

CRYSTALLIZATION BEHAVIOR OF VAPOR-DEPOSITED HEXANITROAZOBENZENE (HNAB) FILMS

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Abstract. Vapor-deposited hexanitroazobenzene (HNAB) has been shown to form an amorphous structure as-deposited that crystallizes over a period ranging from several hours to several weeks, depending on the ambient temperature. Raman spectroscopy and x-ray diffraction were used to identify three distinct phases during the crystallization process: the as-deposited amorphous structure, the HNAB-II crystal structure, and an as-yet unidentified crystal structure. Significant qualitative differences in the nucleation and growth of the crystalline phases were observed between 65°C and 75°C. While the same two polymorphs form in all cases, significant variation in the quantities of each phase was observed as a function of temperature.

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INTRODUCTION

Hexanitroazobenzene (HNAB) is an interesting material for microenergetic research on explosive behavior at sub-millimeter geometries due to its small critical thickness for detonation and its chemical stability at temperatures above its melting point [1,2], which allows for fast deposition rates using vacuum thermal evaporation (VTE). We have observed that HNAB films fabricated using VTE have a highly reproducible dense amorphous structure that is largely independent of substrate material or small changes in deposition conditions, provided the substrate remains sufficiently cool during deposition. Unfortunately, this amorphous structure is not stable and the films crystallize over a period of hours to weeks, depending on the ambient temperature.

HNAB is known to have a number of different polymorphs that are stable or metastable at ambient conditions [3-5]. It is not clear *a priori* which crystal structure(s) will form or if we can exert

some amount of control by varying processing conditions. To this end, several films were deposited to a thickness of approximately 100 μm and subjected to a variety of temperatures ranging from 30–75°C to observe variations in crystallization behavior using time-lapse optical microscopy. Films were also characterized *ex situ* using x-ray diffraction and Raman spectroscopy to identify crystal structures present and examine variations in crystallization behavior with increasing temperature.

EXPERIMENTAL PROCEDURE

HNAB films were deposited in a custom designed high-vacuum deposition system. HNAB powder was loaded into an effusion cell thermal deposition source, and the chamber evacuated to a base pressure of $\sim 10^{-6}$ Torr. The effusion cell was heated to a maximum temperature of $\sim 230^\circ\text{C}$, at which point the HNAB completely evaporated over a period of approximately 30 minutes. Substrates consisted of 1 cm squares of (100) oriented single

crystal silicon held on a water-cooled copper block to reduce heating during deposition. Substrates were rotated at 25 rpm during deposition to produce a uniform film thickness. Shadow masks were used such that uncoated 1–2 mm wide regions around the edges of the substrate could be used as a reference for accurate film thickness measurements.

Films were characterized using time-lapse optical microscopy, x-ray diffraction, and Raman spectroscopy. Time-lapse optical microscopy was performed by placing HNAB films onto a custom heater stage controlled using a Lakeshore model 325 temperature controller under a Keyence VHX-1000 microscope using a VH-Z20R lens. Films were heated to temperatures from 30–75°C, and images were taken at a 50× magnification at time intervals ranging from 15 seconds to 2 hours until crystallization was complete. A Bruker D8 diffractometer equipped with a General Area Detector Diffraction System (GADDS) was employed for the x-ray diffraction measurements. This system used a copper x-ray source ($k\alpha$ wavelength of 1.54059 Å) operated at 40 kV and 40 mA with a 0.3 mm spot size. Raman spectroscopy was performed using a 785 nm laser with a 2.4 μm spot size. Spectra were collected over a 138 $\mu\text{m} \times$ 148 μm region in a 75 \times 75 array with an integration time of 0.11 seconds per point.

RESULTS AND DISCUSSION

Time-lapse optical microscopy

Images showing the progression of crystallization at 40°C, 65°C, and 75°C are shown in Figure 1. Initially, the as-deposited films are transparent and dark red in color. The films crystallized at 40°C and 65°C show a similar nucleation and growth process, with both orange and yellow nuclei forming, growing, and coalescing over time. The distinct coloration is likely the result of the film forming different crystal structures in the yellow and orange regions.

The difference in temperature causes the crystallization to occur much faster in the film at 65°C, with crystallization completing in \sim 2.5 hours, compared with \sim 3 days for a film at 40°C and 3 weeks for a film at room temperature (not shown). In addition, it appears that the growth rate

of the orange phase increases faster with increasing temperature than the yellow phase does, resulting in a larger volume fraction of the orange phase in the crystallized film as temperature increases. Note that films crystallized at intermediate temperatures (not shown) appeared to follow similar nucleation and growth processes with trends consistent with those discussed above.

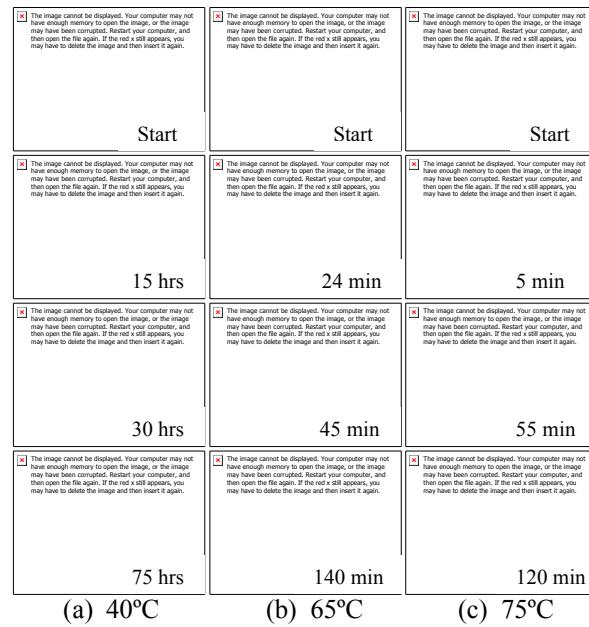


Figure 1. Time-lapse images showing crystallization of an amorphous HNAB film at (a) 40°C, (b) 65°C, and (c) 75°C. Each image depicts an area 7 mm wide, with the elapsed time noted in the lower right of each image.

The film crystallized at 75°C shows a much different behavior than films crystallized at lower temperatures. Over the first five minutes at this temperature, the surface of the film changes from transparent red to opaque black. Furthermore, crystallization is no longer dominated by the nucleation and growth process seen at lower temperatures, but instead occurs primarily by the movement of a large crystalline front from the edges of the film towards its interior. Total time for crystallization to complete is similar to the film crystallized at 65°C. Note that while there is contrast in the coloring of the crystallized film, we no longer see only two distinct colors in the crystallized material, as was evident at lower

temperatures, and instead have more subtle variations in coloration.

X-ray diffraction

X-ray diffraction patterns were collected at various locations in films crystallized at both 60°C and 75°C, as shown in Figure 2. Locations were chosen to represent regions with distinct coloration. Despite having a fair amount of color contrast, films crystallized at 75°C showed only minor changes in the diffraction pattern with location; the pattern shown below is representative of scans performed in a number of different areas. Films that crystallized at 60°C, however, show distinct differences in their diffraction patterns in the yellow and orange regions, as can be seen in the lower two scans in Figure 2.

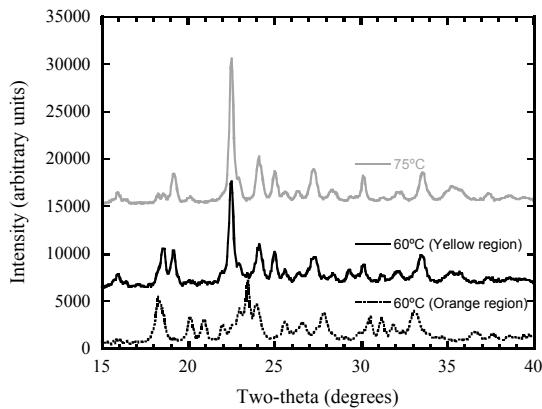


Figure 2. Representative x-ray diffraction patterns from an HNAB film crystallized at 75°C, and from the orange and yellow regions of an HNAB film crystallized at 60°C. Patterns offset for clarity.

Diffraction patterns collected from orange regions appear consistent with the monoclinic ($P2_1/a$) HNAB-II crystal structure. Diffraction patterns from yellow areas (crystallized at 60°C) and from all regions of the film crystallized at 75°C are very similar and suggest that these regions have the same crystal structure. Unfortunately, we have not been able to identify which polymorph this is. While the primary peaks are consistent with the monoclinic ($P2_1$) HNAB-III crystal structure, there are a number of additional peaks that do not match

this structure. It is possible that the additional peaks are due to the large spot size ($\sim 300 \mu\text{m}$) sampling areas containing multiple crystal structures. Additional experiments are currently underway in an attempt to identify this unknown crystal structure.

Raman Spectroscopy

Raman spectroscopy was performed on three different HNAB films, one that was in the process of crystallizing at room temperature, one that had crystallized at 60°C, and one that had crystallized at 75°C. Spectra were collected over a $138 \mu\text{m} \times 148 \mu\text{m}$ region. Scanned regions were chosen so as to encompass areas with multiple distinct microstructural features. The area scanned in the room temperature film contained regions of dark amorphous phase, orange HNAB-II crystallites, and the unidentified yellow phase. The area scanned in the film crystallized at 60°C contained regions of orange HNAB-II crystallites and the unidentified yellow phase. The area scanned in the film crystallized at 75°C did not have distinctly colored regions, but rather contained roughly circular features of a few hundred microns in diameter, likely crystallized in a nucleation and growth process, surrounded by a matrix that likely formed from growth inward from the edges of the film. Representative results from each region are shown in Figure 3.

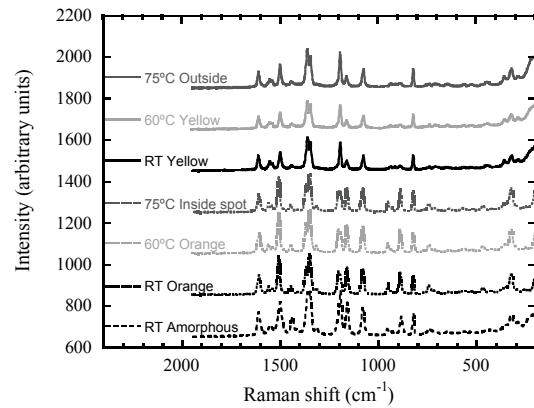


Figure 3. Comparison of Raman spectra representative of various regions of HNAB films crystallized at room temperature, 60°C, and 75°C. Data are offset for clarity.

The Raman spectra clearly show three distinct patterns that we can correlate with the amorphous structure, the orange HNAB-II crystal structure, and the unidentified yellow crystal structure. The spectra from the orange regions in the films crystallized at room temperature and at 60°C are indistinguishable, as are the spectra from the yellow regions in these same films. Interestingly, the film crystallized at 75°C, despite not having the distinct differences in coloration seen in films crystallized at lower temperatures and showing little change in the x-ray diffraction pattern with the specific location that was interrogated, appears to contain both of these same structures as well. Spectra collected from the “matrix” region (that grew in from the edges of the film) are identical to those from the unidentified yellow crystal structure, while spectra from the material inside of the 100-200 μm spots (that crystallized from nucleation and growth in the interior of the film) are identical to that of the orange HNAB-II crystal structure. Note that this suggests that the x-ray diffraction patterns collected from the film crystallized at 75°C and from the yellow regions in the film crystallized at 60°C were actually interrogating regions containing multiple phases (due to the large spot size of the incident x-ray beam). Identification of the unknown crystal structure may be possible by either scanning in an array of locations and performing a multivariate analysis to separate out distinct diffraction patterns for each phase, or by interrogating a film that was crystallized at lower temperatures that may have sufficiently large yellow regions to completely contain the x-ray beam.

CONCLUSIONS

Vapor-deposited hexanitroazobenzene (HNAB) has been shown to form an amorphous structure as-deposited that crystallizes over a period ranging from several hours to several weeks, depending on the ambient temperature. Raman spectroscopy and x-ray diffraction were used to identify three distinct phases during the crystallization process: the as-deposited amorphous structure, the HNAB-II crystal structure, and an as-yet unidentified crystal structure. Significant qualitative differences in the nucleation and growth of the crystalline phases

were observed between 65°C and 75°C. While the same two crystal structures emerged in all of the films investigated, significant variation in the quantity of each was observed as a function of temperature.

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