

## Thermionic emission microscopy of Scandium thin film dewetting on W(100)

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Scandium thin films of 5 -30 nm thickness deposited on clean W(100) surfaces de-wet from the tungsten surface when heated to temperatures  $< 0.5 T_{\text{melt}}$ . The dewetting temperature and the resulting droplet size are a function of the initial scandium film thickness.

Scandium is an additive in vacuum electronic devices, used to enhance performance of barium based thermionic cathodes, known as “scandate cathodes” [1]. The function of the scandium addition is not well understood. Model cathode studies using scandium have been reported [2-6]. Calculations have been made to understand the function of scandium on the surface of porous tungsten cathode surfaces, using the W(100) surface as a foundation [7]. Thick (100 nm) oxide layers containing barium and scandium oxides have been proposed, although no evidence for these layers was found by Kirkwood, et al. [1]. Stacked thin film layers of  $\text{Sc}_2\text{O}_3$  and BaO, and co-sputtered layers of  $\text{Sc}_2\text{O}_3$  and BaO were shown to de-wet from polycrystalline tungsten foil in [6]. The emissive areas on these surfaces were at locations occupied by the oxide films before dewetting, prompting the current study with pure scandium metal films.

A theory of work function reduction by a charged adsorbate dipole layer is usually invoked to explain the action of alkali metals on a metal surface [8]. In this model, the alkali is adsorbed onto the metal; charge is transferred to the metal from the alkali to produce a positively charged adsorbed alkali ion. When the alkali is adsorbed, a sharp decrease in the work function is observed, with a work function minimum at between  $\frac{1}{4}$  and  $\frac{1}{2}$  monolayer (ML) coverage. The alkali metal experiments often rely on Low Energy Electron Diffraction (LEED) to determine the adsorbate coverage. The addition of more alkali atoms creates new diffraction patterns as the adsorbate atoms are compressed on the surface. Beyond the minimum in the work function, the increased alkali coverage results in depolarization of the adsorbate atoms, and at 1 ML, the surface work function reaches the work function of the bulk adsorbed alkali metal. The compression structures observed in LEED suggest that the alkali atoms are free to move laterally on the surface. The charge associated with the alkali atom provides a repulsive force that allows the alkali adsorbates to remain as separate atoms as the coverage is increased rather than to agglomerate into islands.

In the specific case of the barium and tungsten model surface for cathodes, an adsorbed oxygen atom is also involved. The model calculations [7] place the oxygen below the level of the Ba on the surface, on top of a tungsten atom, and barium over a tungsten hollow site. The

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Ba-O dipole is produced with the positive Ba ion on the vacuum side; oxygen on tungsten on the opposite side. On W(100) with adsorbed barium, the work function decrease from 4.65 eV to a minimum below 2 eV, then increase to 2.5 eV, the value for bulk barium. In a study of cesium adsorption on W(100), the addition of adsorbed oxygen to the W(100) surface shifted the work function minimum slightly, due to increased bonding of cesium which increased the surface coverage of cesium [9]. Adsorbed oxygen was eliminated or minimized in the experiment reported below.

Dewetting would seem to preclude the basic physical requirements of the dipole model for work function reduction: there is no diffusion along the surface to form progressively dense surface structures. Droplet formation would preclude a repulsive force between adsorbate atoms, and droplets would not be formed from like-charge ions. While scandium is not an alkali, a similar work function minimum as for barium has been calculated in [7]. These calculations postulate a homogeneous distribution of barium, scandium and oxygen on the tungsten surface. The calculations in [7] do not require a vertical W-O-Ba or W-O-Sc-Ba stack. The ad- atoms are at adjacent sites, with differing distances from the W surface.

Nano scale scandium oxide particles and liquid synthesis using scandium precursors in the tungsten mix have been successful in scandate cathodes [1]. Scandate cathodes also use a relatively low percentage loading of scandium in the cathode mix, less than 5 at. %. We conclude that the film thickness vs. droplet size in scandium de-wetting explains why low scandium concentrations and nano-sized distributed scandium inclusions in cathodes are effective.

The experiments reported here were performed using the Elmitec Low Energy Electron Microscope V (LEEM V) at the Center for Functional Nanomaterials at Brookhaven National Laboratory. The W(100) crystals (99.999%), about 9mm in diameter and 0.25 mm thick were purchased from Accumet Materials Co. (Ossining, NY). The crystal was cleaned in a separate chamber by repeated heating in  $5 \times 10^{-7}$  Torr oxygen at 1800 C and flashing to over 1800 C. The temperature during cleaning cycles was measured using an optical pyrometer. In the LEEM, a thermocouple attached to a tungsten plate in contact with the crystal was used to measure the temperature. Sharp 1x1 LEED patterns were observed using LEED. Scandium (99.9%) was evaporated by placing a small piece (2x2x5 mm) of scandium metal in a 5 turn coil of 0.375 mm diameter tungsten wire with a 4-5 mm loop diameter with the end loops constricted to hold the scandium in place. The wire coil and scandium were mounted on a 2 conductor electrical feedthrough and mounted on a port on the sample transfer chamber of the LEEM V. Before each scandium deposition, the W(100) crystal was cleaned ( 2 minutes  $5 \times 10^{-7}$  Torr oxygen) and flashed to the maximum that could be achieved in the LEEM V (nominally 1600-1700 C). The surface was imaged in LEEM and LEED to check cleanliness, then the W(100) crystal was moved to the transfer chamber. The scandium was preheated at 5-7 Amperes for a few minutes, and then the current was raised to 10.4 amperes. The crystal was then placed in front of the filament (20 mm distance) and the dose was determined by timing the exposure. Times of 1, 3 and 6 minutes were used, roughly corresponding to 5, 15 and 30 nm. Initially, scandium deposition was confirmed by measuring the work function change in photoelectron emission

microscopy. The thickness of deposited scandium using a similar filament in a different chamber equipped with a quartz crystal microbalance was also used to calibrate the thickness of the scandium layer. Auger electron spectroscopy performed on the scandium layers showed only scandium. The scandium covered W(100) crystal was then transferred to the LEEM chamber. The surface was observed in LEEM and in thermionic emission microscopy (ThEEM) while being heated from the back side of the crystal. Surface coverage fractions were estimated from the dewetting images using ImageJ. Dewetting was observed in dozens of experiments. Measurements made specifically for Figure 3 include 3- 1 minute, 4- 3 minute and 3- 6 minute deposits. For a review of the different imaging methods used in emission microscopy, see [10].

The clean W(100) surface in LEEM is characterized by step bunches that are a result of the small deviation from (100) due to the crystal preparation. Some features are caused by the retreat of steps pinned by defects during sublimation or evaporation. This is a result of the oxygen cleaning process. The clean crystal (Figure 1a) and the crystal surface covered with scandium metal (Figure 1b) imaged in LEEM are shown in Figure 1.

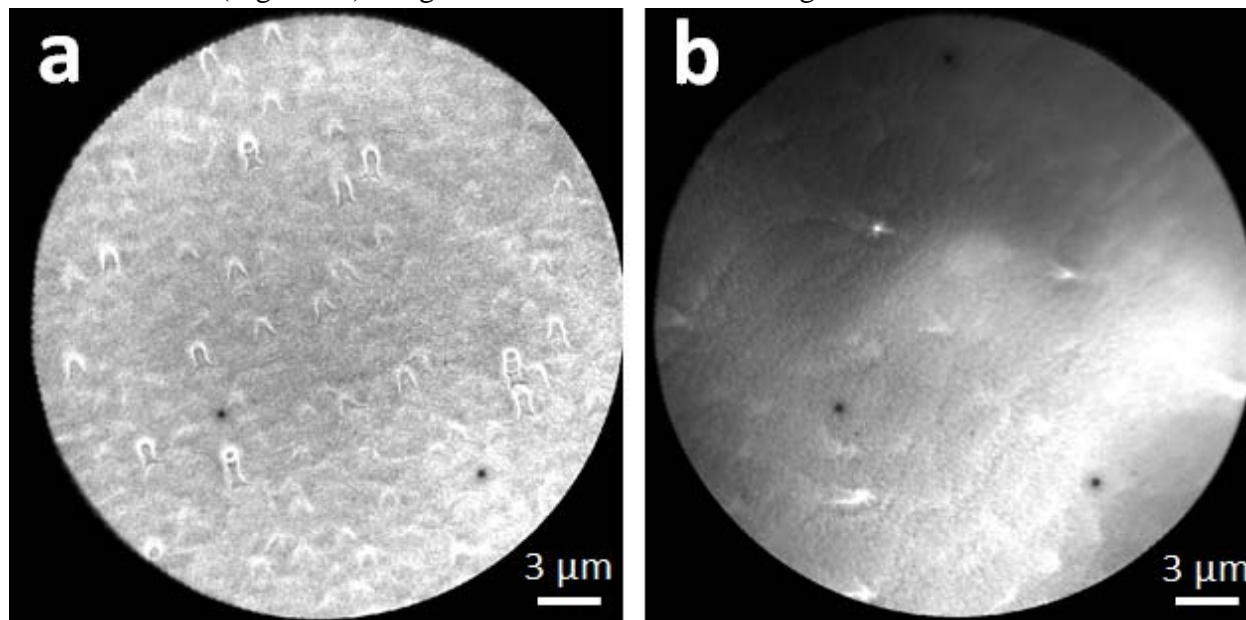


Figure 1: a) LEEM image of clean W(100), Starting Voltage = 0.1V, b) LEEM image of W(100) with 3 minutes (15 nm) scandium as deposited (not at the same location), Starting Voltage = 1.48V.

Dewetting was observed as the crystal was heated; the dewetting on thick layers is visible in ThEEM images (c. 800 C). Figure 2 shows the image in ThEEM of three layers, 1, 3 and 6 minutes of scandium exposure. The droplet size is correlated with the initial scandium layer thickness. Thompson [11] gives the relationship between dewetting temperature,  $T_d$ , and the thickness of the film,  $h$ , as  $T_d \propto 1/\ln(ch^{-3})$ , where  $c$  is a constant. Thinner layers de-wet at lower temperatures, and are observable in mirror microscopy mode below the thermionic

emission threshold, and subsequently in ThEEM as the temperature increases. The correlation between layer thickness, droplet size, and dewetting temperature is shown in Figure 3.

Scandium melts at 1541 C. There is an hcp to bcc transition at 1337 C. There is an eutectic between Sc and W at 1.38 % tungsten in 98.63 % scandium that reduces the melting point by 26 C (1541 to 1515 C) [12]. Therefore, for all tungsten–scandium compositions, the melting point is at or above 1515 C. At all three coverages of scandium investigated in our experiments, the dewetting temperature is below 800C, which is about 0.5  $T_{\text{melt}}$ . The scandium is solid at all of the dewetting temperatures reported here; it is not liquid and does not melt.

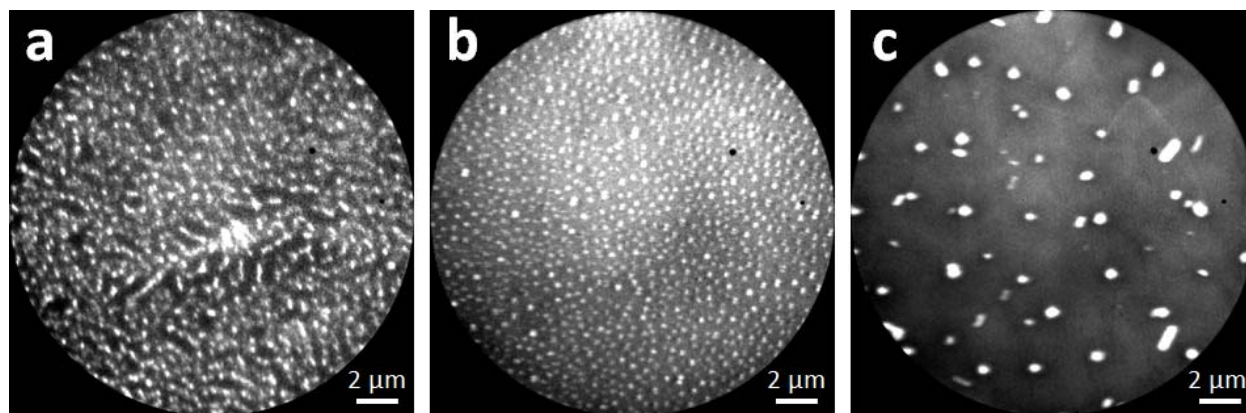


Figure 2: a) 1 minute Sc deposit,  $T=590$  C, b) 3 minute Sc deposit,  $T=760$  C, c) 6 min Sc deposit,  $T=720$  C. All images are of de-wetted scandium, imaged in ThEEM mode.

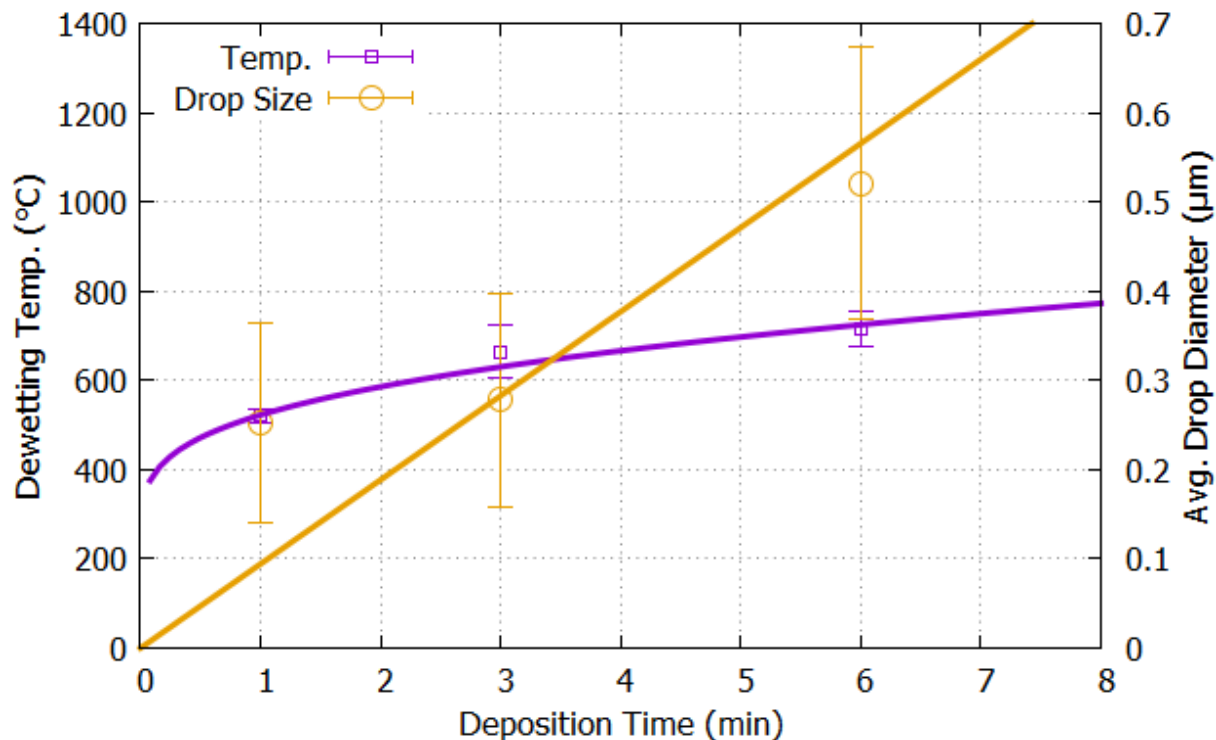


Figure 3. De-wetting temperature and average droplet diameter for Sc on W(100). The curve for the dewetting temperature follows the equation given in [11],  $T_d \propto 1/\ln[ch^{-3}]$ , where  $h$  is the film thickness and  $c$  is a constant. The fit to the data requires two constants, a constant of proportionality,  $a$ , and  $c$ . For the fit to our data,  $a= 10066.9$ , and  $c= 2.91446 \times 10^{10}$ .

A significant aspect of the ThEEM images in Figure 2 is the relative brightness of the background W(100) in each image. The image brightness cannot be compared between images a)-c), but each individual image represents a map of the electron emission from the surface. The scandium droplets are the brightest, hence highest emission, features in each image. In figure 2c) the scandium droplets sweep up all of the scandium. *There is no low-work function, high emission layer on the W(100) surface after dewetting.* The scandium is not liquid, and the surface tension that drives the dewetting is opposed to wetting the surface with a smooth, homogeneous layer. In Figure 2a), however, there is some background emission intensity that roughly follows the step bunches on the W surface. For small droplets, the step edges may provide a second surface for bonding, and the droplets that are on the scale of the step bunches, 50-75 nm, may form a droplet that is not round, elongated in the direction along the step bunches. At some small thickness, it may no longer be energetically beneficial to de-wet. The 1 minute scandium depositions in Figure 3 show a deviation of droplet size relative to thickness that may be a result of higher coordination of the smallest droplets on the step bunches. We have observed “tails” on some droplets that suggest a lower contact angle parallel to the step bunches [13]. In addition, the time resolved images of the dewetting in Figure 2c) show a phase where the droplets elongate parallel to the (100) directions on the surface.

Figures 4a)-d) show a part of the dewetting sequence for a 6 minute deposit (multimedia view). The dewetting along the  $\langle 100 \rangle$  directions and the elongation and eventual pinch-off of the droplets is clear in Figure 4 b) and c). Similar phenomena have been described for Si(001) on SiO<sub>2</sub> [14]. The edges of the square features in Figure 4b are bright. In [11] it is noted that the edges of the dewetting film thicken. The droplets (Figure 4d) are also bright relative to the background tungsten. Geometric enhancement factors for field emission calculate the enhancement factor for a hemisphere to be 3 [15]. The emission current density difference due to the work function difference between scandium and W(100) is also about 3, so that an increased emission of about a factor of 9 would be expected for the scandium droplets relative to the W(100) surface. If the work function minimum of the scandium dipole layer were estimated to be about 2.5 eV[7], the scandium droplets ( with geometric enhancement of 3) should be about 1.1 times brighter than the scandium monolayer. This estimate would require that the droplets and the scandium dipole layer would be about the same intensity (droplets slightly brighter) in Figure 4d. The image in Figure 4d) is consistent with complete dewetting of the scandium film. A rough estimate of the brightness variation in Figure 4c from ImageJ is at least a factor of 10 greater brightness for the droplets (even though the brightness of the droplets in the image appears to be saturated).

The image in Figure 2a is also consistent with these emission current estimates. If the smallest droplets are on top of a local scandium monolayer film, they would appear as bright droplets on a slightly less bright background, as in Figure 2a.

Because a vertical W-O-Sc-Ba stack is unlikely, a side by side geometry for scandium and barium is the more probable geometry on the tungsten surface. The scandium droplets would have barium atoms around their perimeter. The smallest droplets that were observed in Figure 2a) cover 40% of the tungsten surface, the ones in Figure 2b) and c) cover 29% and 12% respectively. Figure 5 shows a histogram of droplet sizes for the three scandium film thicknesses (deposition times). The two thinner films, 5 and 15nm, are similar, consistent with the data in Figure 3. The droplet size deviates in the thinnest film, probably due to the influence of the step bunches. Oxide droplets of 10 nm diameter were reported in [1]. On a flat surface, we would expect small droplets on that order for scandium. The smaller droplets allow for more interaction between barium and scandium. Thin layers produce more uniformly covered surfaces after dewetting, suggesting that small scandium concentrations mixed in the precursor materials or into the cathode oxide mixture results in better scandate cathode performance.

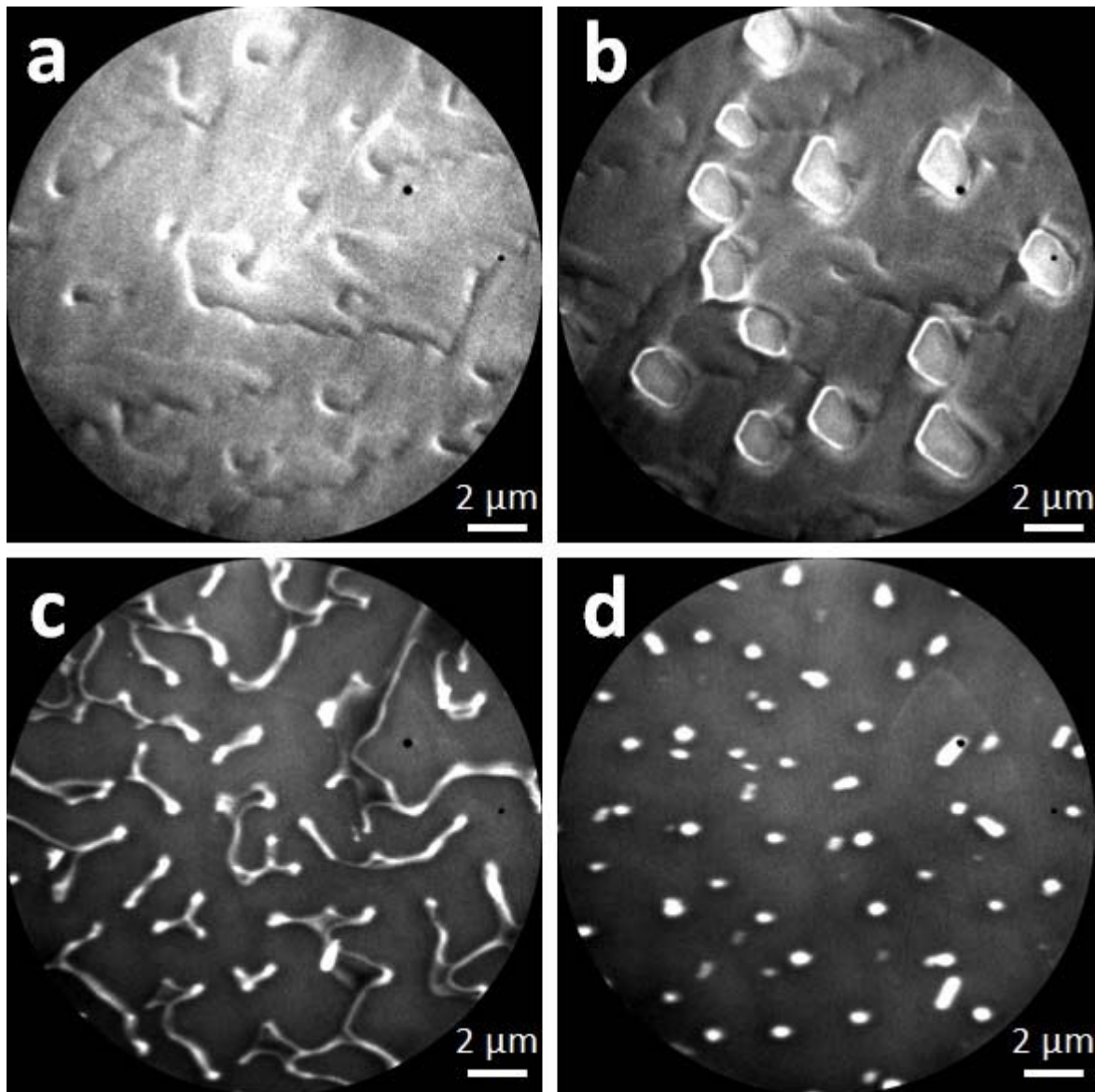


Figure 4. ThEEM (thermionic emission) images of the dewetting of a 6 minute deposit of scandium on W(100). The scandium layer thickness is about 30 nm. The image in a) shows the as-deposited layer. The image in b) shows dewetting in a square pattern, consistent with the  $\langle 100 \rangle$  direction of steps on the W(100) surface. Image c) show the thinning and pinch off of the remaining scandium layer. Image d) shows the final droplets. All images are at  $T=770$  C. (Multimedia view, video, format: .mov).



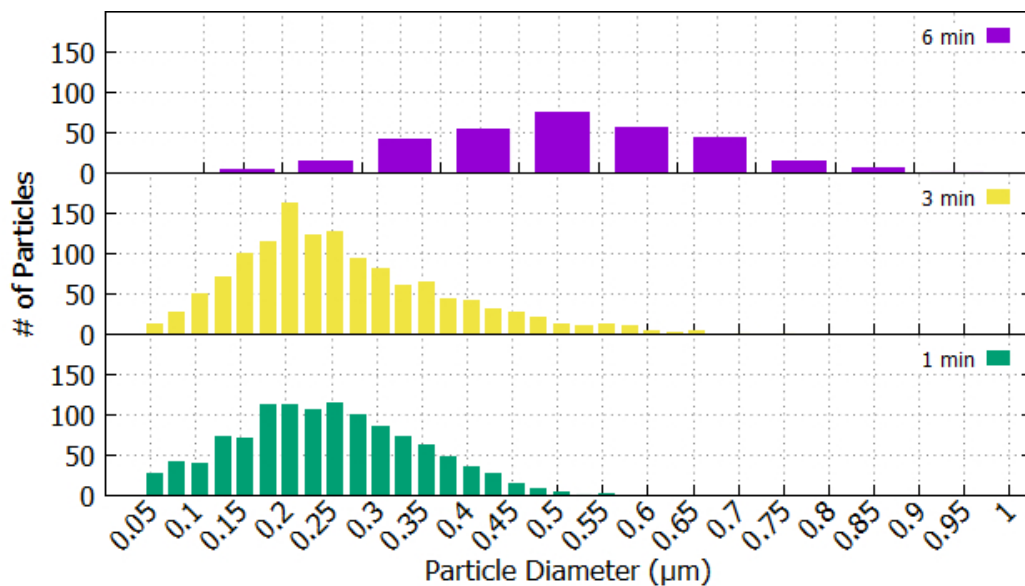


Figure 5. Particle diameter distributions from the images in Figure 2. The bin size for the 6 minute deposition is larger than for the 1 and 3 minute depositions.

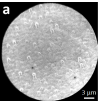
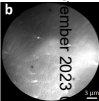
### Acknowledgements

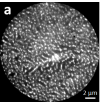
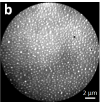
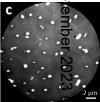
This work was supported by DARPA INVEST grant number N66001-16-1-4040. This research used resources of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

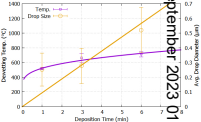


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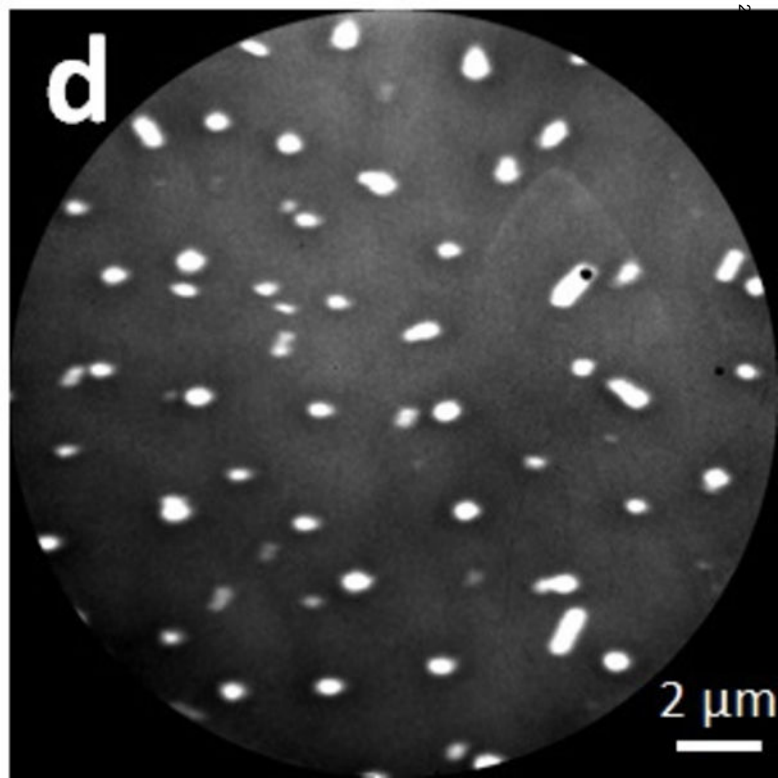
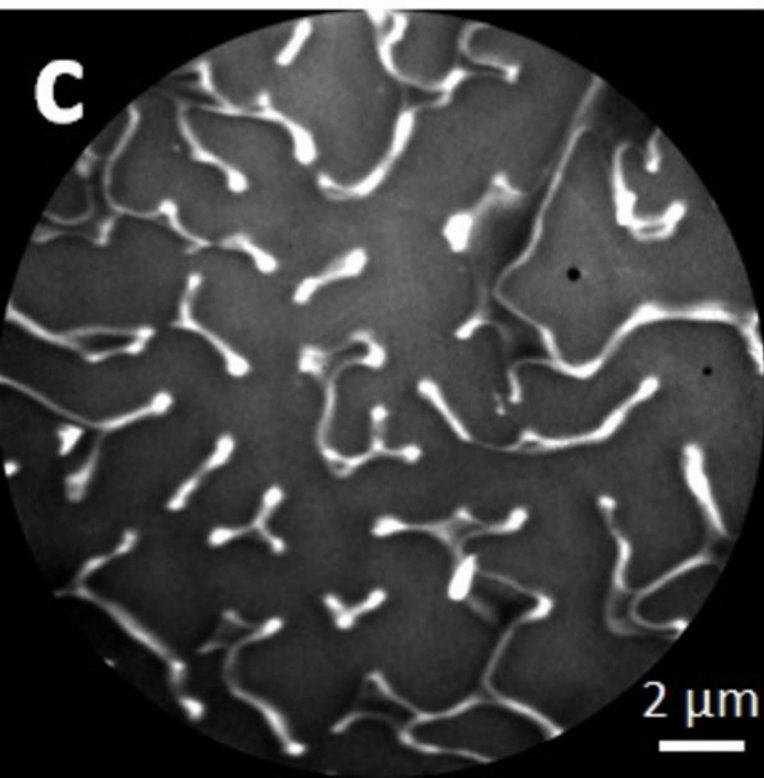
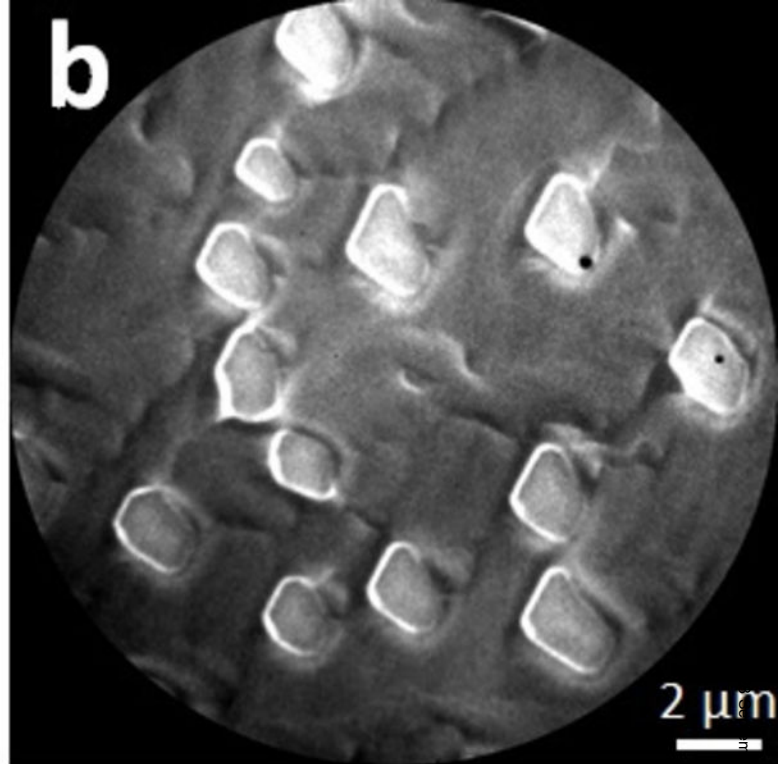
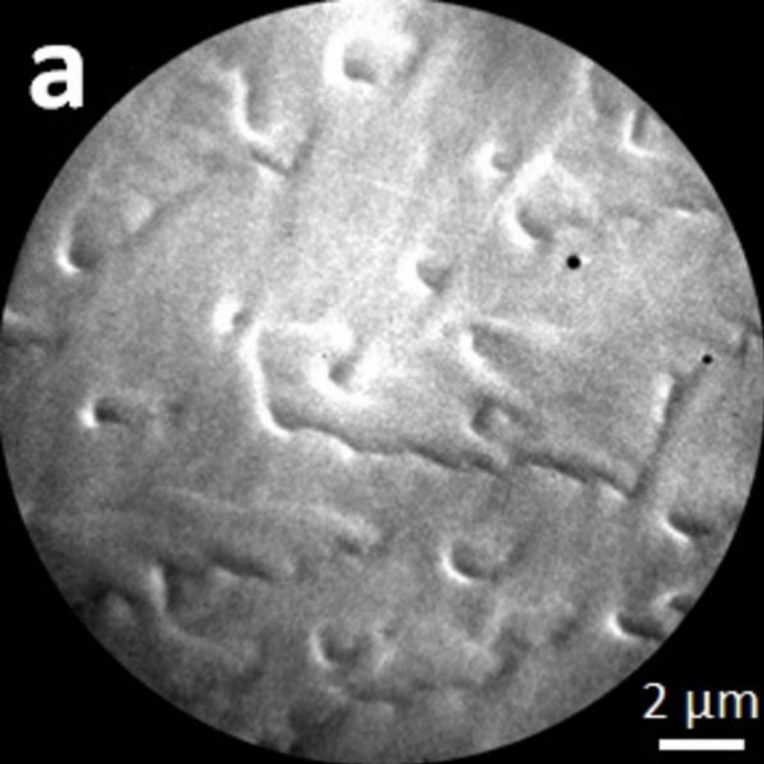
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