Chemical-force microscopy for materials characterization

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Chemical force microscopy (CFM) is an extension of atomic force microscopy (AFM) that employs a chemically-functionalized tip, which makes it possible to control chemical interactions between tip and sample, so CFM can be used to probe local chemical information on the surfaces of materials and biological samples under near-native environments at nanoscale spatial resolution. We describe applications of CFM for materials characterization, including measurements of single intermolecular interaction forces and investigations of nanoscale heterogeneity of surface-chemical properties of polymeric materials.

Keywords: Biological sample; Chemical-force microscopy; Host-guest chemistry; Materials characterization; Nanoscale heterogeneity; Polymer; Single intermolecular interaction force; Surface characterization; Surface-chemical property

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1. Introduction

Atomic force microscopy (AFM) has been widely used to measure nanoscale topographic images of sample surfaces under environments (e.g., ambient air and solution) close to systems in materials and biological research [1,2]. In AFM (Fig. 1a), a very sharp tip made of Si or Si_3N_4 is used to probe local information on the sample surface. The tip is brought close to the sample surface, and the force between tip and surface (of the order of 10^{-12}–10^{-7} N) is measured as the deflection of a microfabricated cantilever having the tip at its end. The tip is raster-scanned over the surface using a piezoelectric device that can control the tip position with sub-nm precision. During raster scanning, the tip-surface force (or distance) is kept constant by means of a feedback system to provide topographic AFM images.

AFM-image formation is significantly affected by the nature of the interaction forces between tip and sample, and by the sharpness of the AFM tip. For example, spatial resolution in AFM imaging deteriorates in the presence of strong attractive forces (e.g., capillary force) and non-specific adsorption of biomolecules onto a tip [1,3]. Surface topographic images have been obtained by probing the interfacial repulsive force at the tip-sample contact area that is independent of surface chemical composition (contact and intermittent contact modes) [1,2]. In ultrahigh vacuum, elemental discrimination of surface atoms was demonstrated using non-contact-mode AFM, because the tip-surface force mainly reflected the short-range chemical force due to the contamination-free environment [4]. By contrast, chemical identification of surface species in air or in solution using AFM is often challenging because of the involvement of various interactions in a measured tip-surface force and contamination-induced changes in tip-surface properties [1,3].

One approach to control tip-sample interactions in AFM is to tailor the surface of an AFM tip chemically with a well-defined organic thin film having a specific terminal group (Fig. 1b) [1–3,5,6]. The use of chemically-functionalized tips for AFM imaging, which is called chemical force microscopy (CFM) [5], enhances a specific intermolecular interaction and suppresses other interfering interactions, so selectively probing surface-functional groups of interest in the range of microscale to nanoscale. Also, CFM makes it possible to measure a variety of non-covalent chemical and biological interaction forces directly as a function of tip-sample distance [1,3,6,7], which is based on the force measurement capability of AFM (Fig. 1c).

In the measurements, the deflection of the cantilever, which can be converted to tip-surface force, is recorded at a single point on a sample during approach and withdraw cycles at a given speed. In the retraction part of the curve, the tip

0165-9936/$ - see front matter doi:10.1016/j.trac.2009.12.008

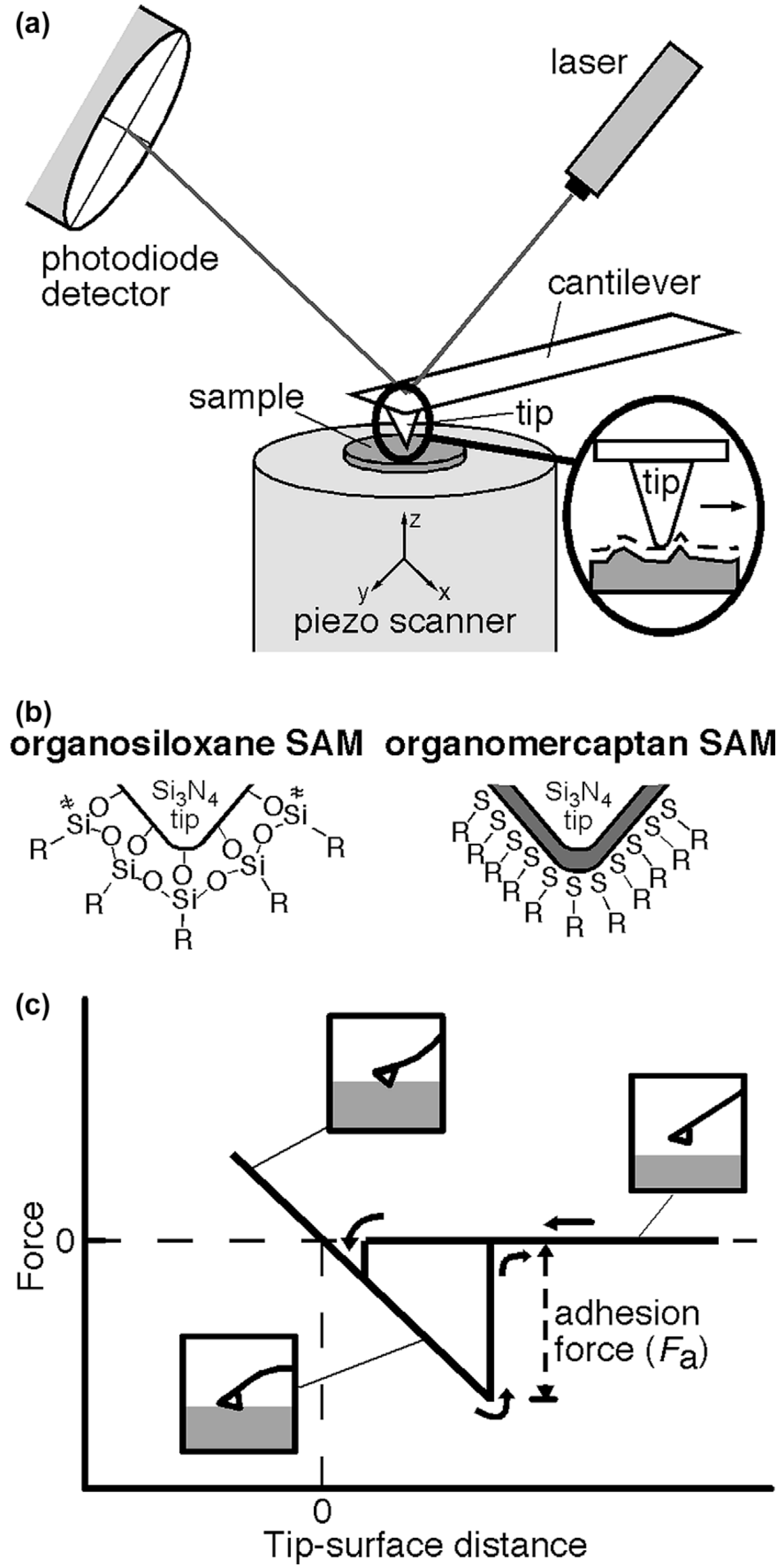

Figure 1. (a) AFM. (b) Chemically-functionalized AFM tips commonly employed in CFM. (c) Force-distance curve.