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Electron Microscopy Investigation of the Microstructure of Nafion Films

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Transmission electron microscopy (TEM) and transmission electron diffraction were used to study the microstructure of recast Nafion films. Zero-loss bright-field (BF) images were obtained, as well as Dage SIT low-light images (minimum specimen damage) and specific sulfur imaging. The results show a nonrandom distribution of the $-SO_3^-$ groups in the polymer film, primarily as ~5 nm clusters. Electron diffraction of deposited Nafion films shows the existence of single crystals, randomly distributed in the film, with an average distance of several microns. The diffraction pattern indicates an orthorhombic crystal structure which is similar to that of polyethylene (PE). The calculated *d*-spacings of the corresponding lattice planes for the two polymers are also quite close, suggesting similarity in their crystal structures. This result indicates that the fluorocarbon backbone of Nafion is in the form of a linear zigzag chain as in PE and not a twisted chain as in polytetrafluoroethylene (PTFE), despite the similarity in the chemical composition of Nafion and PTFE.

Introduction

Nafion (a registered trademark of E. I. du Pont de Nemours and Co.) ion-exchange polymer is one of the most widely investigated and used ionomers. Among other applications, recast Nafion films have been commonly used for the modification of electrode surfaces (see ref 1 and references therein).

The microstructure of Nafion has been widely investigated by a variety of techniques, a complete list of which is beyond the scope of this Introduction. A commonly accepted model for the microenvironment in Nafion is the three-phase model, first suggested by Rodmacq and co-workers[2] and later improved by Yeager and Steck.[3] It consists of three regions: (a) a fluorocarbon hydrophobic backbone; (b) an interfacial region; (c) ionic clusters. Region a contains the fluorocarbon backbone material, some of which may be in a microcrystalline form. Region c is formed by the ionic clusters and contains the sulfonate ion-exchange sites, counterions, and the majority of sorbed water. Region b is of intermediate character, containing pendant side chains, some unclustered sulfonate groups, and a certain amount of absorbed water and counterions.

Transmission electron microscopy (TEM) has been used by several investigators to obtain a direct view of the microstructure of Nafion, particularly of the shape and size of the ionic clusters. All these studies were performed with Nafion membranes, which were ultramicrotomed (to ca. 60 nm) and stained with various metal cations. Ceynowa[4] examined sections of Nafion EW1200 membranes, stained with lead ions. The resultant micrograph was composed of uniformly distributed dark points, 3−6 nm in diameter. These were interpreted as traces of ionogenic groups, homogeneously distributed in the membrane. To support this interpretation, the author re-examined the same microsections after exchanging the Pb^{2+} ions with H^+ and could not observe any of the previous features. Gierke and co-workers[5] examined sections of Nafion EW1200 which were stained by various techniques. They always observed a spongelike microstructure with approximately circularly stained

regions of 3−10 nm in diameter. Hashimoto and co-workers[6] obtained a similar micrograph from Nafion EW1100, stained with Cs^+ ions. It exhibited dark particles of ca. 4 nm in diameter, assumed to be domains rich in cesium ions. This assumption was supported by the observation that these particles were progressively growing in size, which was attributed to crystallization of cesium, caused by interaction of the electron beam with the ions.

Crystallinity in Nafion was tested by wide-angle X-ray diffraction, but the reports are rather inconsistent. Yeo and Eisenberg[7] reported that no evidence for crystallinity was found. Gierke and co-workers[5a] estimated that the amount of crystallinity in Nafion ranged between 0 and 40%, and although it somewhat decreased upon hydrolysis, the hydrolyzed polymer was still partially crystalline. Moore and Martin[8] distinguished between as-received Nafion and solution-cast films, which also exhibited different physical and chemical properties. As-received Nafion showed a crystalline reflection superimposed as a shoulder on an amorphous halo, indicating the existence of both crystalline and amorphous regions. However, recast Nafion was found to contain much less (if any) crystallinity, which could be reintroduced to the film by a thermal treatment.

In the present paper the microstructure of recast Nafion films is studied using TEM and electron diffraction. It is shown that these techniques, when carefully executed, can provide valuable information on the microstructure of the polymer and particularly on its crystallinity.

Experimental Section

Nafion-H^+ deposition solutions were prepared as previously described.[1] Samples for electron microscopy were prepared by two methods from solution of Nafion EW1100 in ethanol/water: (a) direct deposition of a small volume of the solution on a carbon-coated TEM grid, followed by evaporation of the solvent ("deposited films"); (b) formation of a Nafion film on mica, which was lifted onto a 700-mesh uncoated TEM grid by floating on water ("floated films").

Method a produced very thin films upon applying a volume of 3 μL of 0.01% Nafion solution onto a carbon-coated grid, followed by removal of most of the liquid after 30 s using filter paper. A thin layer was left, which dried quickly to produce a

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Nafion film with an estimated thickness of 30−40 nm. With larger volumes it was difficult to obtain films of uniform thickness, as the solution tends to accumulate in a small drop on the hydrophobic surface of the grid.

Method b included transfer of 3 μL of 0.7% Nafion solution onto a freshly cleaved mica surface, spread over an area of ca. 2 cm^2. Room-temperature evaporation of the solvent left a film of an average thickness of 60 nm. This film was floated in a water bath and lifted onto an uncoated grid.

Bright-field (BF) images of floated films were obtained with a Zeiss EM 902 analytical electron microscope, at 140000× magnification using 80 keV. The microscope was fitted with an energy filter so that inelastically scattered electrons could be removed from the final image. This markedly enhances the contrast between atoms of different atomic number.[9] The use of Dage SIT camera allowed images to be obtained at a very low beam intensity. At 50000× magnification it was possible to examine the film for a period of 2 min without detectable mass loss from the polymer film.

Specific imaging for sulfur was carried out using a three-window method in the total energy loss spectrum. The net sulfur distribution was obtained by image subtraction using the Freelance Image Manager (Sight Systems, U.K.) following collection of averaged (20) images around the sulfur $L_{2,3}$ edge at 164.8 eV, using windows centered at $\Delta E = 140$, 155, and 175 eV, over a 50−60 s period. A 60 μm objective aperture and a 15 eV electron energy window at a magnification of 50000× resulted in a spatial resolution of about 2 nm. Using a relatively small objective aperture reduced the mass loss and collection efficiency for electron energy loss spectroscopy imaging, and therefore the detection limits of the analysis, but increased the final spatial resolution of the elemental map. Images for sulfur mapping were collected before the corresponding zero-loss images.

Electron diffraction patterns were obtained with a Jeol 1200EX electron microscope, operated at 120 keV, and recorded on Kodak X-ray films.

In all aspects of microscopy precautions were taken to minimize the exposure of the polymer film to the electron beam. Degradation of the specimen could be observed as loss of crystallinity in the diffraction pattern or mass loss in the analytical microscope.

Results

A BF zero-loss image of a floated film, prepared from a solution of Nafion in ethanol/water (90:10), is shown in Figure 1. It exhibits a dense texture of dark areas, ca. 5 nm in diameter, which are homogeneously distributed in the film.

The 90:10 Nafion sample was also examined with the Dage SIT low-light camera, which allows images to be obtained using a much lower beam intensity, thus inducing specimen damage at a significantly lower rate. Multiple images were collected at a magnification of 50000× over a period of 2 min using an unfocused beam, without any apparent mass loss in the film. A typical image is shown in Figure 2A, where the observed texture is essentially similar to that in Figure 1, but the contrast and resolution are substantially improved. The image appears to show quite clearly the cluster-network microstructure of Nafion.

Imaging specifically for sulfur with the three-window method, using its energy loss peaks, produces a net elemental map, as shown in Figure 2B. The sulfur appears to be localized in areas of several nanometers in size, which presumably comprise the $-SO_3^-$ groups in the ionic clusters. The distribution of sizes
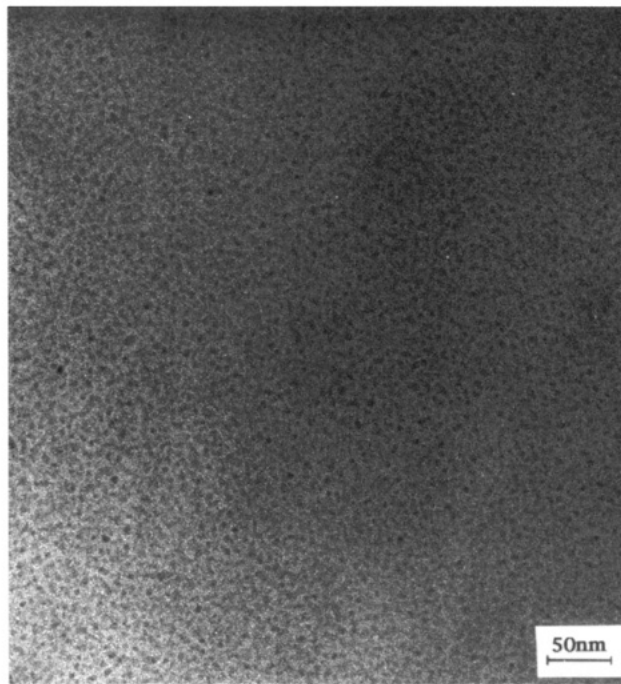

Figure 1. Zero-loss, contrast-enhanced BF micrograph of a floated Nafion-H$^+$ film, prepared from a solution of Nafion 1100 in ethanol/water (90:10).

and contrasts in Figure 2B may indicate an inhomogeneity in the distribution of sulfonate groups in the clusters.

The crystallinity of Nafion (in the H$^+$-form) was examined by transmission electron diffraction. The crystals were found to be very sensitive to radiation damage, with the diffraction pattern disappearing within 1−2 s, even under conditions of low-intensity illumination. Therefore, the diffractograms were recorded at very short times on X-ray film (more sensitive than the regular EM film).

A typical electron diffraction pattern of deposited Nafion is shown in Figure 3A. It is organized in a near-hexagonal symmetry with one axis longer than the other two, indicating an orthorhombic crystal lattice. A similar diffraction pattern indicating orthorhombic structure was obtained by Revol and Manley[10] from polyethylene (PE) crystals. On the other hand, polytetrafluoroethylene (PTFE), which resembles the fluorocarbon backbone of Nafion, has a hexagonal crystal lattice and was found by Chanzy et al.[11] to give rise to a perfectly symmetrical hexagonal diffractogram. The assignment of the reflections in the Nafion diffraction pattern is similar to that of PE. Careful examination of the diffractogram shows some weak reflections of higher order, which are presented and indexed in Figure 3B. The calculated d-spacings, corresponding to these planes, are given in Table 1 and compared with those of PE, calculated from the diffraction pattern in ref 10.

The very close values of the d-spacings, together with the symmetry in the crystal lattice of the two polymers, suggest that the crystal structure of Nafion is very similar to that of PE. The lattice parameters a and b are obtained using the formula for the orthorhombic crystal system,

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

giving $a = 7.54$ Å and $b = 5.02$ Å. The lattice parameter c cannot be determined, since all the reflections are perpendicular to the plane of observation, so that the third dimension is missing.
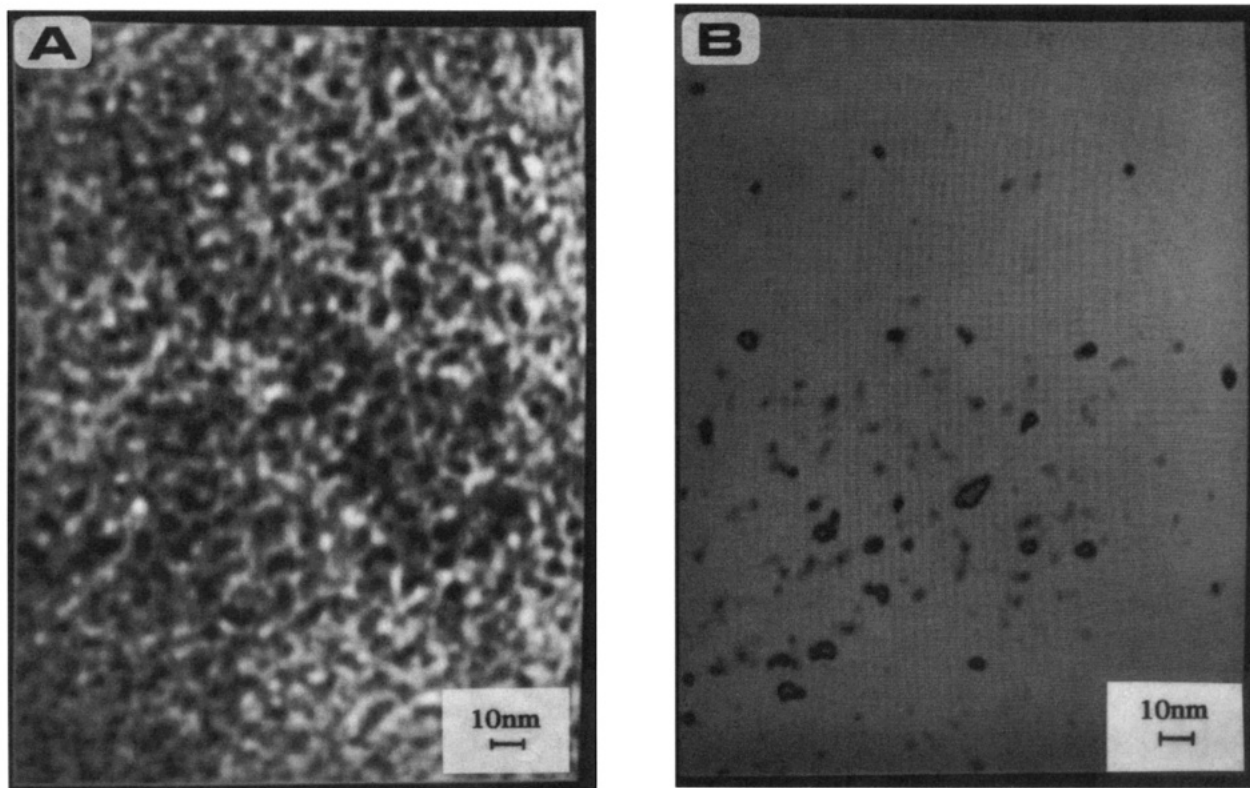
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Figure 2. (A) Zero-loss image of a Nafion-H$^+$ film, obtained via a Dage SIT 66 video camera by averaging 20 frames and recorded onto 35 mm B/W film from a video monitor screen. (B) Same field as in part A, showing specific electron energy loss spectroscopy imaging for sulfur.
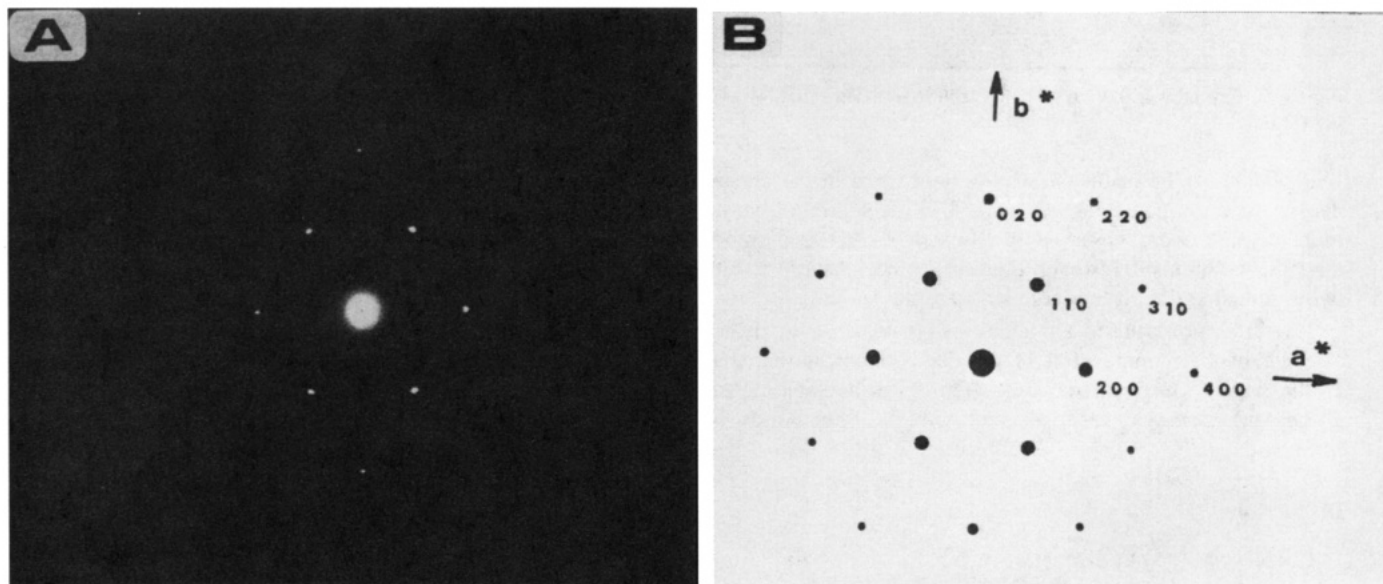

Figure 3. Electron diffraction pattern of Nafion crystals in a deposited Nafion-H$^+$ film: (A) original diffractogram, recorded on X-ray film; (B) schematic representation of the full diffraction pattern.

Mapping of the crystal distribution in the polymer was attempted by systematic scanning of sections of deposited films and recording the locations of the crystals by their coordinates on the grid. The microscope was operated in the diffraction mode, so that the presence of a crystal was evidenced by the appearance of the near-hexagonal diffraction pattern. Since the crystals are highly beam sensitive, care had to be taken not to destroy crystals lying near the path of scanning, which were to be examined later. The diffraction aperture is located below the specimen in the microscope column and cannot control the area of the specimen being exposed, and therefore the beam was diminished to the size of the diffraction aperture image (1.7 μm) so that only the observed area was actually exposed

to the beam. A typical mapping result is shown in Figure 4, where each spot represents the location at which a diffraction pattern was observed, indexed by the coordination units of the microscope. The crystalline domains appear to be randomly distributed in the polymer with an average distance of several microns from each other.

An attempt to find a correlation between the degree of crystallinity and the amount of water in the depositing solution[1] was made by comparing the mapping results of three kinds of films, deposited from Nafion solutions of ethanol/water compositions of 90:10, 50:50, and 10:90. The comparison was based upon the average density of crystals in each kind of film, i.e. the number of crystals per scanned area, averaged over four or

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TABLE 1: Lattice Planes and *d*-Spacings in Nafion Crystals and in Polyethylene (PE) Crystals

(*hkl*)	*d*-spacing (Å), Nafion[a]	*d*-spacing (Å), PE[b]
(110)	4.15	4.1
(200)	3.77	3.7
(020)	2.49	2.4
(310)	2.24	2.2

[a] Calculated from Figure 3. [b] Calculated from ref 10.
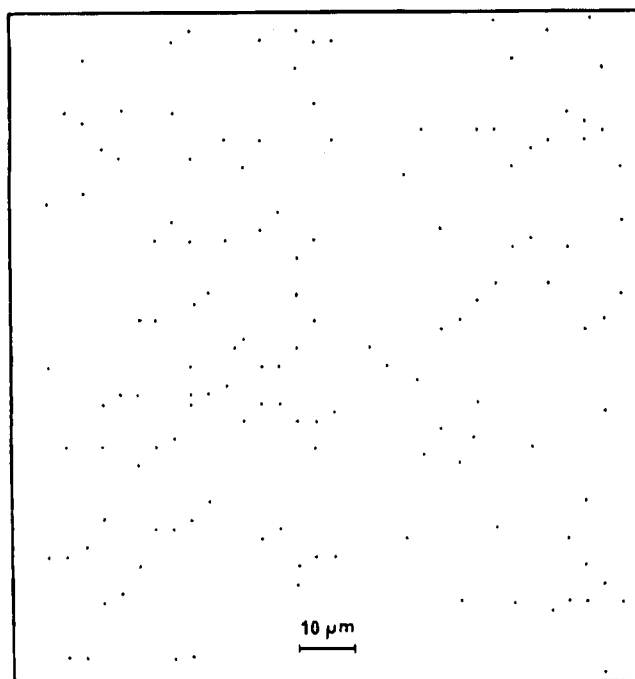
Figure 4. Crystal distribution map in a section of a deposited Nafion-H$^+$ film.

five samples. The results show a certain trend in the crystal density with the percentage of ethanol in the solution; that is, more crystals were observed in films deposited from more alcoholic solutions. However, the significance of these results is questionable due to the large standard deviations.

The diffraction pattern, and hence the crystal structure, is not affected by the composition of the deposition solution; that is, the same form of diffraction pattern with the same orientation and spacings was observed with all three kinds of films.

Discussion

The present study of the microstructure of recast Nafion films could not be carried out in an aqueous medium, and the analysis was necessarily done on specimens which may have suffered a certain distortion due to high-vacuum conditions and possible radiation damage in the microscope. Therefore, the utmost efforts were made to minimize these effects and to ascertain when damage had occurred. The possible distortion implies that the separation of contrast areas may not exactly represent that in the solvated film, although the distribution of specific ions should be reliable.

Three major conclusions can be derived from this study:

(a) The distribution of $-SO_3^-$ groups in the film is in the form of distinct areas of ca. 5 nm in size, consistent with the previously suggested models of hydrophobic and hydrophilic regions.

(b) The fact that recast Nafion films exhibit clear crystallinity and show characteristic single-crystal diffraction patterns indi-

cates that the film contains large domains (corresponding to the crystals) in which ordered functional groups are in the same orientation.

(c) The crystal structure is very similar to that of polyethylene.

The contrast enhancement with this microscope enabled deductions to be made about the atomic number distribution in the film, which are usually not possible with conventional microscopy. The contrast ascribed to the ionic clusters is within the resolution of the instrument, although the absolute size cannot be stated accurately. The separation of the clusters as measured in the microscope is not indicative of their separation in the film in an aqueous medium, because of swelling, but their distribution supports the cluster-network model proposed by Hsu and Gierke.[5b]

The existence of crystals is evidenced from the characteristic electron diffractions, which were found to be rather abundant in the examined sections. On the other hand, both Moore and Martin[8] and Gebel et al.,[12] who used X-ray diffraction techniques, reported poor crystallinity in recast Nafion with respect to as-received Nafion membranes, which could be reintroduced by thermal treatment. The probable reason for the success of the presnt study in observing substantial crystallinity in recast Nafion is the higher sensitivity and localized nature of electron diffraction compared with X-ray diffraction. The crystal size that can be detected by the electron diffraction is smaller, and diffraction patterns can be obtained from very thin specimens.

Although the number of reflections evident in the diffraction patterns was small, their symmetry and intensities suggest a similarity in crystal structure between Nafion and polyethylene. This would imply that the fluorocarbon backbone, which forms the crystalline part of Nafion, is in the form of a linear zigzag chain and not a twisted chain as in PTFE.[13] Linear chain polymers generally have a very similar structure. To have this linear structure would require that the side chains of Nafion prevent the twisting of the backbone and stabilize the configuration of the backbone in a plane zigzag, as found in hydrocarbons. The reproducibility of orientation in the films, i.e. with the *c*-axis perpendicular to the plane of the film, shows that this is a normal growth habit. Neither carbon nor mica induced strong interactions with hydrophobic or hydrophilic groups to cause epitaxial growth, and the orientation of growth observed here is the same as that which occurs in paraffins and polyethylene on these substrates.

It should be mentioned that Gebel et al.[12] also found similarity with polyethylene, but of the thermally treated Nafion. They described it as a "more well-defined crystallinity inside larger crystallites with a long range order characterized by a repeat distance of the order of 200 Å, a distance that compares well with polyethylene".

The effect of the solvent composition on the microstructure of the films was not clear in this study. Electrochemical measurements show that the diffusion coefficient of Ru(bpy)$_3^{2+}$ in Nafion films on electrodes increases substantially with the percentage of water in the depositing solution.[1] This effect was attributed to a more porous texture of the films or wider interconnecting channels between the ionic sites. However, no prominent differences could be observed with the TEM resolution. Moreover, the crystal structure, as seen by electron diffraction, was unaffected by the composition of the solution. The fact that the distribution of crystalline domains appears rather similar for the three deposition solutions used may suggest that the crystallite size, rather than distribution, is the main difference.

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A point worth noting is the marked reproducibility of the diffraction patterns throughout the extensive crystal mapping. This shows a highly preferred c-axis orientation normal to the plane of the film.

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