

Tip Induced Crystallization Lithography

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S Supporting Information

ABSTRACT: We demonstrate a new technique for efficiently fabricating large-area organic crystal arrays on substrates using tip induced crystallization lithography (TICL). This technique depends on coating an amorphous organic thin film on a substrate and then inducing crystallization of the thin film using an atomic force microscope tip. After the noncrystalline materials are removed from the substrate by heating or washing, the organic crystal arrays are stable on the substrate. In this communication, the size of the smallest feature made using TICL technique is less than 1 μm .

The preparation of uniform large-area organic crystal arrays on substrates plays an important role in material sciences, such as producing high-quality organic thin film based semiconductors, solar cells, field-effect transistors, light-emitting diodes and promoting the sensitivity of chemical and biological sensors.¹ It also aids in providing an environment to understand the thermodynamics, kinetics, sensitivity, and detonics of energetic materials in micro- or nanoscale.² To date, various techniques such as soft-lithography,^{2a} inkjet printing,³ microchannel growth,⁴ optical lithography,⁵ and template-based fabrication⁶ have been applied to fabricate organic crystal arrays on various substrates.

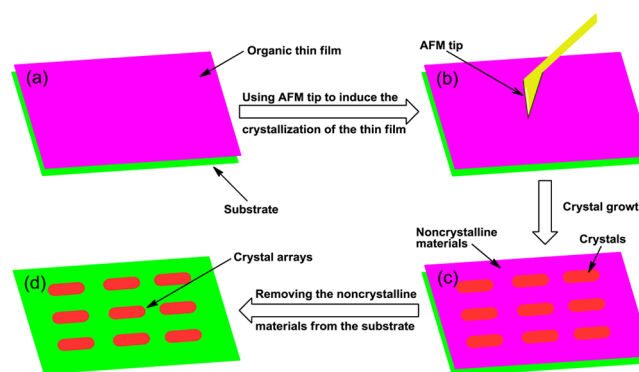
Among these developed techniques, template-based fabrication is the most popular technique to produce large-area organic crystal arrays with a well-controlled structure because the physical or chemical properties of templates can be adjusted beforehand to tune the microstructure formation of organic crystals. The templates can be micropatterned self-assembled monolayers (SAMs), which can easily be lithographically defined through microcontact printing ($\mu\text{-CP}$). The organic material, which has an affinity (hydrogen bonding, $\pi\text{-}\pi$ stacking, electrostatic interactions, or van der Waals interactions) with the patterned material, is deposited on the SAM pattern to form the crystal arrays.⁶ Crystalline arrays can also be generated through capillary drying between the meniscus formed between a PDMS template and a substrate.⁷ Template based techniques have the advantage that large areas can be readily patterned, but it is impossible to quickly change the stamp to make arbitrary patterns.

Atomic force microscopy (AFM) is a high-resolution type of scanning probe microscopy. It uses a microcantilever with a sharp tip, which is normally used to collect high resolution images of the surface.⁸ However, AFM can also be used for various forms of lithography without the use of a template. One example is deposition of materials through dip-pen nanolithography (DPN).⁹ The AFM tip acts as a reservoir of 'ink'

which can be written on various substrates. DPN can be used to deposit a wide variety of soft materials including alkane thiols, organic molecules, polymers and even metals.⁹

By using AFM, we demonstrate a novel technique for effectively fabricating large-area organic crystal arrays on various substrates by tip induced crystallization lithography (TICL). This technique relies on coating an amorphous organic thin film on a substrate and then inducing the crystallization of the thin film using the AFM tip. The process can be controlled by removing the remaining noncrystalline materials from the substrate, leaving crystalline areas defined by where the AFM tip was in contact. The schematic illustration of the experimental procedure for the TICL technique is shown in Scheme 1. Currently, the size of the smallest feature made using TICL is less than 1 μm .

Scheme 1. Schematic Illustration of the Experimental Procedure for the TICL Technique



Pentaerythritol tetranitrate (PETN) is a typical monomolecular crystal and is used as a pharmaceutical and as benchmark material for high explosives.¹⁰ The sensitivity, performance and stability of PETN are heavily influenced by the crystal habit.¹¹ The first observation TICL was with PETN and is presented in detail as a model molecular compound and to provide guidance for fabricating various organic materials with this method. Amorphous PETN thin films can be prepared by thermal evaporation of PETN at atmosphere¹² or spin coating low concentration PETN solution.^{2b} The amorphous PETN thin films are proposed to be kinetically formed nano/microscale supercooled droplets.¹³ Although these droplets are remarkably stable for days or weeks, they are likely deposited in a metastable liquid state.^{12,14} After some form of perturbation,

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the droplets grow into dendritic crystals. Previous studies reported that AFM tips can be used as a perturbation source to induce nucleation and crystallization of PETN thin films. As the AFM tip scans the amorphous PETN thin film surface, nucleation is induced from the interaction of the tip with the metastable droplets. A possible mechanism to explain how the AFM tip induces crystallization is a 2-D heterogeneous nucleation model, where the tip serves as a defect to enhance the crystal growth by reducing the nucleation barrier.¹⁴ Crystals then grow due to diffusive mass transfer. The crystals formed will continue to grow until the entire surface was void of any remaining islands.

To use TICL as a lithographic tool, methodology needs to be included to stop the growth of the crystallites. The most sensible method is to quickly remove any remaining amorphous islands from the substrate. Two simple methods have been observed to stop the growth process, by heating the sample after nucleation or washing the substrate. Heating the substrate up to 50 °C removes the amorphous droplets that quickly shrink and finally disappear. The disappearance of these droplets is likely because the noncrystalline droplets have a faster sublimation rate than the crystalline material. The disadvantage of heating is that the growth of the crystalline area does not immediately stop and will continue growing as the islands shrink. If left at elevated temperatures too long, the crystalline area will shrink by sublimation and thermally sensitive compounds may be adversely affected.^{12,15} Another simple method is washing the surface with a solvent. For these studies, deionized water was used. After nucleating the growth, the substrate is placed into the spin coater at 3000 rpm, and several milliliters of water are added dropwise removing the noncrystalline droplets. The mechanism of droplet removal is not fully understood but is likely due to weak interactions of the islands with the substrate. Regardless of the technique used to remove the amorphous islands, feature size is ultimately controlled by stopping the crystal growth.

Figure 1 shows various PETN crystal arrays, including linear crystal arrays with different widths and arbitrary shapes formed through TICL. The size of the crystallites formed in these images is controlled by the time between scanning with the AFM and heating the sample. Additional images are shown in Supporting Information.

In this study, the primary factor controlling line width is the period of time between nucleation by the AFM tip and removal of the amorphous droplets. We observed no obvious influence on the tip size since it was small compared to the line width observed. The smallest line width we have been able to fabricate was less than 1 μm when the sample was immediately removed from the AFM and washed with water as shown in Figure 2.

To expand applications of TICL, we also explored the patterning of other organic chemicals, including two other high explosives and two important organic building blocks and intermediates in material science¹⁶ on various substrates. These chemicals are trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), triphenylamine, and 2,5-diphenyloxazole. All of these materials can be patterned and readily form crystal arrays on different substrates as shown in Figure 3. The primary factor observed in this study for choice of an organic material is that it must be deposited as a supercooled/metastable material and is not universal for all materials.

In conclusion, we have developed a novel technique referred to as TICL for effectively constructing uniform organic crystal

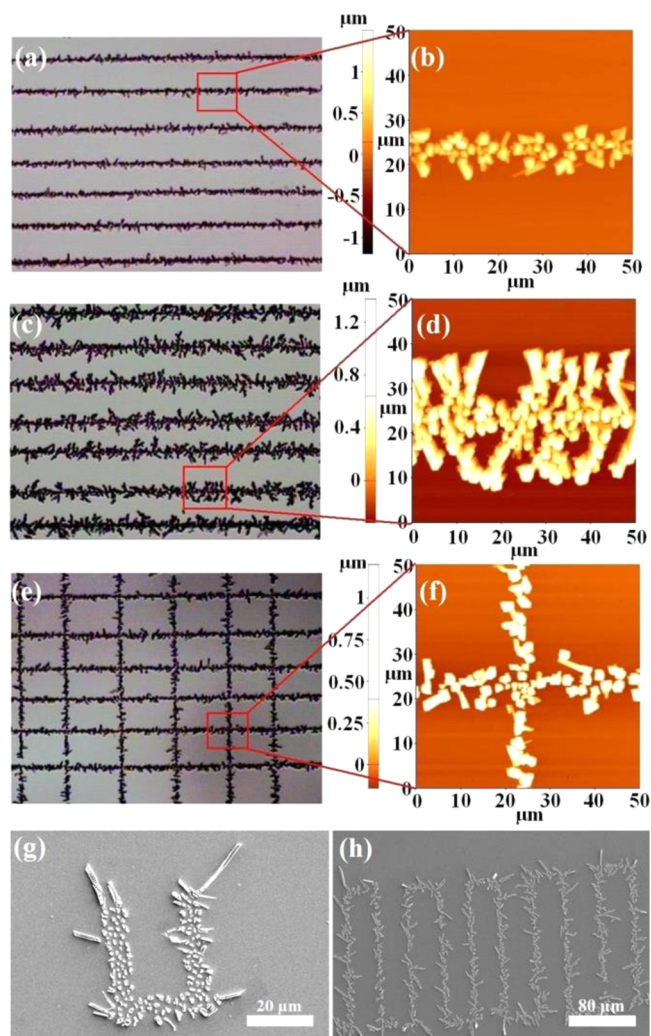


Figure 1. Various PETN crystal arrays on glass substrates. Optical images of linear PETN crystal arrays with different size (a) $\sim 10 \mu\text{m}$ and (c) $\sim 30 \mu\text{m}$ (the growth time for (a) and (c) was 5 and 20 min, respectively) and (e) clathrate PETN crystal array; (b, d, f) AFM images of the respective sample; SEM images of PETN crystal arrays (g) U shape and (h) continuous line. All thin films are prepared using spin coating. The noncrystalline PETN droplets are removed by heating at 50 °C. The size of all optical images is $370 \times 270 \mu\text{m}^2$.

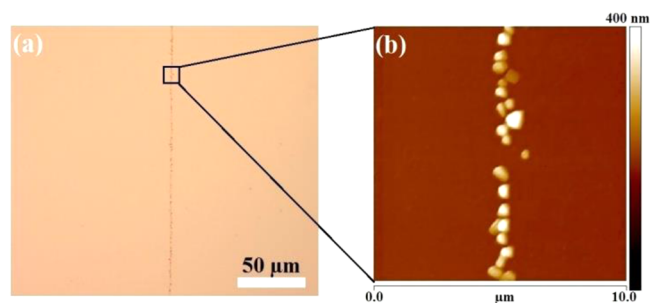


Figure 2. Optical (a) and AFM (b) images of $\sim 1 \mu\text{m}$ lines. The noncrystalline PETN droplets are removed by water washing.

arrays on various substrates. By controlling the crystal growth time, this technique can be used to define the shape, size and distribution of these organic crystal arrays. The experimental procedures of the TICL technique are simple, low cost and could potentially be scaled up with cantilever arrays.¹⁷

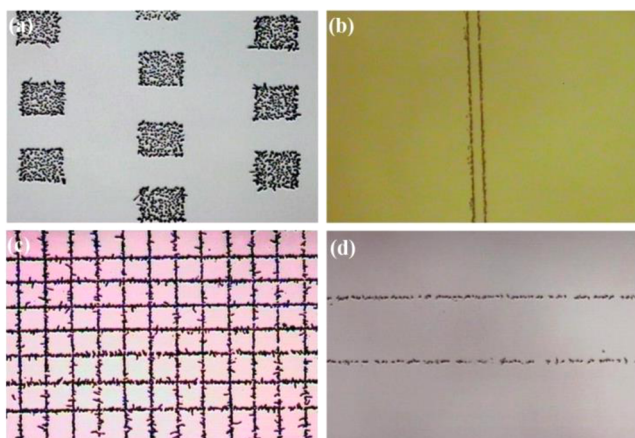


Figure 3. Optical images of various organic crystal arrays: (a) TNT square crystal arrays on Cr substrate; (b) RDX linear crystal arrays on Au substrate; (c) triphenylamine clathrate crystal arrays on glass substrate; and (d) 2,5-diphenyloxazole linear crystal arrays on glass substrate. The noncrystalline materials are removed by heating. The size of all images is $420 \times 300 \mu\text{m}^2$.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and additional results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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