Scanning Microscopy

Volume 9 | Number 3 Article 7

9-12-1995

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Scanning Microscopy, Vol. 9, No. 3, 1995 (Pages 701-704) 0891-7035/95$5.00+.25
Scanning Microscopy International, Chicago (AMF O'Hare), IL 60666 USA

THERMAL STABILITY OF POLYSTYRENE LATEX SELF-ASSEMBLED ARRAYS STUDIED BY ATOMIC FORCE MICROSCOPY

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(Received for publication May 18, 1995 and in revised form September 12, 1995)

Abstract

Preliminary observation of the heat softening of self-assembled polystyrene latex arrays on the submicron scale using atomic force microscopy is reported. Samples of latex self-assembled arrays have been studied in the temperature range from the room temperature up to 120°C. It has been shown that the submicron scale structure remains stable up to the softening point of polystyrene. The experimental set-up used is described and the results obtained are discussed.

Key Words: Scanning force microscopy, polystyrene latex particles, thermal stability.

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Introduction

Latex submicron-size polymer particles have numerous uses including calibration of microscopes and electronic particle sizing equipment, model systems for studies in basic colloid chemistry, and general biomedical studies [1, 4]. With the growing interest in the possible utilization of organic and biological compounds as basic elements for nanometer-scale solid-state electronic devices, latex microspheres become a good candidate for model studies of the arraying procedures for those compounds and as a constructive element for the devices themselves.

Here, an investigation of self assembled arrays of latex particles is reported using a scanning force microscope (AFM) and a sample holder with a heating option. This sample holder (heater) was specifically designed in order to observe, by AFM, the same local area of the sample before and after the heating cycle.

Experimental Details

A schematic structure of the sample holder is shown in Figure 1. The heating element is made of 0.1 mm diameter tungsten wire and mounted on a Teflon base; this plate is in contact with the scanner, and ensures a minimal heat flow from the heater to the piezo element. The heating element is covered by a copper plate in order to provide uniform heat distribution to the sample. The latter is fixed onto this copper plate by means of plane springs (not shown in Fig. 1). The temperature is monitored with a accuracy of ± 3°C by a temperature sensor AD590JH (Analog Devices, Nordwood, MA, USA) attached to the copper plate. The square copper plate is larger than the sample one, and cooling is carried out mainly by heat dissipation in air from uncovered areas of the copper plate.

The sample was prepared by spreading an 8 μl drop of a 1% solution of 144 nm diameter sulfate polystyrene latex particles in water (Interfacial Dynamics Corp., Portland, OR, USA) onto the freshly cleaved surface of mica. Then, the sample was dried in air for 20 minutes

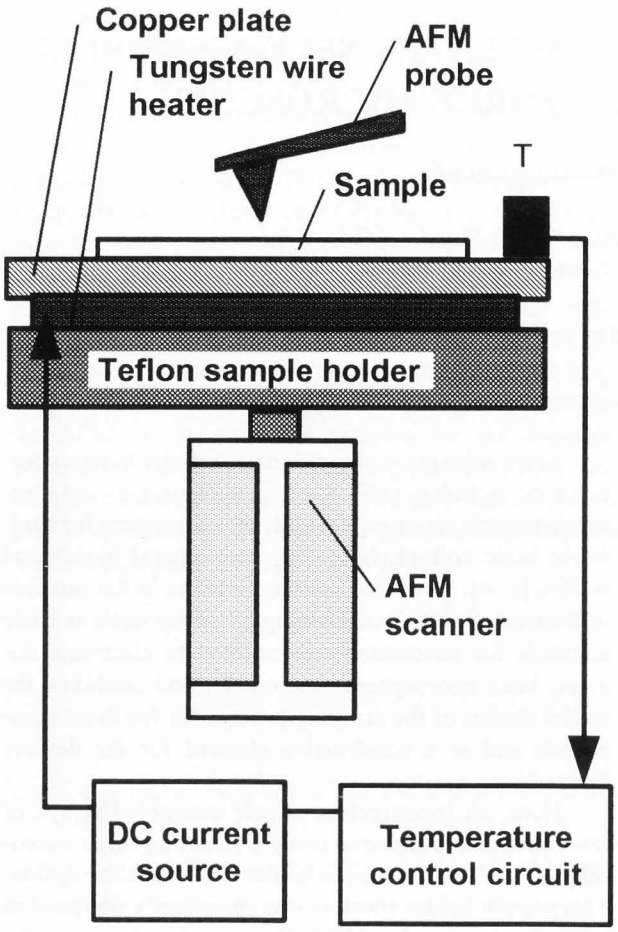

Figure 1. AFM sample heater design.

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at a temperature of 35°C. Sulfate polystyrene monodisperse microspheres form close-packed ordered layers on the hydrophilic surface while the water is evaporating [2, 3]. The areas with various numbers of monolayers can be located easily by means of an optical microscope as different color zones, when the optimal diffraction contrast is set. The AFM study of these samples shows that areas of several μm^2 of uniformly arrayed microspheres can be obtained by the mentioned deposition method.

The sample was fixed onto the heater, and then mounted onto the scanner tube of AFM (SFM-BD2, Park Scientific Instruments Inc., Sunnyvale, CA). V-shape cantilevers (Microlever, Park Scientific Instruments) with a spring constant of 0.064 N/m and a probe curvature radius of about 40 nm were used. All images have been obtained in "contact mode" in air. After the images at the ambient temperature had been obtained, several heating-cooling cycles were carried out.

Each heating-cooling cycle was performed according to the following procedure. First, the AFM image at room temperature (25°C) was acquired. Then, the AFM feedback was switched off in order to prevent the probe from contacting the sample surface during heating. The sample was heated to the desired temperature at a rate of approximately 1°C per second. The sample was heated to the temperature below and above the glass transition temperature of polystyrene (90°C), but below the polystyrene melting point (240°C). Then, the sample was cooled to room temperature in about 20 minutes. The sample temperature must be stable before a new image is acquired because the heat flow caused by the temperature gradients greatly disturbs the AFM probe. The cooling of the sample was achieved by heat dissipation in air from the uncovered parts of the heater's copper plate. All images, presented below, were obtained at room temperature.

Results and Discussion

In order to observe the influence of the defects on the microsphere array melting process an area of the sample containing different types of defects (vacancy defects, intergrain cracks) was selected (Fig. 2a). No changes were observed in the microsphere ordering, nor around the grain boundary cracks or vacancy defects when heating the sample up to 75°C and cooling it down to room temperature (Fig. 2a). After the maximum temperature of the heating-cooling cycle was set to 99°C, the apparent RMS roughness of the ordered areas was diminished to 67% (Fig. 2b) with respect to the RMS roughness at the beginning (RMS roughness is defined as the standard deviation of the data from the best fit line). A small growth in the apparent particle size was observed on the edge of the grain.

After further temperature cycles increasing to a maximum of 112°C (Fig. 2c), the RMS roughness became 32% of the corresponding value of a fresh sample (Fig. 2c). At the same time, the array cluster boundaries became smoother. Another phenomena observed during the heating of the sample to 112°C is that the single microspheres, which are found over the arrays, become fixed (Fig. 3). This observation was made on another area of the sample several micrometers away from the area where ordered arrays were studied. The measurements were made simultaneously with heating cycles discussed above. On the freshly prepared sample, such particles can be moved by the AFM probe along the scanning axis, resulting in images with long strips of increasing height. After heating, the interaction between the single microparticle and the underlying array increased and the lateral component of the tip-particle interaction force was too small to move the microsphere.

In Figure 2d, the result of heating up to 120°C is

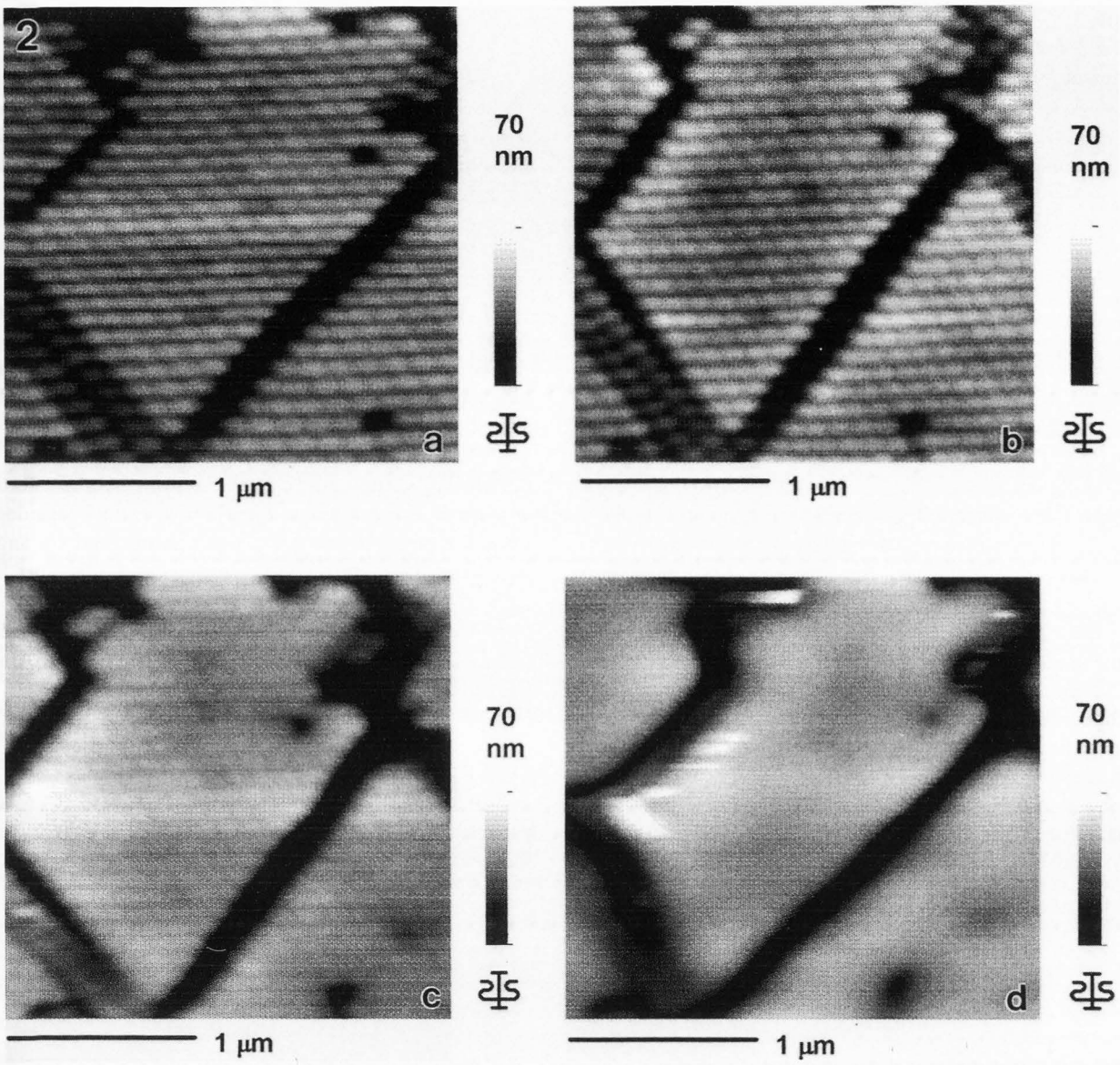

Figure 2 (above). Latex self-assembled arrays observed by AFM after heating to various temperatures: (**a**) 75°C; (**b**) 99°C; (**c**) 112°C; and (**d**) 120°C. Roughness changes, as well as array structure degradation, are clearly visible at higher temperatures. The latex particles show up distorted in Figure **2a** mainly due to the lateral drift of the sample during the acquisition of the image.

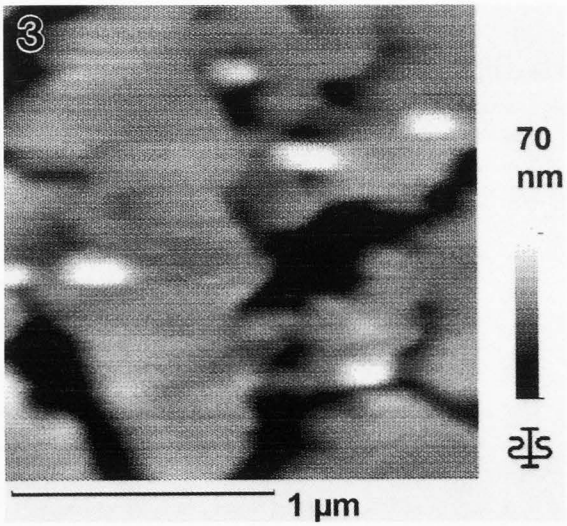

Figure 3 (at right). AFM image of single microspheres that were fixed on the microsphere array after heating to 112°C. This image was obtained several micrometers away from the area presented in Figure 2.

Table 1. RMS roughness values of polystyrene particle self-assembled array when heated up to different temperatures below the melting point.

Heating cycle maximum temperature (°C)	RMS roughness (nm)
75	6.5
99	4.3
112	2.1
120	< 1

shown. This image has changed dramatically with respect to the previous ones. The fine uniform ordered structure was no longer visible. Traces of this structure can be seen on the image at higher magnification, but the roughness of this trace is less than 1% of the fresh sample. The cluster edges become smooth and also the vacancy defects become the centers of much larger depressions. Nevertheless, the structure is almost the same, no clusters or grain boundary cracks were destroyed. The RMS height values for various heating cycle temperatures are presented in Table 1.

In conclusion, the ordered lateral structure of self-assembled latex arrays remain stable in all the range of temperatures from ambient to the softening point of polystyrene. Short-time heating of a polystyrene particle can be used to fix it onto a polystyrene surface or to attach it strongly to another particle without destroying the particle itself.

Acknowledgements

We wish to acknowledge P. Faraci and M. Scarselli for their help in mounting the temperature control system, D. Nardelli for the help in heater design, and Dr. M. Sartore for the helpful discussion and comments regarding this work.

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Editor's Note: All of the reviewer's concerns were appropriately addressed by text changes, hence there is no **Discussion with Reviewers.**