowire. When the temperature is increased above 700 K, the thermally activated carrier generation prevails the nanowire surface oxidation and conductivity stabilizes. Above 780 K, the conductivity of SnO_2 increases linearly with time after the temperature step due to the beginning of thermal reduction of SnO_2 to SnO_{2-x} or SnO in vacuum. The activation energy of for conductance can be estimated from the corresponding Arrhenius plot (inset in the Figure 4). The estimated value of ≈ 0.6 eV is somewhat larger compared to previously reported. This is due to systematic overestimation of the nanowire

temperature occurring due to significant lateral temperature gradient on the membrane between two meander heaters.

Electron beam induced effects and current measurements as a function of ambient conditions

Electron beam induced current (EBIC) measurement is a powerful SEM imaging modality which allows for visualization of the charge transport channels in semiconductor devices^{28, 29}. However, this powerful technique was never used under elevated pressure conditions. We studied the effects of different environments (including vacuum and air) on electron beam induced current through the model SnO₂ nanowire. Figure 5(a) and (b) shows SEM images of a SnO₂ nanowire in vacuum and air under atmospheric pressure respectively. As in the previous case, the nanowire is electrically connected to the platinum electrodes by electron beam induced Pt deposition. The SnO₂ nanowire is placed inside of the SEM environment cell where the ambient pressure can be altered between vacuum and air at atmospheric pressure. SEM images were taken at 10 keV electron beam energy, imaging through the SiN membrane. No significant changes in resolution or contrast is observed between the images recorded in vacuum and air. The EBIC image of the nanowire collected under ambient air conditions is shown in the Figure 5c. Schottky barriers when formed between moderately doped nanowire and electrode usually manifest themselves as submicron long bright (dark) areas on EBIC images³⁰. In our case, the gradual EBIC signal change along the length of the nanowire is indicative of resistive EBIC contrast with no obvious Schottky barriers being detected³¹. The quasi-linear I-V characteristics of the device (not shown here) corroborate this observation.

The environment however has a big effect on electron beam induced electron transport in reducible oxides such as SnO₂. Figure 5 shows the effect of 10 keV electron beam irradiation on the resistance of the SnO₂ under different gaseous environments.

When the SnO₂ nanowire is excited by an electron beam in vacuum, the conductivity of the nanowire increases abruptly, until reaching a plateau, as shown by the red curve in Figure 5d. This fast increase in conductivity originates from the electron-beam induced desorption of residual O₂ from the SnO₂ surface. Preabsorbed oxygen species act as an electron acceptors on a SnO₂ surface causing electron depletion near the surface and thus narrowing the conduction channel and lowering the nanowire conductivity (Figure 5e). Electron beam irradiation of SnO₂ stimulates oxygen desorption³² resulting in expansion of the conductance channel and an increase in SnO₂ conductivity. When the electron beam is turned off, the conductivity of the SnO₂ nanowire decreases reaching eventually its original value due to the re-adsorption of background water (OH-groups) and oxygen.

The response of the nanowire to irradiation in air at atmospheric pressure is quite different, as shown by the black curve in Figure 5d. The conductivity of the nanowire, upon electron beam irradiation, shows a small transient increase followed by immediate decreases to its original value upon longer beam irradiation (170 s). As in the previous case, the adsorbed species such as water (H₂O), oxygen (O₂) and dissociated water (OH) govern the band bending in the nanostructure but the surface kinetics under irradiation becomes more complicated. Both O₂ and OH groups act as electron acceptors while adsorbed water

molecules act as an electron donor. Thus, the degree of nanowire depletion in air depends on adsorption partitions between these species. Somewhat higher initial conductivity in air exposed nanowires implies that donor species dominate the surface coverage. When the nanowire is irradiated, the electron beam causes (i) desorption of O₂ and (ii) dissociation of water. While desorption of O₂ increases the conductivity, newly formed OH⁻ groups on the SnO₂ surface act like acceptors decreasing the conductivity. These processes compete resulting in much smaller changes in conductivity during electron beam irradiation, compared to that in vacuum.

Summary

We developed a nanocalorimeter sensor which is coupled with SiN membrane based SEM environmental cell. The design enables measurements of the heats of various processes with simultaneous observations of the morphology changes and electric measurements. The samples can be imaged and characterized in pressures ranging from vacuum up to atmospheric pressure. Our results demonstrate that the through membrane SEM high resolution imaging can be conducted at atmospheric pressures and was used to study in *situ* phase transitions in polymer film, charge transport in nanostructures in air and vacuum by EBIC. This technique can be easily integrated with any existing SEMs. We believe this technique will find applications in material science, catalysis, microelectronics, chemistry, and biology.

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Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose. Nanocalorimeter fabrication was performed in part at the NIST Center for Nanoscale Science & Technology (CNST).

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Figure 1.

(A) schematic cross-section of the nanocalorimeter sensor which consists of a 50 nm thick SiN membrane, 10 nm Ta adhesion layer, 150 nm thick Pt as heaters and electrodes, and 30 nm alumina protection layer fabricated on a silicon frame. The amorphous SiN membrane is highly transparent to electrons and is used to separate the sample's environment from the high vacuum of the SEM. (B) top view of the nanocalorimeter sensor showing two pairs of heaters and four sets of electrodes. Two guard electrodes are located between the heaters and electrodes. (C) sensor in a ceramic chip carrier sealed using a silicone gasket; the sample is located inside the cell where it can be imaged using SEM through the SiN membrane and samples measured in different gas/liquid environments.

Figure 2.

SEM images of PEO film melting process recorded in vacuum during nanocalorimetry measurement. T_m is reported based on peak melting temperature. From left panel to the right: (a) as-deposited PEO film, (b) the film in melted state and (c) the film after solidification. (d) nanocalorimetry measurement results with baseline heat losses subtracted. Insets are zoomed in areas ($\approx 50 \mu\text{m} \times 50 \mu\text{m}$) where characteristic oriented fibrillar crystals can be resolved.

Figure 3. SEM images (15 keV) of PEO film (a) before and (b) after the melting during *in situ* nanocalorimetry measurement; c) Monte Carlo simulation of the electron trajectories in 2 μm thick PEO deposited on top of 150 nm Pt. The energies of the electrons along the collisions trajectories are color coded. E_B stands for the electron beam energy.

Figure 4.

Step annealing (red curve) of SnO₂ nanowire in vacuum. Blue curve corresponds to conductivity change under 2 V bias. Inset: the Arrhenius conductance plot. The horizontal error bars correspond to calibration temperature uncertainty of the heaters (plus/minus one standard deviation of the measured values). The vertical error bars correspond to measured current noise level.

Figure 5.

SEM image of SnO₂ nanowires in (a) vacuum and (b) air. The SEM images were taken with 10 keV electron beam energy through a 50 nm thick SiN_x membrane. (c) Beam induced current image (uncalibrated) of the nanowire recorded under the same conditions. High gray scale values at the top electrode correspond to electron beam absorbed current. (d) I-t measurements on the nanowire in 2 × 10⁻³ Pa vacuum (red curve) and in air (black curve) before, during and after electron beam irradiation with 10 keV energy. During the irradiation, the beam was scanning along the nanowire length. Higher initial conductivity in air exposed nanowires is due to surface adsorption of water molecules acting as donor species.) The proposed mechanism of electron beam induced effects on the SnO₂ nanowire conductivity in vacuum and in air under atmospheric pressure.