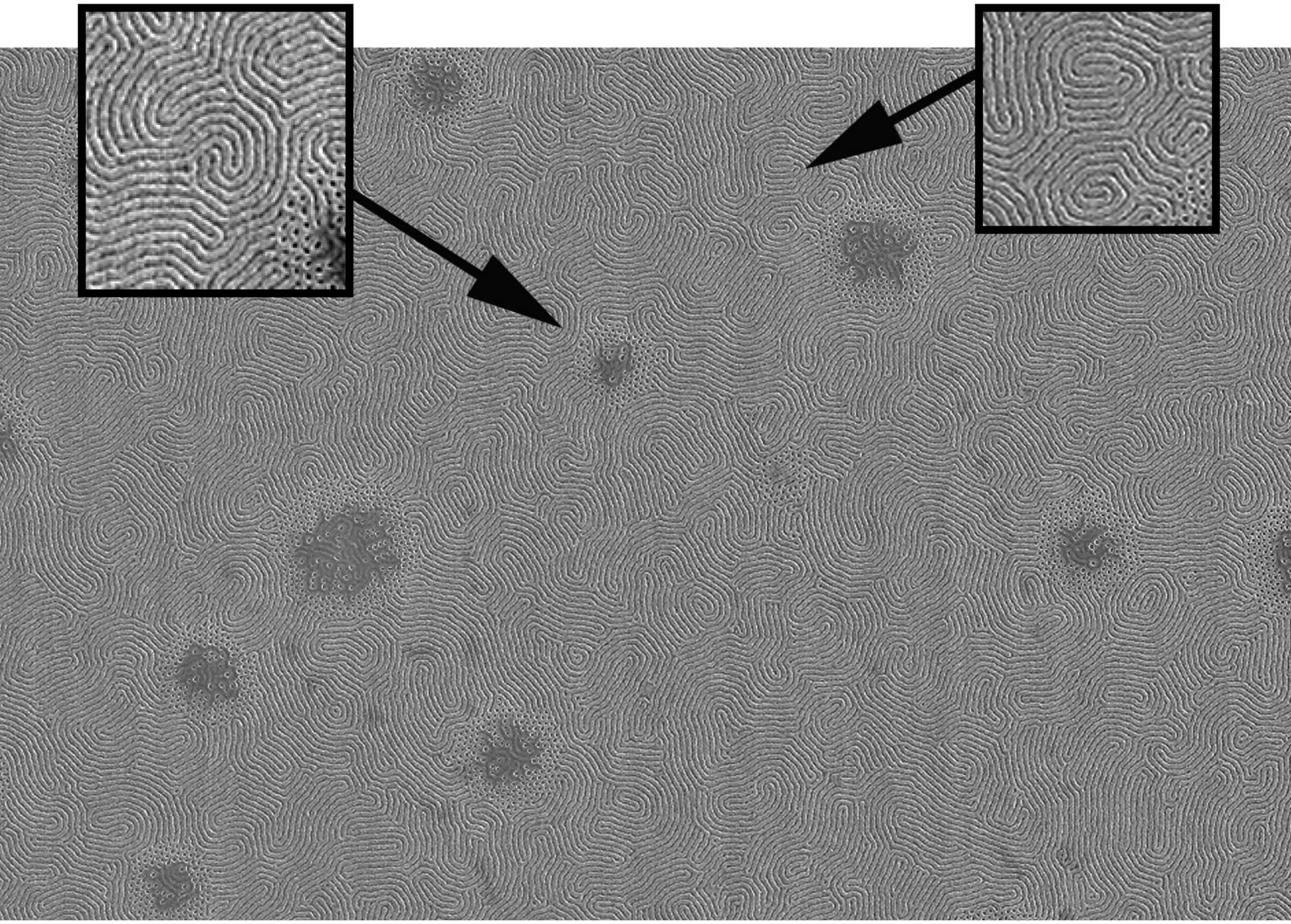
Application Note



Imaging Polymers with a Helium Beam

ZEISS ORION NanoFab

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ZEISS ORION NanoFab provides high resolution imaging of complex polymer structures with high resolution, high contrast, and no charging artifacts. The helium ion beam's unique advantages are attributed to the unique sample interaction of helium ions with low atomic number materials. Researchers using polymers can gain new insights into their polymer materials using the ORION NanoFab's focused helium ion beam.

Introduction

Disadvantages of the Conventional Imaging of Polymers

Due to nanometer scale features, the imaging of polymers in optical microscopy is not suitable. It is not suitable in TEM and scanning probe methods either as the polymers can be arranged in potentially complex, three-dimensional structures. Heavy ion beams, such asgallium, also present imaging problems because of the high sputter rate and the likelihood of implanting conducting metal atoms.

The electron beam from a conventional SEM provides only limited resolution because the electrons scatter under the surface and produce an abundance of type 2 secondary electrons with limited resolution [1]. Electron beams can induce damage such as radiolysis and subsurface dipole fields (from positive surface charge and buried negative charge) and can even cause dielectric break down [2].

Application Example: Diblock Copolymers

A diblock copolymer consists of a mixture of two distinct polymer components. If the temperature is gradually lowered below the characteristic melt temperature, the polymers arrange themselves into characteristic patterns to minimize their energy. Depending on the polymer types, mix ratio, and boundary conditions; the components can separate themselves into complex three-dimensional structures (e.g. spheres, cylinder, gyroids or lamella).

A lamella type of self organization of a diblock copolymer on a flat substrate was imaged with the helium ion beam (Figure 1(a)). The same type of structure was imaged with an electron beam (Figure 1(b)) and showed artifacts arising from sub-surface charge [3]. The helium beam shows great advantages in contrast, resolution, and reduced damage. Such directed self-assembly processes can be used to engineer large scale structures with nanometer scale features. In this application, ORION NanoFab's helium beam was operated between 20 keV to 40 keV, and 0.1 pA to 1.5 pA.

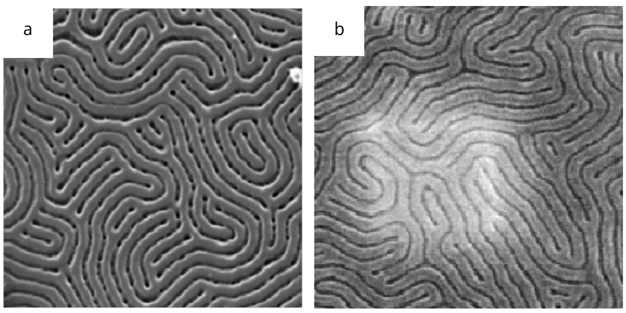

Figure 1 *Diblock copolymer as imaged with the helium ion microscope (a) and a traditional SEM (b) [3]. The field of view is 1 micron.*

Application Example: Electrospun PLLA Fibers as a Substrate for Bone Mineral Growth

ORION NanoFab's helium ion beam has also proven to be valuable for imaging complex, three-dimensional polymer networks. In this case, Poly L-Lactic Acid (PLLA) was electrospun to produce a fibrous network that was immersed in a simulated body fluid with mineral precursors. After varying time intervals, the sample was withdrawn and examined with the focused helium ion beam. The bone mineral, hydroxyapatite (HA) was found to begin forming in the first hour. High resolution images of the fiber network were captured (Figure 2).

The image shows a remarkable depth of field and high contrast which facilitates detailed examination. Specific sites on the fiber surface show the nucleation of HA minerals which can then be examined at higher magnification (Figure 3). In both of these helium ion beam images, there are no signs of charging artifacts despite both materials being electrical insulators.

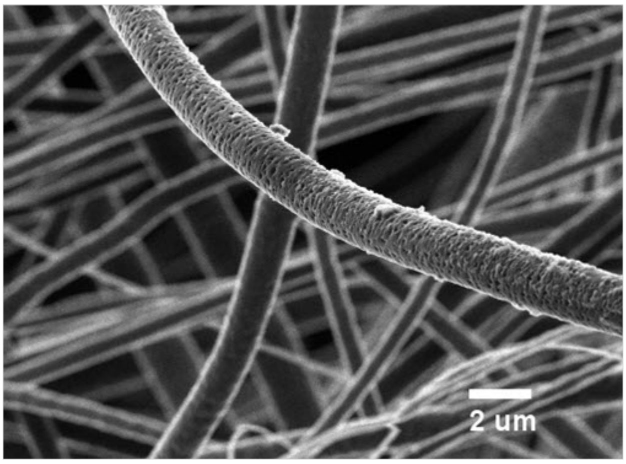

Figure 2 *PLLA fiber network imaged with the helium ion beam.*

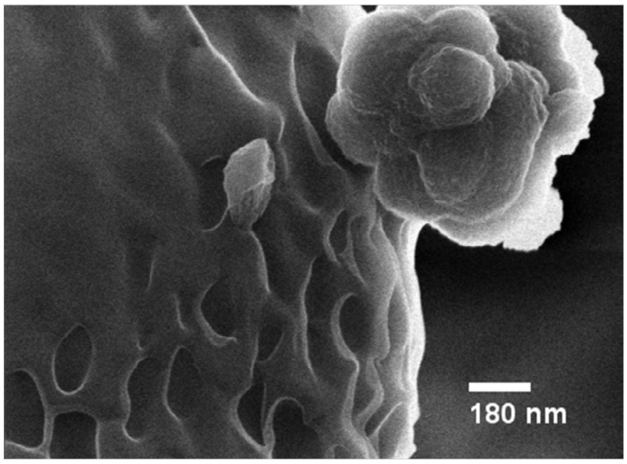

Figure 3 *HA nucleation on the surface of a PLLA fiber, as imaged with the helium ion beam.*

Summary

The Advantages of Helium Beams

The absence of charging artifacts when imaging insulators arises from the unique manner in which the helium ion beam interacts with the sample. As it enters the surface, the helium ion captures an electron and is neutralized for the remainder of its trajectory deeper into the sample. This leaves the surface of the sample with a net positive charge. Similarly, the production of secondary electrons at the surface also leaves the sample with a net positive surface charge. This residual charge is easily neutralized with operation of the incorporated electron flood gun.

Typically, the electron flood gun is configured to provide neutralization after each completed line scan or frame scan of the helium beam. Under these conditions, the helium ion beam provides high resolution images with strong contrast, even when imaging insulating samples such as polymers.

In contrast, SEMs are not well suited for imaging polymers at high magnification, and tend to cause thermal damage, charge induced damage, and radiolysis [2].

References:

[1] Ludwig Reimer, Scanning Electron Microscopy, 2nd edition, p.162 (Springer Verlag, New York) (1998).

[2] Radiation Damage in the TEM and SEM by R.F. Egerton, P. Li, M. Malac in Micron (35) (2004).

[3] The Morphology of Ordered Block Copolymer Patterns as Probed by High Resolution Imaging, Borah et al., in Nanomaterials and Nano technology 4(25) (2014).

[4] Case Study: Growth of Bone minerals on PLLA. Unpublished ZEISS collaboration with Ian Smith of U. of Michigan (2010).

Front cover image:

Diblock copolymers organize themselves into rich, complex patterns that are influenced by relative abundance of the two comprising monomers, and the underlying substrate.

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