Sequence-Defined Peptoids as Next-Generation EUV Photoresists

CNF Project Number: 2733-18
Principal Investigator(s): Christopher K. Ober
User(s): Chenyun Yuan, Rika Marui, Erina Yoshida

Affiliation(s): Materials Science and Engineering, Cornell University

Primary Source(s) of Research Funding: U.S. Department of Energy, Office of Science, Basic Energy Sciences

Contact: cko3@cornell.edu, cy479@cornell.edu

Research Group Website: https://ober.mse.cornell.edu

Primary CNF Tools Used: JEOL JBX-6300FS E-beam Lithography System, JEOL JBX-9500FS E-beam Lithography System, ASML DUV Stepper

Abstract:

Photoresists face substantial challenges as photolithography advances into the extreme ultraviolet (EUV) era. Traditional polymeric photoresists struggle with chemical randomness due to variations in polymer chains' molecular weight, composition, and sequence, as well as the unpredictable distribution and potential aggregation of photoacid generators (PAGs) within the polymer matrix. Additionally, the use of PAGs has sparked growing environmental concerns worldwide, especially since most commercially used PAGs are per- and polyfluorinated substances (PFAS). We have engineered sequence-defined polypeptoids to function as photoresists, addressing many existing limitations.

We developed a resist system that is a single-component monomolecular system composed solely of polypeptoids. The polypeptoids were synthesized by the solid-phase submonomer synthesis method [1]. The sequence typically includes phenol derivatives that induce solubility changes upon exposure to ionizing radiations including electronic beam (e-beam) or extreme UV (EUV), along with inactive building blocks, all precisely controlled at the molecular level. This design ensures uniform length, composition, and sequence, greatly minimizing compositional stochastics. The developed photoresist platform, incorporating phenol derivatives, is inherently patternable under EUV or e-beam lithography, removing the need for PAGs or other additives in the resist formulation. This innovation addresses problems related to uneven PAG distribution and tackles environmental, health, and regulatory concerns associated with PAGs in photoresist formulations. EUV patterning experiments demonstrated that the photoresist could achieve patterning at a 14 nm half-pitch or smaller resolution using an aqueous tetramethylammonium hydroxide solution as the developer.

Summary of Research:

We have developed a novel sequence-defined polypeptoid photoresist to address challenges in EUV lithography. Traditional polymeric photoresists struggle with compositional stochasticity originated from the random nature of conventional polymers in terms of molecular weight, composition and sequence, and there are also environmental concerns due to the use of PAGs with are mostly fluorinated compounds [2]. The new polypeptoid photoresist system, synthesized via solid-phase submonomer synthesis, features precisely positioned functional groups and exhibits uniform chain length, composition, and sequence. This can be proven by liquid chromatography–mass spectrometry (LC-MS) measurements (Figure 1). The wide variety of building blocks we can choose also allows us to explore new patterning mechanisms that have not been applied in advanced EUV photoresist design. This system mitigates stochastic effects and allows for intrinsic patternability under EUV radiation, eliminating the need for PAGs and thereby addressing related environmental concerns.

Our research involves extensive screening of peptoid sequences with various building blocks, such as tBOC-protected phenols, t-butyl esters, and unprotected phenols. Initial testing revealed that certain peptoid sequences demonstrated a negative tone pattern when developed in highly dilute aqueous base solutions, despite being designed to mimic the composition of conventional chemically amplified photoresists. This negative tone was first observed in peptoid sequences during development in a diluted tetramethylammonium hydroxide (TMAH) solution, and further confirmed using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

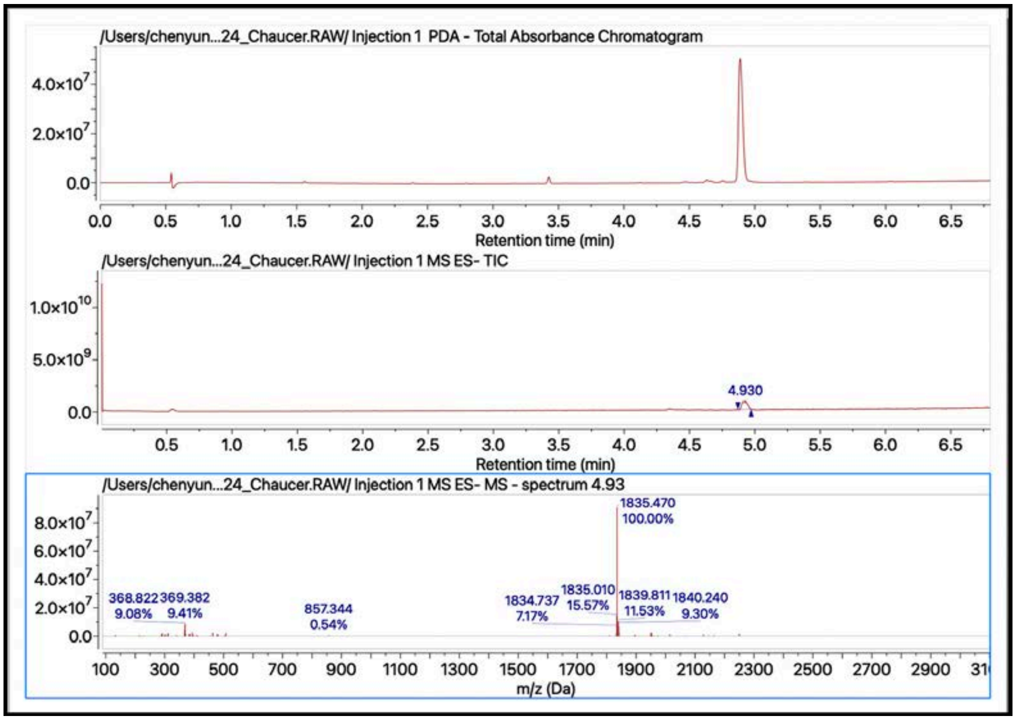


Figure 1: LC-MS data of one example polypeptoid sequence with theoretical molar mass 1836.96 g/mol.

Experiments indicated that these peptoids could be patterned in a negative tone under e-beam and EUV lithography, both with and without the presence of PAGs. However, the resolution improved significantly without PAGs, achieving a resolution of 24-nm half-pitch (hp) under e-beam lithography (Figure 2). Further testing at Lawrence Berkeley National Laboratory (LBNL) demonstrated that the peptoid sequences achieved a 14-nm hp resolution under EUV exposure without PAGs (Figure 3).

Our current efforts focus on understanding the underlying mechanisms and high-throughput synthesis of diverse peptoid sequences. The research confirmed that the negative tone mechanism is due to phenol groups in the structure, with chemistry occurring during exposure and potentially obviating the need for post-exposure baking (PEB). This phenol-based patterning mechanism has not been used in photoresist design previously, marking a significant advancement in photoresist technology.

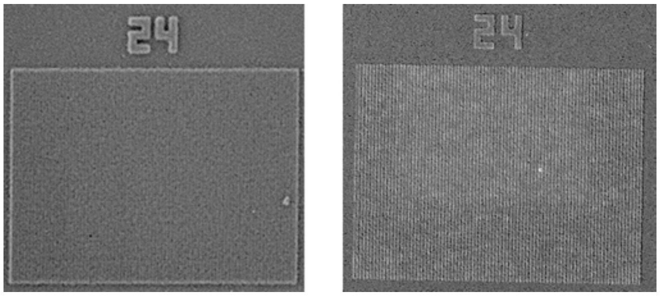


Figure 2: 24-nm half-pitch e-beam patterns of the polypeptoid resist. Left: with 10 wt% PAG. Right: without PAG. The no PAG sample required ~ 3 times dosage than the PAG containing sample.

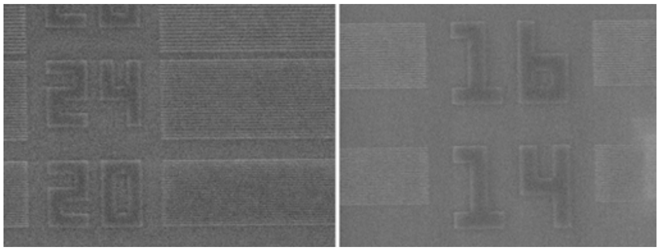


Figure 3: EUV patterns generated from the polypeptoid resist. Left: with 10 wt% PAG, 27 mJ/cm². Right: without PAG, 45 mJ/cm².

References:

[1] R. N. Zuckermann, J. M. Kerr, S. B. H. Kent, and W. H. Moos, "Efficient method for the preparation of peptoids [oligo(N-substituted glycines)] by submonomer solid-phase synthesis," J. Am. Chem. Soc., vol. 114, no. 26, pp. 10646-10647, 1992, doi: 10.1021/ja00052a076.

[2] C. K. Ober, F. Käfer, and C. Yuan, "Recent developments in photoresists for extreme-ultraviolet lithography," Polymer, vol. 280, 2023, doi: 10.1016/j.polymer.2023.126020.

Direct Functionalization of Polyethylene Surfaces with High Density Polymer Brushes

CNF Project Number: 3040-22
Principal Investigator(s): Brett Fors
User(s): Anna Ringuette

Affiliation(s): Chemistry and Chemical Biology, Cornell

Primary Source(s) of Research Funding: This work was supported by the NSF under Award CHE-1752140

Contact: bpf46@cornell.edu, aer286@cornell.edu

Research Group Website: https://fors.chem.cornell.edu/

Primary CNF Tools Used: Ramé-Hart Goniometer

Abstract:

Introducing functionality into PE surfaces is a longstanding challenge in polymer science, driven by the need for polymer materials with improved adhesion and antifouling properties. Herein, we report surface-initiated hydrogen atom transfer-reversible addition-fragmentation chain transfer (SI HAT-RAFT) as a robust method to grow high-density brush polymers from PE surfaces. We demonstrate that under mild conditions, direct initiation from the C-H bonds of PE surfaces allows for the graft polymerization of a variety of (meth) acrylate monomers. The resulting polymer brushes reached several hundred nanometers in thickness with densities of ca. 0.62 chains/nm2, compared to the current standard of ~ 0.28 chains/nm2. Finally, we show that our method is capable of dramatically improving the adhesive properties of PE surfaces. This work enables the preparation of PE with diverse surface functionalities for potential use in biomedical, industrial, and battery applications.

Summary of Research:

Polyethylene (PE) is ubiquitous in our society, with over 100 million tons produced annually. The widespread use of PE is enabled by its superior bulk properties and low cost; PE is strong, tough, light weight, and chemically resistant. Despite these advantages, poor surface properties such as low adhesivity and wettability limit its use in applications such as battery membranes, packaging, and automotive materials, all of which require interfacing with other plastics, metals, and solvents. Furthermore, the surface of PE contains only unactivated C-C and C-H bonds, making it challenging to modify.

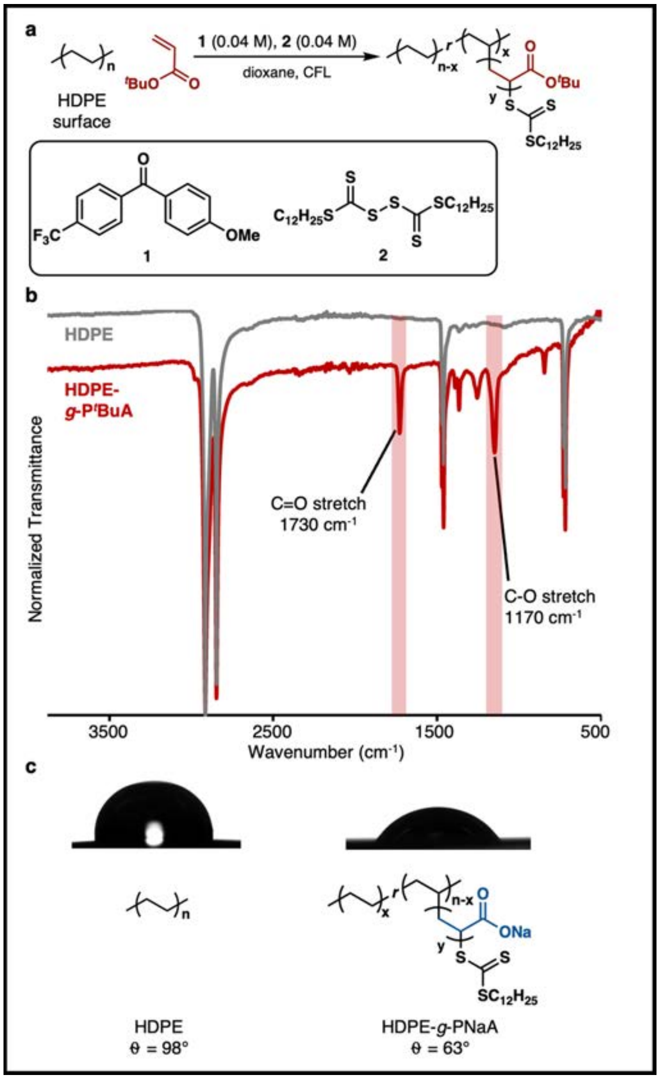
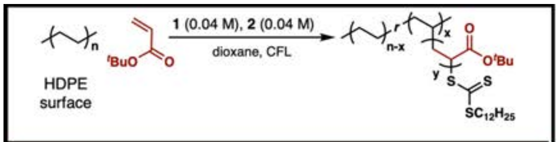
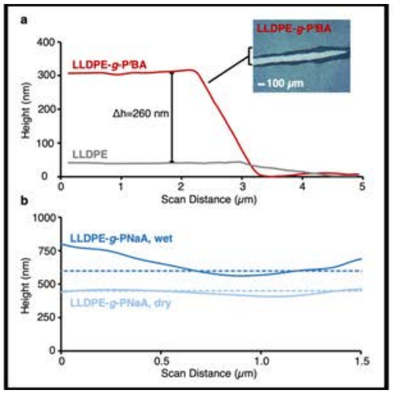


Figure 1: (a) Standard reaction conditions for SI HAT-RAFT from PE. (b) IR spectra of unfunctionalized HDPE and HDPE-g-PtBuA. (c) Static water contact angle for HDPE and HDPE-g-PNaA.

This difficulty in functionalization hampers the synthesis of PEs with high-performance surfaces such as antifouling biomedical implants, antibacterial high-touch surfaces, or chemically selective filtration membranes. A method to imbue PE surfaces with improved or novel properties would facilitate the development of next generation polymeric materials.



Conditions	Strong IR stretch at 1730 cm^{-1}
Standard Conditions	+
Drop cast PᵗBuA onto HDPE	-
Thermal RAFT	-
No light	-
No disulfide	-
PET instead of HDPE	-



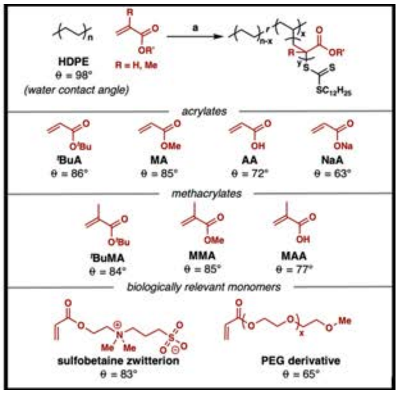


Table 1, left: *SI HAT-RAFT Controls.* ***Figure 2, middle:*** *(a) AFM measurement of LLDPE-g-PtBuA brush thickness. Brush thickness is assessed by comparing the depth of a scratch (pictured here by optical microscopy) in an LLDPE film before and after graft-ing. (b) AFM swelling study of LLDPE-g-PNaA in pH 9 buffer solu.tion shows the wet film swells 63% relative to the dry film. The dashed lines denote the average film height over the scan distance.* ***Figure 3, right:*** *Monomer scope of SI HAT-RAFT, where a is the standard reaction condition: photocatalyst 1 (1 equiv.), CTA 2 (1 equiv.), monomer (200 equiv.), and dioxane (0.04 M in CTA) irradiated with a CFL at room temperature in a nitrogen atmosphere for 16 hours. For the sulfobetaine zwitterion and the PEG derivative, water was used in place of dioxane. For the sulfobetaine zwitterion, the reaction was run at half the overall concentration due to poor monomer solubility.*

We began our studies by layering a solution of benzophenone derivative [1], bis(trithiocarbonate) disulfide species [2], tert-butyl acrylate, and dioxane on top of a high-density polyethylene (HDPE) film and covering it with a glass slide before irradiating with visible light from a compact fluorescent light (Figure 2a, reaction setup depicted in SI). Following irradiation, we detected carbonyl and C-O bond stretches in the IR, indicating that poly(tert-butylacrylate) (PtBA) was successfully installed on the surface of PE (Figure 1). Upon basic hydrolysis of PtBA to poly(sodium acrylate) (PNaA), the static water contact angle of the surface decreased from 98° to 63°, indicating a dramatic increase in the hydrophilicity of the surface (Figure 1).

We then carried out a series of control experiments to verify that the polymer observed on the surface was in fact grafted covalently via the HAT-RAFT process. Free PtBA drop-cast onto an HDPE surface washed away easily, suggesting no adhesion of PtBA to HDPE in the absence of covalent bonds between the surface and the grafted polymer (Table 1). Additionally, subjecting HDPE to thermal RAFT polymerization conditions yielded no polymer on the surface, confirming that generation of radicals alone is not enough to graft from HDPE. We also found that under standard SI HAT-RAFT conditions but in the absence of light, polymerization does not proceed.

Having shown that we can grow acrylates from a PE surface, we set out to better characterize the brush polymers produced through microscopy experiments. A silicon wafer was spin-coated with linear low-density polyethylene (LLDPE) to form the substrate and then grafted with PtBA. Atomic force microscopy (AFM) was used to assess brush thickness (Figure 2). For our LLDPE.g-PtBA sample, we achieved a brush thickness of 260 nm. We also used AFM to characterize brush density. Our SI HAT-RAFT method achieves a grafting density of 0.62 chains/nm2. Currently, there are no other methods for grafting from PE surfaces that report such a high grafting density.

To demonstrate the diversity of PE surfaces accessible with SI HAT-RAFT, grafted polymer surfaces were prepared using a variety of acrylate and methacrylate monomers (Figure 3). Static water contact angles ranging from 63° to 86° are accessible, showing that hydrophilicity is tunable by the choice of monomer. Hydrophilicity can also be tuned by protonating or deprotonating the brushes. For example, in their protonated form, PAA brushes have a water contact angle of 72°. In their deprotonated, water-soluble PNaA form, the water contact angle falls to 63°. In the interest of synthesizing biomedically relevant surfaces, we examined a sulfobetaine zwitterion acrylate and a PEG acrylate.

Conclusions and Future Steps:

We developed a robust, highly diversifiable method to grow high density brush polymers from PE surfaces. The SI HAT-RAFT method presented achieved the highest reported brush thicknesses and densities grafting from PE surfaces, and we can access brush polymer surfaces composed of a wide variety of (meth) acrylate monomers. Improving the surface properties of PE opens the door to using PE in applications including battery science, antimicrobial surfaces, and filtration. This work addresses the long-standing challenge in polymer science of facile and robust access to PEs with enhanced surface properties.

New High-Resolution Resists for EUV Lithography

CNF Project Number: 3137-23
Principal Investigator(s): Christopher Kemper Ober
User(s): Madan Rajendra Biradar, Huseyin Cem Kiliclar

Affiliation(s): Department of Materials Science and Engineering, Cornell University

Primary Source(s) of Research Funding: DuPont and SK Hynix

Contact: cko3@cornell.edu, mrb348@cornell.edu, hck46@cornell.edu

Research Group Website: https://ober.mse.cornell.edu/index.html

Primary CNF Tools Used: ASML 300C DUV Stepper,
JEOL 6300 E-Beam Lithography, P10 Profilometer, Optical Microscope

Abstract:

The semiconductor industry depends on photoresists to manufacture advanced chips. To meet the industry's growing demands for precise pattern fidelity and resolution, scissionable polymeric materials with chain end groups that can trigger depolymerization are crucial. A promising solution is photodegradable polymer material based on poly(phthalaldehyde) (PPA), having acetal linkages highly sensitive to acids. When exposed to deep ultraviolet (DUV) or electron beam light, these end groups generate acids that induce depolymerization of PPA into its monomers. In this report, we describe the design and synthesis of bromo-substituted PPA and demonstrate its effectiveness as a photoresist through DUV lithography, achieving well-defined line-space patterns.

Summary of Research:

In 1983, IBM's research laboratory developed depolymerizable photoresists, including end-capped poly(phthalaldehyde) (PPA). These photoresists contain photolabile groups that generate acids when exposed to light. The acids then catalyse the chain cleavage of the PPA [1]. In the literature, various research groups have investigated the potential of PPA under DUV and EUV radiation. The Ober research group has demonstrated that functionalized poly(phthalaldehyde)s (PPAs) can serve as degradable polymer backbones. Additionally, this group has explored PAG-tethered phthalaldehyde to achieve exceptional results across several lithography techniques [2-4].

In this report, we have described the development of photoresists containing active end groups, which show high stability, low outgassing and extreme sensitivity under DUV exposure. The development and depolymerization mechanism of functionalized linear Br-PPA is shown in Figure 1. After exposure of EUV radiation, the EUV active end group initiates depolymerization via a cascade mechanism.

Result and Discussion:

The synthesized Br-PPA polymer was examined with 1H NMR spectroscopy to determine its structural confirmation and evaluate its stability, while its thermal stability was evaluated through thermogravimetric analysis. The molecular weight of the polymer was characterized via gel permeation chromatography.

For photoresist testing, 35 mg of the polymer was dissolved in 1 mL of cyclohexanone and spin-coated onto a silicon wafer at 2500 rpm for 60 seconds. The coated wafers were then subjected to DUV radiation using an ASML 300C DUV stepper. After radiation exposure, the film was baked at 90°C and developed in isopropyl alcohol for 30 seconds. The resulting line-space patterns were examined using Atomic Force Microscopy (AFM), as depicted in Figure 2.

Conclusions and Future Work:

In this work, we demonstrate the synthesis of bromo-substituted poly(phthalaldehyde) (Br-PPA) with active end groups and observed its potential as a photoresist for deep ultraviolet (DUV) lithography. The initial results with the Br-PPA are promising. Moving forward, we will further explore the lithographic performance of various functionalized PPA photoresists.

References:

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[2] Deng, J., Bailey, S., Jiang, S., Ober, C. K. High-Performance Chain Scissionable Resists for Extreme Ultraviolet Lithography: Discovery of the Photoacid Generator Structure and Mechanism. Chem. Mater. 2022, 34, 6170.6181.

[3] Deng, J., Bailey, S., Ai, R., Delmonico, A., Denbeaux, G., Jiang, S., Ober, C. K. Synthesis of End-Cap Enabled Self-Immolative Photoresists For Extreme Ultraviolet Lithography. Macro Lett. 2022, 11, 1049.1054.

[4] Deng, J., Bailey, S., Jiang, S., Ober, C. K. Modular Synthesis of Phthalaldehyde Derivatives Enabling Access to Photoacid Generator-Bound Self-Immolative Polymer Resists with Next-Generation Photolithographic Properties. J. Am. Chem. Soc. 2022, 144, 42, 19508-19520.

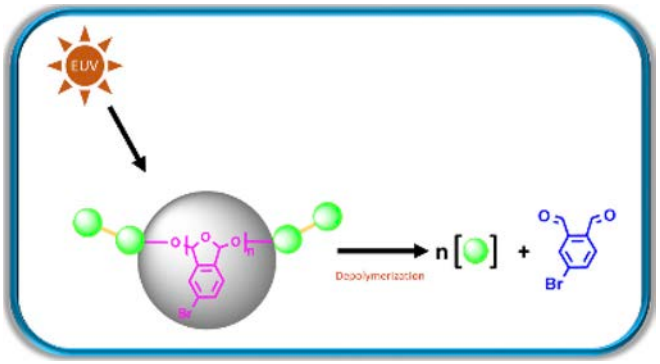

Figure 1: Functionalized linear Br-PPA with photoactive end groups.

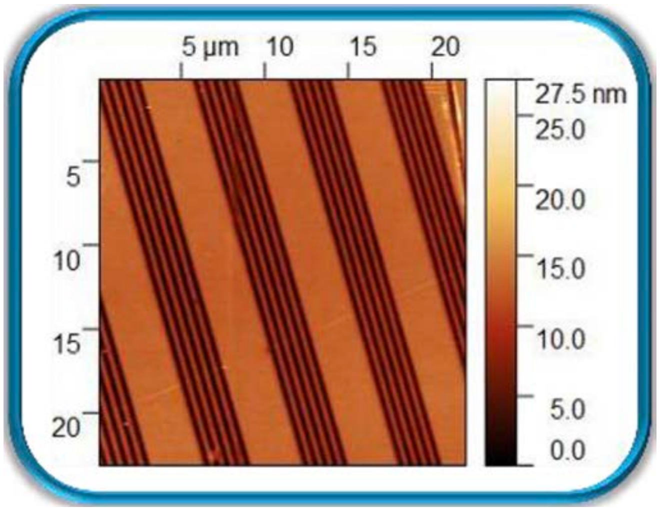

Figure 2: Line-space patterns characterized using AFM.