Gradient Reference Surfaces for Scanning Probe Microscopy*

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INTRODUCTION

Scanning Probe Microscopy (SPM) techniques promise micrographs that map specimen properties with nanometer scale resolution. While current SPM images generally provide qualitative information, some progress has been made in quantifying SPM data. A prime example in this regard is AFM topography data. In this case two factors, scanning piezo non-linearity and unknown probe tip shape hamper precision measurements of specimen surface features. Now, linearized/calibrated piezo systems ensure micrograph dimensions[1]. In addition, specialized substrates with ultra sharp features can measure tip geometry so that, in principle, tip-shape effects on topographic data can be removed[2]. Indeed, such reference specimens are now available commercially.

In recent years, a new generation of SPM techniques, which intend to measure chemical, mechanical, and electro/optical properties on the nanoscale, have been developed. Based upon sample/probe interactions that are more complex than in AFM, contrast in these new SPM images is difficult to quantify. In particular, the development of quantitative SPM techniques require methods to gauge the following factors:

• *Resolution and Sensitivity*: The lateral resolution, measurement volume, and sensitivity to measured properties must be determined.

• *Probe quality*: Many new SPM techniques depend upon custom-made probes, the fabrication of which often is not reliable or uniform. Accordingly, convenient means to characterize these probes are needed.

• *Combination Effects*: SPM measurements of, for example, chemical properties are convoluted with local mechanical, topographic and other effects. Effective reference specimens would serve to separate the impact of these "combined" effects on image contrast.

In response to these needs, a new research effort initiated by the NIST Combinatorial Methods Center (NCMC) aims to provide a suite of reference specimens useful for the quantification of next-generation SPM data. By design, these specimens gauge the quality of SPM probes, calibrate SPM image contrast through "traditional" surface measurements (e.g. spectroscopy, contact angle) and provide information useful for modeling complex probe/sample interactions. The design and production of these specimens uses bench-top microfabrication routes, used in conjunction with the combinatorial gradient-specimen fabrication toolbox developed by the NCMC[3].

REFERENCE SPECIMEN DESIGN

An example reference specimen design is illustrated in Figure 1. Such a specimen would useful for quantifying chemically sensitive SPM techniques such as friction-force AFM, or Chemical Force Microscopy (CFM), which employs a chemically functionalized AFM probe[4]. The reference specimen includes a pattern of micron-scale lines that gradually change in their chemical contrast (e.g. surface energy) with respect to a constant matrix. Wide "calibration" fields, which bound the patterned area, directly reflect the changing (or static) chemistry of the lines (or matrix); so traditional measurements along the calibration fields gauge chemical differences in the gradient micro-pattern. Accordingly, for SPM micrographs acquired along the patterned region, the specimen calibrates the image contrast and illuminates the sensitivity (minimum contrast) with respect to traditional measures. In addition, for techniques like CFM this specimen serves as a tool for comparing the quality of tip-functionalization.

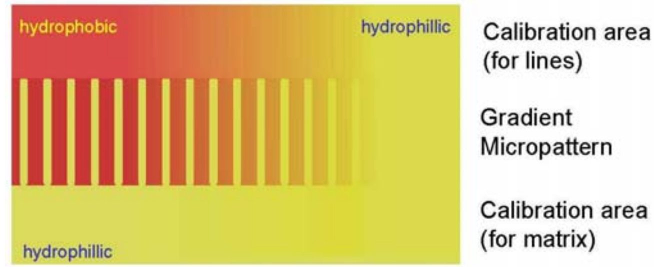

Figure 1. Schematic of gradient reference specimen for gauging tip quality, for calibrating image contrast, and for determining sensitivity in chemically-sensitive SPM techniques. Chemical contrast in the patterned area is gauged via traditional measures along the calibration areas.

DISCUSSION OF SPECIMEN FABRICATION

Fabrication of gradient-pattern specimens requires soft-lithography of appropriate SAM molecules onto a planar substrate. A composite stamp, which has both flat and corrugated areas, allows printing of the micropatterned strip with the adjacent solid calibration field. Next, a graded UV-ozonolysis (UVO), gradually modifies the chemistry of the patterned SAM (and calibration field) along one direction. For example, methyl-terminated alkyl chain monolayers (hydrophobic) can be gradually converted into carboxylic acid terminated (hydrophilic) chains[3,5]. Subsequent "filling" with a hydrophilic SAM completes the "matrix" of the specimen. To test this design and process, traditional micro-contact printing of thiol-SAM "inks" onto gold substrates followed by gradient UVO provided quality specimen prototypes. While this validated the specimen design, ultimately the use of delicate gold/thiol chemistry will not result in specimens that can be stored, cleaned and reused. Accordingly, the next generation of reference specimens will be fabricated using more robust substrates and chemistries, thereby making them viable candidates for applications such as NIST Standard Reference Materials.

In this presentation, we will demonstrate novel routes for the graded patterning of monochlorosilane (MCS) SAMs on SiO_2-terminated silicon substrates; and we will discuss the fabrication and testing of reference specimens created through these new fabrication approaches. The utility of these specimens will be demonstrated with respect to emerging SPM techniques such as CFM and Atomic Force Acoustic Microscopy. In addition, we will show how graded pattern specimens can be useful for the high-throughput analysis of surface-directed behavior in thin films of homopolymers, polymer blends and block copolymers.

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