nano-TA™: Nano Thermal Analysis

Application Note #4
Heated Tip-AFM of Energetic Materials: Nano-dectonics
Author: William P. King Ph.D.
Georgia Institute of Technology

Introduction

Energetic Materials are materials that exhibit dramatic release of stored chemical energy as thermal and mechanical energies. The primary difference between an energetic material and any material that undergoes a chemical decomposition process is the rate at which the decomposition occurs. The decomposition rate is determined by a number of factors including the particle characteristics (chemical composition, size, morphology), the magnitude and duration of the reaction stimulus, and material confinement. For explosives, the rate and amount of energy released is normally sufficient to establish a self-sustaining shock known as detonation. Energetic materials often have nanometer-scale polycrystallinity, voids, and / or defects, and it is widely believed that nanoscale properties and phenomena within these materials play a key role in their macroscopic behavior. (1-3)

One example of nanometer-scale phenomena in energetic materials is 'hot spots,' which are nano- to micro-scale voids within the energetic material, which play a key role in energetic material decomposition. (4) When exposed to an initiation stimulus, these hot spots act as ignition sites that grow in temperature, size, and pressure leading to a deflagration or detonation. The formation of voids within an energetic material is not easily controllable during materials synthesis, but has dramatic impacts on the sensitivity and performance of the energetic material. The hot spots are but one of several important nanoscale thermomechanical properties of energetic materials, none of which have been extensively studied due to the lack of nanoscale thermal probes. Nanodectonics techniques, (5) could enable improved design of energetic materials and ultimately yield safer and more powerful explosives.

This application note describes local thermal decomposition in an energetic material with a heated tip, and shows the effects of tip temperature on the energetic material response.

Heated Tip AFM (HT-AFM) refers to any AFM operation where a heated tip is used instead of a normal tip. Nearly any AFM imaging mode (tapping / contact / Force-Volume etc) can accommodate a heated tip to yield new information tied to the thermal properties of the sample. HT-AFM includes the family of techniques known as nano-TA, explained below.

nano-TA is a local thermal analysis technique which combines the high spatial resolution imaging capabilities of atomic force microscopy with the ability to measure the thermal behaviour of materials with a spatial resolution of 100nm or better. The conventional AFM tip is replaced by a special nano-TA probe that has an embedded heater and is controlled by the specially designed nano-TA hardware and software. This nano-TA probe enables surface visualization with nanoscale resolution through the AFM's standard imaging modes, which permits the user to select the specific locations where thermal measurements are desired. The user may direct the probe to locally applying heat at the desired location, measuring its thermomechanical response.

Experiment

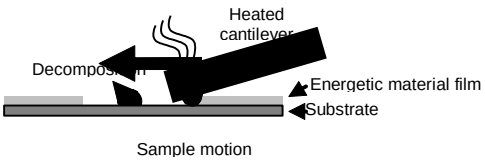

Fig 1. Experimental Setup

HT-AFM and nano-TA have enabled studies of local decomposition of energetic materials (5). Figure 1 shows the basic experimental configuration. A thin film of Pentaerythritol Tetranitrate (PETN) was prepared at a thickness of ~250 nm on a glass slide. When the heated AFM cantilever tip was scanned in contact with the energetic material, heating from the tip could induce nanoscale melting and/or decomposition in the energetic material film. It was possible to perform metrology of the energetic material using a cold tip, both before and after thermal writing.

Results and discussion

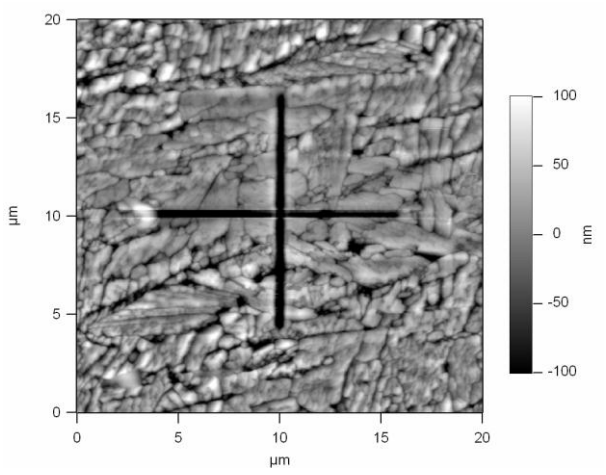

Fig 2. Pattern written using heated tip

Tailoring Voids in Energetic Materials: Local thermal decomposition with a heated tip provides a unique method of controlling both the size and spatial resolution of voids in the energetic material. The ability to tailor synthetic voids could enable new ways to interrogate and control energetic phenomena. Figure 2 shows a simple "+" pattern written in the PETN film,

demonstrating the high special resolution and registry of the technique. For each of the two lines of the "+," the cantilever was held at 215 °C and scanned at 0.1 Hz for 60 seconds. The depth of the feature was ~300 nm which closely matched the film thickness. There was no noticeable pileup or residue, indicating that the material was completely decomposed or evaporated during the thermal writing.

Energetic Material Response to Tip Temperature: Figure 3 below shows the effect of tip temperature on the energetic material response. In this experiment, the heated tip was scanned along lines at five different temperatures. The lowest temperature tested, 54 °C, produced no lithographic mark on the PETN. However, at 99 °C and above the heated tip was able to write into the PETN. The region of PETN reaction was wider for increasing temperature. The increased reaction area may have been due to increased heating from the tip, or by diffusion of a thermo-mechanical reaction in the PETN film. For the areas decomposed at higher temperatures, the PETN crystals near the decomposed area were noticeably larger than in the unmodified sample regions, suggesting that this type of measurement may be useful for studying grain coarsening and aging in energetic materials.

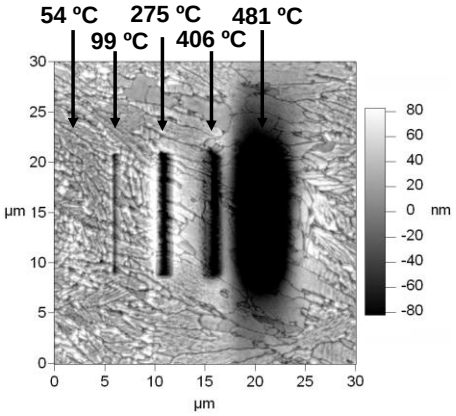

Fig 3: PETN response to different tip temperatures

A second experiment (Fig 4.) tested the rate of material reacted by scanning the heated tip over a 5 µm square of the PETN film. In the images of Fig. 4, the slow scan began at the "south" end of the image and moved "north," in only one pass such that the tip did not scan over the same region twice. For these experiments, the cantilever was heated to 215 °C. For the first experiment, the heated tip scanned over the sample in 1290 seconds. In the post-reaction metrology of Fig. 4, much of the PETN that was heated was removed, but unlike the decomposed lines of Figs. 2 and 3, some of the PETN filled in behind. Furthermore, it appears as if the polycrystalline structure of the PETN orients in a columnar fashion in the north-south direction in Fig. 4. A second 5 µm square was written on a fresh area of PETN, under identical conditions, except for an increased scan speed that resulted in a total scan time of 660

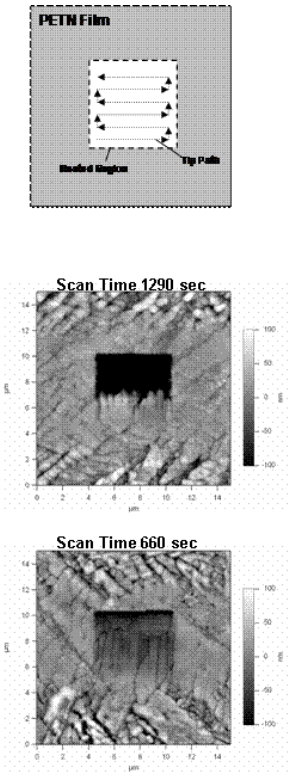

Fig 4. Effect of varying scan rate

seconds. For this second, faster experiment, significantly less PETN was removed and the columnar grain structure of the PETN is even more apparent. When heated, the PETN can either go through a phase transition (sublimation or melt/evaporation) into the gas phase or decompose. We hypothesize that the PETN was melted or evaporated at the heated tip, and subsequently recondensed onto the previously scanned area. However, not all the material was recondensed, which suggests that some of the PETN may have decomposed. The recondensed PETN is mostly in the south of the region where the tip scan began because the north end was heated last leaving a temperature gradient. The high temperature of the tip drove the liquid or vapor PETN away from the tip, which resulted in PETN condensed on the southern end of the scan only which was cooler. The condensed PETN formed columnar structures that generally lie in the north-south direction, which is behavior that is consistent with the temperature gradient being strongest in the north-south direction. Less material condensed within the scanned square for the longer scan and slower tip speed. The longer dwell time of the heated tip may have allowed the melted / evaporated PETN to diffuse farther from the heated source. This technique for manipulating the micro/nanostructure of polycrystalline energetic materials could be used to study phenomena such as diffusion rates and produce controlled nanoscale features of arbitrary shape and spacing to investigate propagation between voids and/or oriented crystallites.

Conclusions:

This application note presents new methods for testing the nanometer-scale thermo-mechano-chemical response of an energetic material via Heated tip AFM (HT-AFM). Thermo-chemical reactions can be induced on the thin film materials by controlling the temperature of the probe. The experiments investigate propagation of the thermo-chemical reaction based on size, shape, spacing, and anisotropy. This technique could be used to investigate thermophysical phenomena in any crystalline or polycrystalline material. The ability to manipulate the micro/nanostructure of polycrystalline materials could be used to study phenomena such as diffusion rates, phase transitions, and perform lithography in a wide variety of nanomaterials beyond energetic materials.

This application note was condensed from reference (5). More details can be obtained from reference (5), from the author, or from Anasys Instruments Inc.

References:

1. Armstrong, R. W. Journal de Physique IV 1995, 5, (c4), 89-102.
2. Dlott, D. D. Materials Science and Technology 2006, 22, (4), 463-473.
3. Armstrong, R. W.; Baschung, B.; Booth, D. W.; Samirant, M. Nano Letters 2003, 3, (2), 253-255.
4. Tarver, C. M.; Chidester, S. K.; Nichols, A. L. Journal of Physical Chemistry 1996, 100, (14), 5794-5799.
5. King, W. P.; Saxena, S.; Nelson, B. A; Weeks, B. L.; Pitchimani, R. Nano Letters 2006, 56, 930-933.