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ORGANIC CONDUCTORS AS NOVEL “MOLECULAR RULERS” FOR ADVANCED MANUFACTURING PROCESSES

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Abstract Future advanced manufacturing equipment used in high technology programs will require ultra-high precision and associated machining tool operations that require placement accuracy of $\sim 1\text{--}100\text{ nm}$ ($1\text{ nm} = 10\text{ \AA}$). There is consensus amongst engineers that this equipment will be based on STM (Scanning Tunneling Microscope) technology. All such STM-based “drivers” must contain a *metrology system* that requires *absolute length standards referenced to atomic spacings* for calibration.¹ Properly *designed* organic conductor substrate crystals have the potential to be *molecular rulers* for STM-based advanced manufacturing equipment.

INTRODUCTION

The focus of this article is to point out a previously unrecognized and highly novel application for conducting organic crystals that could play a very significant role in future advanced ultra-high precision manufacturing processes (positioning and micromachining). A widely held notion is that much future advanced manufacturing equipment will be based on STM technology for ultra-high precision operations that will require placement accuracy of $\sim 1\text{--}100\text{ nm}$ ($1\text{ nm} = 10\text{ \AA}$).^{1,2} Any such STM-based machine must contain a *metrology system* that itself will require calibration by materials in which repeat distances are $1\text{--}100\text{ \AA}$ or more. Thus, calibration requires *absolute length standards references to atomic spacings*,¹ and for the reasons to be described shortly, conducting organic crystals are ideal *molecular rulers* for such purposes. A prototype STM-based system known as the Molecular Measuring Machine, or M-cubed, has been constructed and tested.¹ Just one important industrial application of such a system is the development of measuring devices to aid semiconductor manufacturers in the alignment of lithography masks for complicated circuit patterns.

A STM is capable of single-atom resolution as it surveys a molecular landscape, and current techniques require the use of a two-compound system consisting of a conducting base (frequently graphite) coated with a second “reference or calibrant” material. A conducting base support is necessary because electrons emitted by the STM probe will not tunnel through the reference material unless the base support is electrically

conducting. In the case of the conducting base, for example, there is often difficulty in reconstructing and interpreting valid STM images derived from a reference material because they may form very nonordered and random structures on the base. Such major problems could be obviated with the use conducting single crystal organic materials because they are perfectly *ordered* over very large distances (many mm), and because they are of known *structure* and *orientation*, which makes them ideal molecular rulers. Furthermore, since the organic systems are *intrinsically conducting*, *no* graphite or metal conducting base is required. Why not simply use an elemental metal such as Cu for a reference material? Simply put, elemental metals have too short ($\ll 10$ Å) and *fixed* (*nonadjustable*) interatomic distances, e.g., 2.6 Å in Cu.

Thus, the STM probe and associated metrology system, and the *direct access* that it provides to the *geometry* of single crystal *surfaces* (and *underlying internal structure* given by the atomic positions and molecular arrays and internal repeat patterns), are able to “read” the internal structures (repeat separations) of conducting organic crystals. Most importantly, organic crystals have *modifiable* internal structures that be easily *tailored*, by varying the size of the organic electron-donor molecule or anion, to provide specific *predetermined* intermolecular repeat distances and *patterns* (based on their *intrinsic crystal symmetry*) thereby likely making them ideal *templates* for use in advanced ultra-high precision manufacturing processes. In practice, the counter-ions (anions) to be combined with the organic molecular “spacer” (electron-donor) molecules, will also serve as the repeat *distance markers* in a fabricated crystal lattice. The advantage of this approach is that the marker separations, and *array patterns*, can be adjusted to 10–50 Å or larger separations by appropriate choice of organic “molecular spacer.”

The most important advantages of this novel approach to *molecular ruler* synthesis are that conducting organic materials uniquely satisfy STM-based equipment requirements, i.e., they are electrically conductive, can be grown defect-free with very large optically flat faces (many mm on a side), are easily and reproducibly prepared, and can be tailor-made to have exact and repeated (necessary for repeat placement and cutting operations) intersolid separations of 10–100 Å. A summary of the conceptual use of an organic *molecular ruler* in a STM-based system is as follows: the molecular ruler may be viewed as a VCR tape encoded with metric data read from the organic crystal, a STM driver and its metrology system as a VCR machine, and a high-precision patterning or machining device may be viewed as a TV set. Finally, recent investigations³ support the technical feasibility of the approach discussed here wherein STM studies of organic conductor crystals produced STM images which represent easily recognizable and precisely *repeated* interatomic and intergroup separations of 10 Å.

The major challenges in future organic conductor research aimed at STM metrology applications are as follows:

- Design and synthesis of a series of large organic molecules (spacers) with conducting organic "cores" that can be *systematically lengthened*.
- No drastic changes in the solubilities and redox characteristics of molecular spacers as the spacer size is increased.
- Synthesis of unusually large anionic species to be incorporated with the organic spacers, and when combined with an anion, the crystallized assembly must be electrically conducting.
- Electrochemical crystal growth of large, defect-free, optically-flat, plate-like single crystals.
- STM characterization of the as-grown conducting organic-anion composite crystals to determine the precise repeat separations therein.

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