Chemical Engineering

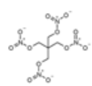
Thermodynamic Analysis of Nanoscale PETN films

Jason Abbott, Rajasekar Pitchimani, and Brandon L.Weeks

Department of Chemical Engineering, Texas Tech University, Lubbock , TX 79409

Introduction

- Pentaerythritol Tetranitrate (PETN, $C_5H_8N_4O_{12}$) is one of the strongest secondary explosive commonly used as an initiator for other primary explosives



- Nanoscale measurements can provide methods of understanding and prohibiting coarsening

•Coarsening
-Alters size distribution
-Particle density
-Modifies crystal habit
-Creates voids
-Detonation properties

- No general agreement on thermal decomposition kinetics and determination of activation energy of evaporation of PETN[1-3]

Experimental

- PETN powders (Lawrence Livermore National Laboratory, UC, California) dissolved in acetone (0.1M) and spin coated on to a piranha-cleaned Si(100) surface and dried in air
- PETN films are prepared by spin coating. (Single Wafer Spin Processor, Laurell Technologies Corp., North Wales, PA)
- Films were annealed isothermally (20-85ºC) in oven (Isotemp Vacuum oven model 282A) at ambient pressures for 6 hours at each temperature
- The film was characterized after annealing at room temperature by AFM (Pacific Nanotechnology, Santa Clara, CA)
- PNI Nano-Rule+ software was used for measuring the volume and surface area of the coarsened region alone

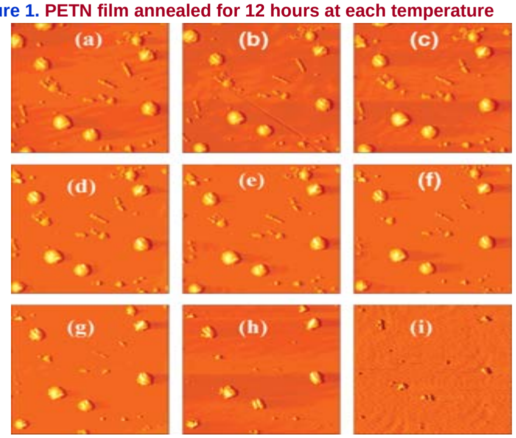
State of the Art

- Work that is presented is a continuation of an earlier work done by R. Pitchimani[5]. Pitchimani's work provided knowledge on the coarsening effects and speed of coarsening of PETN. This work will show how doping PETN will slow the coarsening effects by adding impurities.
- Zinc doped PETN has an increase in activation energy of sublimation thus stabilizing PETN at low temperatures.

Results

- Figure 1 shows the AFM image of the PETN film prepared at room temperature and the images after annealing for 12 hours each
- The AFM image taken 2 hours after preparation shows already some coarsening at some areas (brighter areas)
- The volume and the surface area of coarsened regions were measured at each temperature; The film vanishes at 70ºC

Figure 1. PETN film annealed for 12 hours at each temperature



(a) At room temperature and (b-i) annealed at 30-85ºC

- Figure 2 shows the doped PETN films prepared at room temperature and the images annealed for 12 hours
- The film height increases continuously as the surface area increases up to about 60ºC and then decreases. At and after 60ºC the sublimation dominates
- Increased stability and decease in coarsening effects shown from 55-65ºC with Zn doped films
- Figure 3 shows the changes in activation energy of evaporation (E_a) with changes of doping levels

[1] Cook, M. A., *The Science of High Explosives*; Reinhold, New York, 1958.

[2] Robertson, A. J. B., *J. Soc. Chem. Ind. (London)* **1948**, *67*, 221.

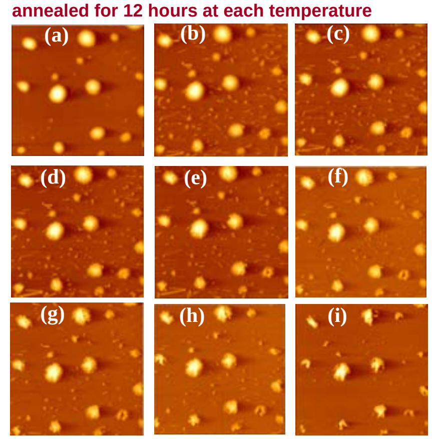
[3] Rogers, R. N.; Dinegar, R. H., *Thermochemica Acta* **1975**, *11*, 131.

[4] Burnham, A.; Gee, R.; Maiti, A.; Qiu, R.; Rajasekar, P.; Weeks, B.; Zepeda-Ruiz, L., "Experimental and modeling characterization of PETN mobilization mechanisms during recrystallization at ambient conditions," UCRL-TR-216963, November 9, 2005.

[5] Pitchimani, R.; Burnham, A.; Weeks, B., "Quantitative Thermodynamic Analysis of Sublimation Rates Using an Atomic Force Microscope," Journal of Physical Chemistry 111,39,9182-9185 Aug 9, 2007

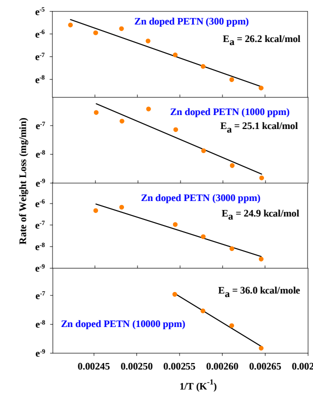
Results (continued)

Figure 2. Zn Doped (1000 PPM) PETN film annealed for 12 hours at each temperature



(a) At room temperature and (b-I) annealed at 30-65ºC

Figure 3. Plot of Rate of Weight Loss versus inverse of temperature at different doping levels



Conclusions and future work

- We have determined the activation energy of evaporation (E_a) for PETN films of thickness few hundred nanometers in the temperature range 60-80ºC
- The E_a values found for films match with that calculated for bulk PETN crystals in the temperature range 110-140ºC
- The works extend the activation energy of evaporation for PETN in the lower temperature region
- Also using thin films for thermodynamic analysis of PETN makes it safer and can be extended to other explosives
- The work will be carried out with smaller temperature steps
- Impurities decrease coarsening effects

Acknowledgements

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