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Influence of Surface Contamination on the Microstructure and Morphology of Vapor-Deposited Pentaerythritol Tetranitrate (PETN) Films

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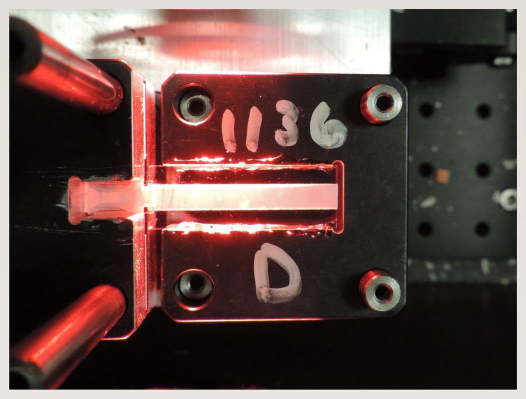
Motivation

Microenergetics

Microscale processing and testing of energetic materials at Sandia National Laboratories has enabled investigation into the field of "microenergetics."

-Small-scale explosive samples can be used for the study of ignition, combustion, and detonation phenomena at sub-millimeter scales.

-Physical vapor deposition (PVD) is one technique for achieving more precise control of explosive morphology and microstructure at length scales of interest.



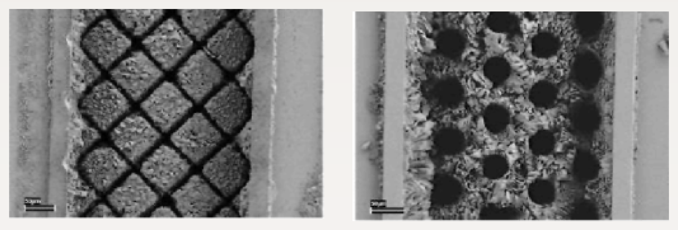
Vapor-deposited PETN film on polycarbonate substrate in microdetonation test setup.

Microstructure and morphology of explosive materials affect resultant detonation characteristics.

-Crystal structure/orientation, porosity, grain size, and local density ultimately dictate key detonation parameters such as detonation velocity, yield, initiation threshold, and critical detonation thickness.

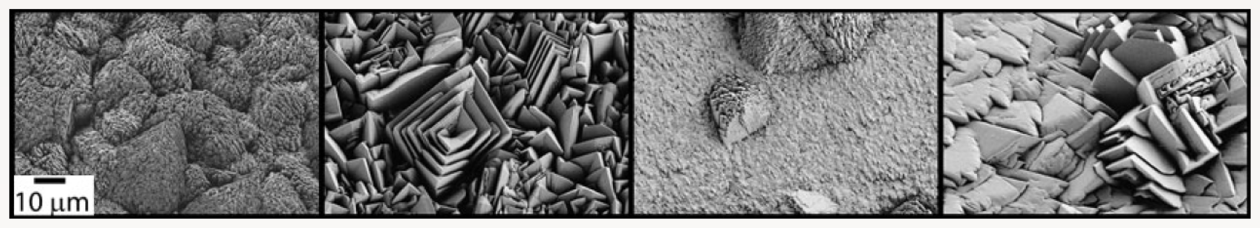
Prior Work

MEMS-based fabrication techniques have been applied to energetic films deposited via PVD to alter detonation characteristics at micron-length scales.



PETN films patterned using femtosecond laser micromachining (far left) and plasma etching (left). Scale bar is 50 µm. *Tappan et al., Int. Det. Symp., 2006.*

Variation in substrate and deposition conditions (homologous temperature, etc.) has been shown to dramatically alter microstructure in PETN films created via PVD.

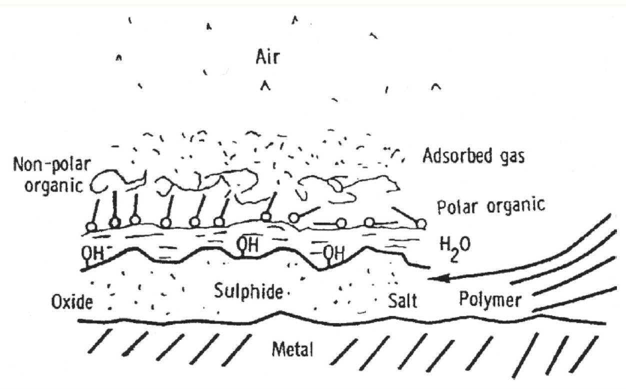


Variation in microstructure of PETN films due to varying substrate conditions (substrate material and temperature). *Knepper et al., J. Mat. Res., 2011.*

Interfacial Effects on Explosive Microstructure & Morphology

Interfacial effects (substrate-energetic interaction) during PVD appear to play a key role in explosive film characteristics.

For practical surfaces, surface energy is largely dominated by atmospheric contaminants. Even at Ångstrom-length scales, these contaminants determine surface energy.



Surface	Surface Free Energy (mJ/m²)
Organic Hydrocarbons	~20
Organic Polymers	~20-30
Epoxides	~50
Metal Oxides	200-500
Metals	1000-5000

Understanding of adsorbed layers on an engineering surface, c. 1968 (left). Typical surface energy values for surface layers (right). Atmospheric contaminants adsorb to surfaces to minimize the free energy of the interface. *Castle, J. Adh., 2008.*

Experimental

Objective

Demonstrate the influence of substrate contamination on surface energy, and in turn, microstructure and morphology evolution of PETN films grown via Physical Vapor Deposition (PVD).

Substrate Preparation

Silicon wafers (1 cm × 1cm, 525 µm thick, <100>, polished) were prepared as follows:

- -**C1,** As-received from vendor
- -**C2**, Aged in room air for one week
- -**C3**, Solvent clean
- -**C4**, Plasma clean, various wait times
- -**C5**, Ar ion etch in-situ
- -**C6**, Glass cleaning
- -**C7**, Piranha etch

Substrate Characterization

Four-liquid contact angle measurement:

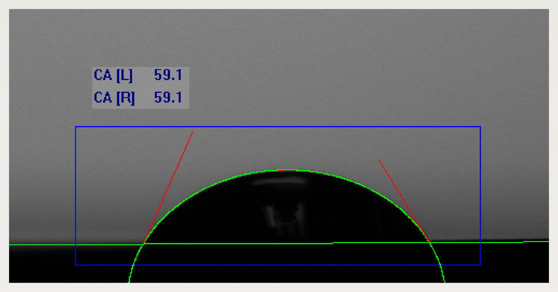
-Provides quantitative value of substrate surface energy prior to deposition.

-Theory of Owens-Wendt:

$$\frac{\gamma_l(1+\cos\theta)}{2\sqrt{\gamma_l^D}} = \left(\frac{\gamma_l^P}{\gamma_l^D}\right)^{1/2}\sqrt{\gamma_s^P} + \sqrt{\gamma_s^D}$$

-Acid-Base Theory:

$$\gamma_l(1+\cos\theta) = 2\left[\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^{+}\gamma_l^{-}} + \sqrt{\gamma_s^{-}\gamma_l^{+}}\right]$$



Contact angle of non-polar liquid on Si substrate.

Angle-resolved X-ray Photoelectron Spectroscopy (AR-XPS):

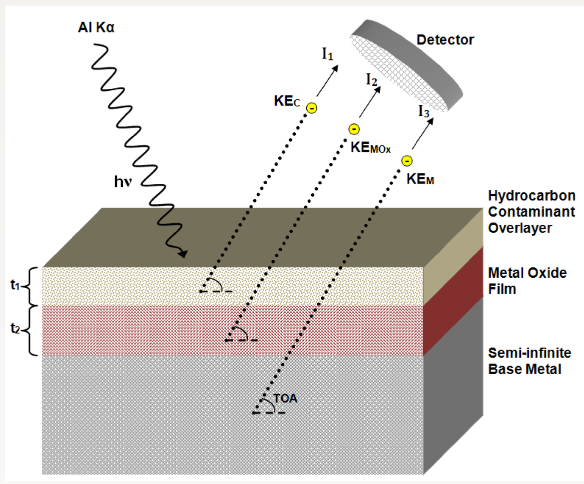
-Provides *quantitative* evaluation of contaminant and oxide profile on substrate at Ångstrom-length scales.

Substrate surface roughness:

-Non-contact 3D profiler.

-All substrate preparations have $R_a < 2$ nm.

→ **Substrate roughness not a factor in depositions.**

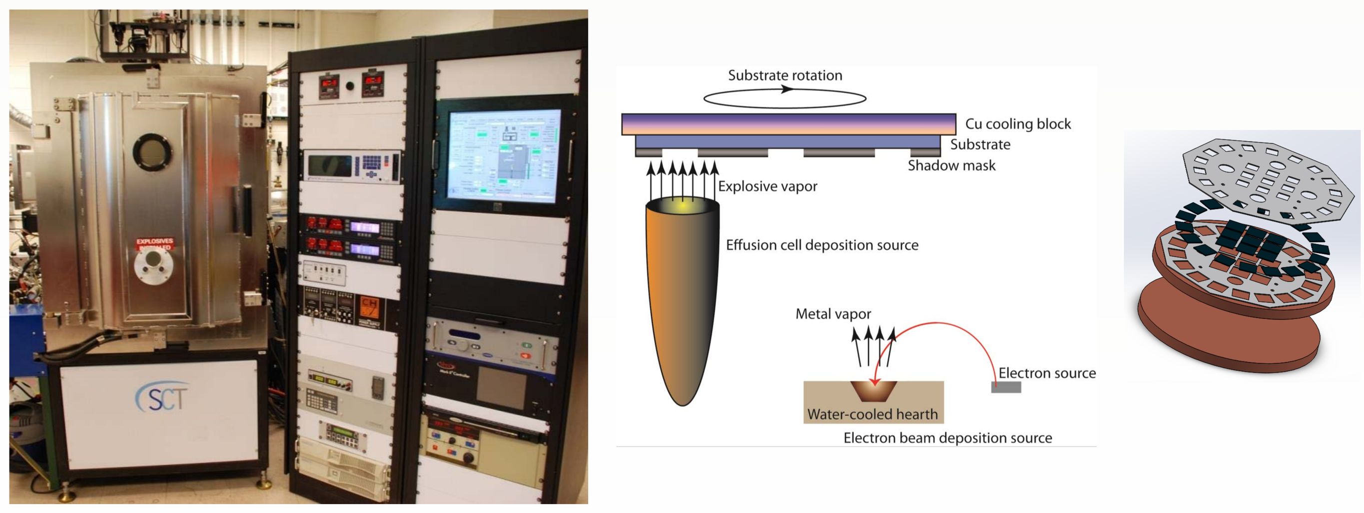


Schematic of AR-XPS measurements. Three layer model valid for substrates ≳100 nm thick.

PETN Film Growth

Deposition chamber can be used to grow organic crystalline energetic films via PVD with carefully controlled deposition conditions.

The unique facility enables cleaning of surfaces in-situ using Ar ion source, followed by PVD of PETN without breaking vacuum (and exposing to atmospheric contaminants).



High Vacuum Chamber for Performing PVD (left), Schematic of PVD process (center), and Model of Deposition Fixture (right).

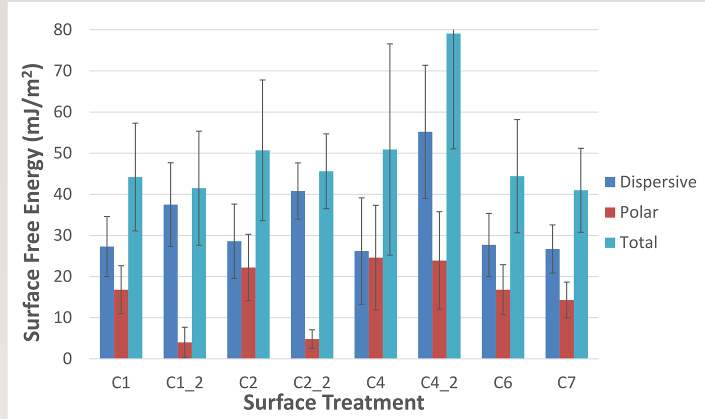
Results & Discussion

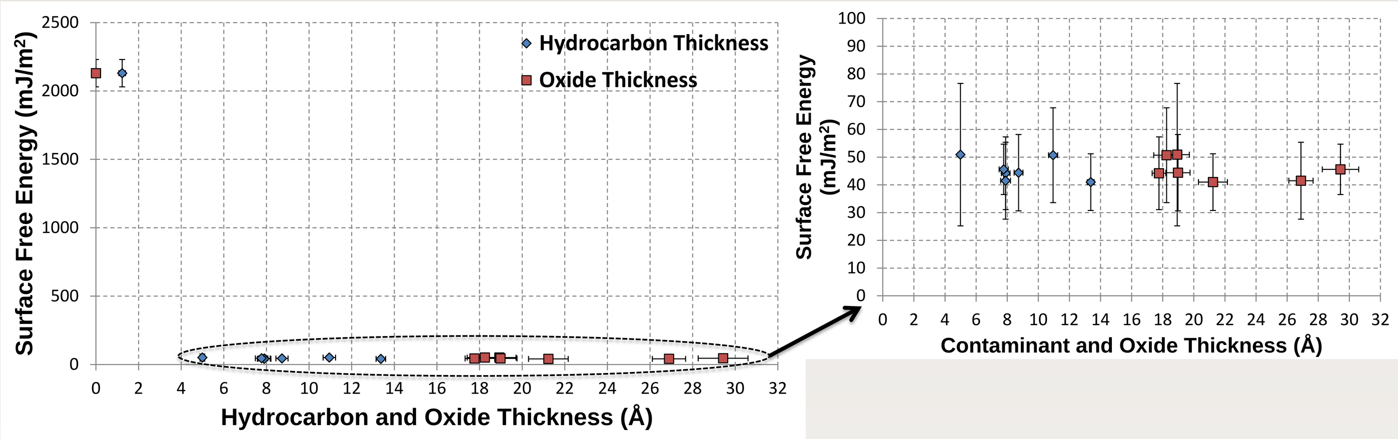
Substrate Surface Energy and Contaminant/Oxide Profile

Cleaning treatments outside of vacuum yield **low surface energy** (<80 mJ/m²).

In-vacuum cleaning treatments yield lowest equivalent contaminant thickness, and therefore **high surface energy.**

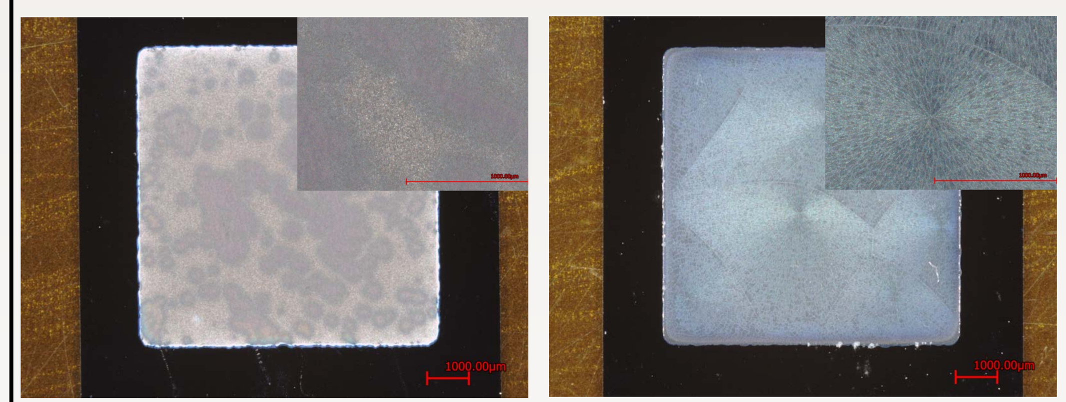
-Theoretical value for 'clean' <100> silicon is 2130 mJ/m².



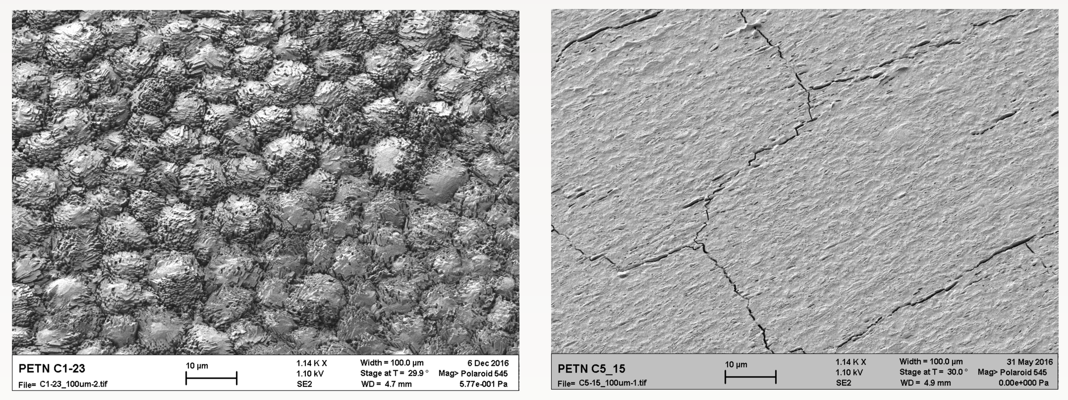


Morphology and Microstructure of PETN Films

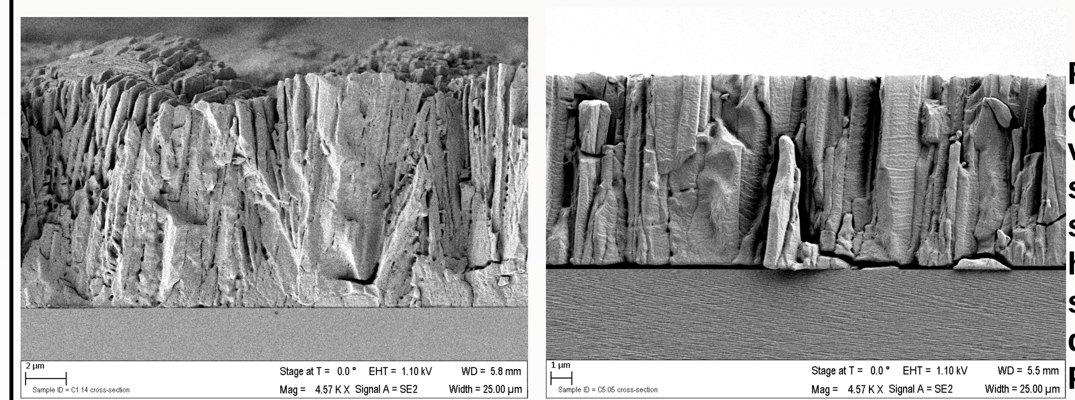
PETN films deposited on substrates cleaned ex-situ all exhibited similar morphology, typical of 3D island growth. Films on substrates cleaned in-situ resulted in smooth, dense films, representative of 2D layer growth.



Optical microscopy of ~10 µm PETN films vapor deposited on low-surface energy Si substrate (far left), and high surface energy substrate (left).



SEM micrographs of top surface of ~10 µm PETN films vapor deposited on low-surface energy Si substrate (right), and high surface energy substrate (far right).



Fracture cross sections of ~10 µm PETN films vapor deposited on low-surface energy Si substrate (far left), and high surface energy substrate (left). Note distinct differences in PETN porosity.

Conclusion & Future Work

- Surface energy plays a key role in microstructure and morphology evolution of PETN films deposited via PVD.
- Densification of PETN films can be achieved using substrate cleaning in-situ to achieve high surface energy during deposition.
- Future work includes study of micro-topographic effects on energetic film morphology, and engineering of interfaces for optimized detonation characteristics in explosive films.

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