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# Near-Failure Detonation Behavior of Vapor-Deposited Hexanitrostilbene (HNS) Films

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**Abstract.** Hexanitrostilbene (HNS) films were deposited onto polycarbonate substrates using vacuum thermal sublimation. The deposition conditions were varied in order to alter porosity in the films, and the resulting microstructures were quantified by analyzing ion-polished cross-sections using scanning electron microscopy. The effects of these changes in microstructure on detonation velocity and the critical thickness needed to sustain detonation were determined. The polycarbonate substrates also acted as recording plates for detonation experiments, and films near the critical thickness displayed distinct patterns in the dent tracks that indicate instabilities in the detonation front when approaching failure conditions.

## INTRODUCTION

Physical vapor deposition (PVD) is an attractive method to produce sub-millimeter explosive samples for studying detonation behavior at near-failure conditions. PVD provides precise control over sample geometry, both in film thickness and lateral dimensions that is extremely difficult to achieve using conventional fabrication techniques, such as pressing powders. PVD also allows one to exert control over film microstructure by varying deposition conditions; changing parameters such as substrate temperature [1-4], substrate material [2, 3], or deposition rate [1, 5] can have substantial effects on the resultant film density, grain size, and/or porosity distribution which can in turn affect properties such as ignition sensitivity, detonation velocity, or critical diameter [6-8].

In this work, we use PVD to deposit films of the explosive hexanitrostilbene (HNS) under two distinct deposition conditions, where the substrate is held at either 10 ºC or 45 ºC during deposition. The resultant differences in microstructure are quantified by analyzing ion-polished cross-sections, and series of detonation velocity experiments are performed on films of various thicknesses in the vicinity of the critical thickness needed to sustain detonation. These experiments can provide insight not only into the near-failure behavior of HNS, but also into the effects of microstructure on detonation performance.

## EXPERIMENTAL METHODS

HNS films were deposited in a custom designed high-vacuum deposition system. HNS powder was loaded into an effusion cell deposition source, and the chamber was evacuated to a base pressure of ~ $10^{-6}$ Torr. Substrates were held against a water-cooled copper block whose temperature could be controlled using an external chiller, and a shadow mask was used to define the geometry of the deposition. Samples were prepared using two different substrate temperatures, 10 ºC and 45 ºC. The effusion cell was heated to a maximum temperature of ~ 260 ºC, at which point the HNS sublimed over a period of several hours. Substrates were rotated during deposition to produce a uniform film thickness. Multiple depositions were required to reach the thicknesses needed for detonation testing.

Films used for detonation velocity experiments were deposited onto 1 × 3 cm polycarbonate substrates in either a single or double line configuration, where 1.6 mm-wide HNS lines extended along the length of the substrate. A polycarbonate lid is assembled with seven optical fibers for each deposited line. This optical fiber probe lid is

constructed by inserting each optical fiber from a multiple-fiber optical fiber probe (Polymicro Technologies) through laser-machined holes. A specialized fixture is used to position the optical fibers orthogonal to the lid, where they are cleaved, positioned flush with the lid, and bonded in place using epoxy. The optical fiber probes are terminated in a 'six-around-one' fashion in an FC optical fiber connector for connection to a silicon photodetector (DET210, Thorlabs) with rise and fall times of 1 ns. Detonation is initiated using a pentaerythritol tetranitrate (PETN) structure that provides an incident shock to the end of the HNS lines. The optical fiber probes detect light as the detonation reaches and destroys each optical fiber on the lid. Additional details can be found elsewhere [9].

Films used for microstructure characterization were deposited onto 1 cm square poly(methyl methacrylate) (PMMA) substrates. PMMA was used due to the ease of ion-polishing compared to polycarbonate. Cross-sections were ion-polished using a Hitachi IM4000 Plus ion milling system operating at 5 kV and 20 $\mu$A with a ± 40º stage swing. The ion-polished cross-sections were then imaged using a Zeiss Crossbeam 340 scanning electron microscope (SEM) operating with a 1.1 kV accelerating voltage and using the secondary electron detector.

## RESULTS AND DISCUSSION

The temperature of the substrate during deposition has a significant effect on the microstructure of an HNS film. Figure 1 shows SEM images of HNS films deposited with the substrate held at either 10 ºC or 45 ºC. Both films have a columnar grain structure with grains oriented perpendicular to the substrate. In the film deposited at 10 ºC, the majority of the porosity appears along the boundaries between the columns with few pores in the column interiors. While the film deposited at 45 ºC also has pores along the column boundaries, now there are a substantial number of pores in the interiors of the columns as well.

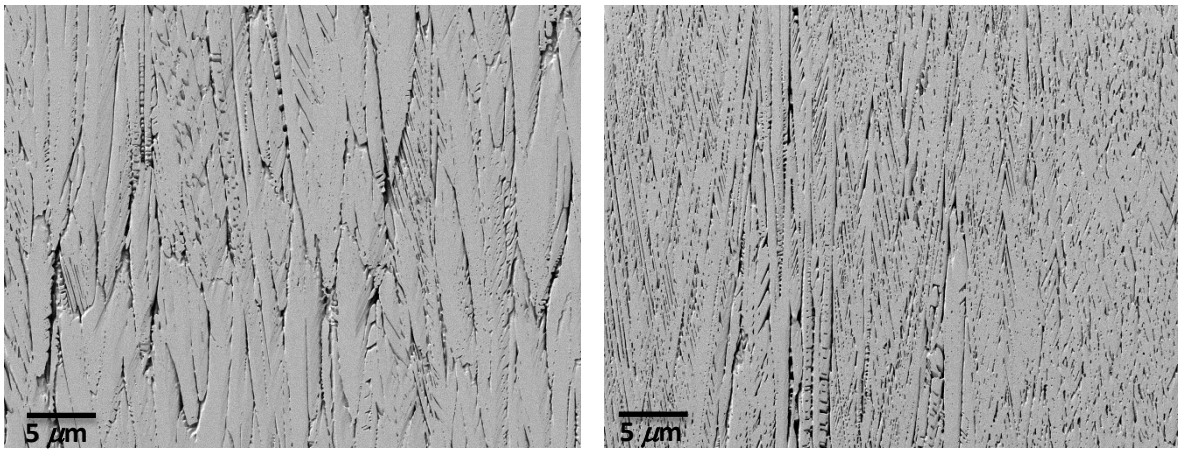


**FIGURE 1.** Representative SEM images of ion-polished cross-sections of HNS films deposited with substrate temperatures of 10 ºC (left) and 45 ºC (right).

Electron micrographs taken of ion-milled cross-sections were digitally processed to segment the void and solid regions. First the contrast was maximized by remapping the grayscale intensities. An adaptive Weiner filter with a 2 by 2 neighborhood was then used to reduce noise before the image was segmented using a simple threshold. The quality of the segmentation was assessed by overlaying the segmented void boundaries onto the original image. While it is difficult to extract realistic distributions of pore sizes and shapes from these two dimensional sections, a 2-D section can be used to estimate the average density of the film. The area fraction of pixels (solid/void) was determined for several images of films deposited at each deposition condition, indicating that the films deposited at 10 ºC and 45 ºC were approximately 91% and 86% dense, respectively. Future microstructure characterization will include using the focused ion beam capabilities in the SEM to sequentially cut thin slices from a cross-section and image the new surface, generating real three-dimensional porosity distributions that can be imported into meso-scale simulations and used to compare experiments with simulated performance [10].

HNS films were deposited to various thicknesses between ~ 190 and 290 $\mu$m to characterize trends in detonation velocity at near-failure conditions. Data for films deposited with substrate temperatures of 10 ºC and 45 ºC are presented in the plot of detonation velocity vs. HNS film thickness shown in Figure 2. The open circles on the axis represent the thickest films that were unable to sustain detonation. In both cases, detonation is unable to propagate at

film thicknesses under ~ 200 $\mu$m and detonation velocities appear to increase from ~ 6.4 mm/$\mu$s to ~ 6.5 mm/$\mu$s with increasing film thickness. While only limited data is currently available for films deposited at 10 ºC, there appears to be little difference in detonation velocity for films deposited under the two different deposition conditions.

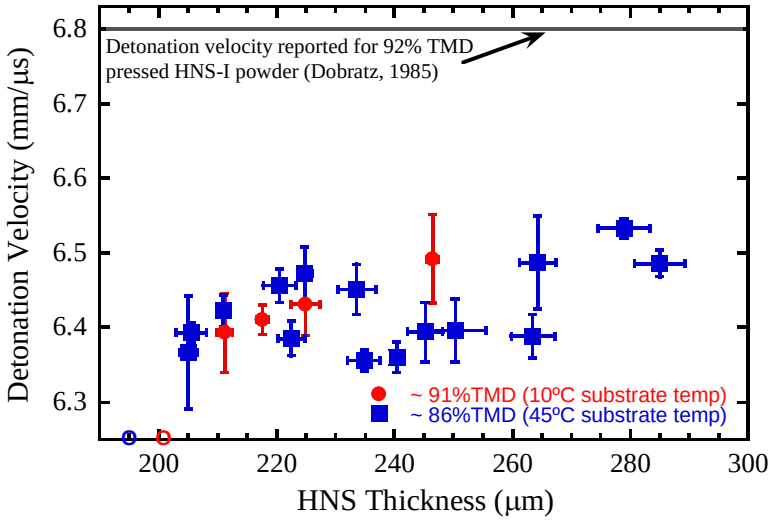


**FIGURE 2.** Detonation velocity vs. thickness for HNS films deposited with different substrate temperatures.

Comparing the detonation velocities measured in the vapor-deposited samples with data for HNS powder pressed to a similar density [11], we see that the velocities for the vapor-deposited films are significantly lower. This suggests that these films are in the "velocity deficit" region of the critical thickness curve, where the detonation velocity drops when approaching the failure thickness [12]. This suggests that we should expect detonation velocities to continue to increase as film thickness increases beyond the range tested thus far, especially for the higher density films deposited at 10 ºC. Future experiments will determine whether this is indeed the case.

Following detonation experiments, the polycarbonate substrates the HNS films were deposited on were not always destroyed, but rather retained a dent track showing the path of the detonation front. Films close to the failure thickness typically produced a cross-hatch pattern in the dent, as shown in Figure 3, similar to patterns often recorded in soot coatings following gaseous detonations [13] or in experiments with TNT [14]. Such patterns suggest instabilities in the detonation front as the film thickness approaches failure conditions. Interestingly, similar behavior was also seen in similar hexanitroazobenzene (HNAB) films tested at near-failure conditions [15], except that the cross-hatching was significantly larger with HNS (cell size ~ 30 – 50 $\mu$m for HNS, ~ 5 – 10 $\mu$m for HNAB), and that while the cross-hatching was only seen near the edges of the dent with HNAB, it extended across the entire track in experiments with HNS.

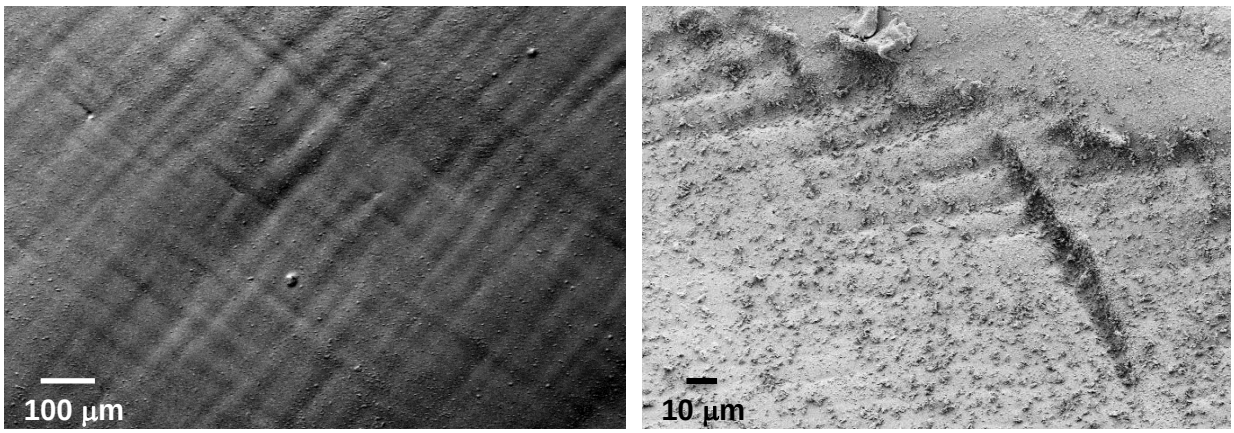


**FIGURE 3.** SEM images of dent tracks from a near-failure detonation experiment in HNS (left) and HNAB (right) films.

## CONCLUSIONS

Altering the substrate temperature during deposition of HNS films can have a significant effect on the resultant density and distribution of porosity, with film density and spacing between pores decreasing with increasing substrate temperature. However, for the films tested thus far, little change in either detonation velocity or failure thickness has been observed. Detonation fails to propagate in films thinner than 200 $\mu$m in all cases, and films near the failure thickness display cross-hatch patterns in the dent tracks that indicate instabilities in the detonation front at near-failure conditions. The data suggest that the near-failure behavior of HNS is relatively insensitive to small variations in microstructure.

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## REFERENCES

1. P. Fenter, F. Schreiber, L. Zhou, P. Eisenberger, and S. R. Forrest, Physical Review B **56** (6), 3046-3053 (1997).
2. F. Schreiber, Phys. Stat. Sol. A **201** (6), 1037-1054 (2004).
3. G. Witte, K. Hanel, S. Sohnchen, and C. Woll, Appl. Phys. A **82**, 447-455 (2006).
4. D. Y. Zhong, M. Hirtz, W. C. Wang, R. F. Dou, L. F. Chi, and H. Fuchs, Physical Review B **77**, 113404 (2008).
5. G. X. Zhang and B. L. Weeks, Appl. Surf. Sci. **256** (8), 2363-2366 (2010).
6. H. Eyring, R. E. Powell, G. H. Duffy, and R. B. Parlin, Chemical Reviews **45** (1), 69-181 (1949).
7. A. W. Campbell, W. C. Davis, J. B. Ramsay, and J. R. Travis, Phys. Fluids **4** (4), 511-521 (1961).
8. B. A. Khasainov, B. S. Ermolaev, H. N. Presles, and P. Vidal, Shock Waves **7** (2), 89-105 (1997).
9. A. S. Tappan, R. Knepper, R. R. Wixom, J. C. Miller, M. P. Marquez, and J. P. Ball, "Critical Thickness Measurements in Vapor-Deposited Pentaerythritol Tetranitrate (PETN) Films," *Fourteenth International Detonation Symposium*, Office of Naval Research, ONR-351-10-185, Coeur d'Alene, ID, 2011, pp. 1087-1095.
10. R. R. Wixom, A. S. Tappan, A. L. Brundage, R. Knepper, M. B. Ritchey, J. R. Michael, and M. J. Rye, Journal of Materials Research **25** (7), 1362-1370 (2010).
11. B. M. Dobratz and P. C. Crawford, "LLNL Explosives Handbook – Properties of Chemical Explosives and Explosive Simulants," *Lawrence Livermore National Laboratory Report UCRL-52997-Chg.2*, 1985.
12. A. W. Campbell and R. Engelke, "The Diameter Effect in High-Density Heterogeneous Explosives," *Sixth Symposium (International) on Detonation*, Office of Naval Research, ACR-221, Coronado, CA, 1976, pp. 642-652.
13. M. I. Radulescu, G. J. Sharpe, C. K. Law, and J. H. S. Lee, J. Fluid Mech. **580**, 31-81 (2007).
14. P. Howe, R. Frey, and G. Melani, Combust. Sci. Technol. **14** (1-3), 63-74 (1976).
15. R. Knepper, M. P. Marquez, and A. S. Tappan, "Effects of Confinement on Detonation Behavior of Vapor-Deposited Hexanitroazobenzene Films," *Fifteenth International Detonation Symposium*, Office of Naval Research, San Francisco, CA, 2014, (in press).