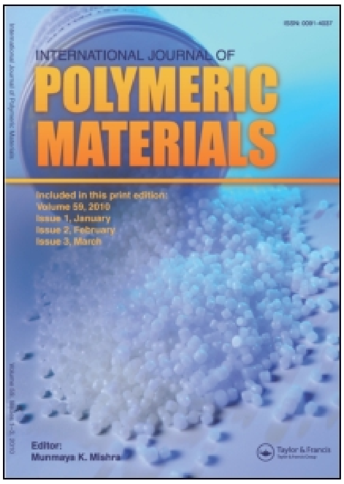

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Effect of Cu^{+2} Doping on the Nano-Scale Surface Roughness of Polyacrylamide Thin Replicas

Mukhles Sowwan[a]; Mayy Magalseh[a]; Imad Ibrahim[a]; Sami Makharza[a]; Wadie Sultan[b]; Hasan Dweik[b]
[a] The Nanotechnology Research Laboratory, Materials Engineering Department, Al-Quds University, East Jerusalem, Palestine [b] Department of Chemistry, Al-Quds University, East Jerusalem, Palestine

To cite this Article Sowwan, Mukhles , Magalseh, Mayy , Ibrahim, Imad , Makharza, Sami , Sultan, Wadie and Dweik, Hasan(2008) 'Effect of Cu^{+2} Doping on the Nano-Scale Surface Roughness of Polyacrylamide Thin Replicas', International Journal of Polymeric Materials, 57: 4, 396 — 403

To link to this Article: DOI: 10.1080/00914030701729099

URL: http://dx.doi.org/10.1080/00914030701729099

International Journal of Polymeric Materials, 57:396–403, 2008

ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030701729099

Effect of Cu^{+2} Doping on the Nano-Scale Surface Roughness of Polyacrylamide Thin Replicas

Mukhles Sowwan
Mayy Magalseh
Imad Ibrahim
Sami Makharza
The Nanotechnology Research Laboratory, Materials Engineering Department, Al-Quds University, East Jerusalem, Palestine

Wadie Sultan
Hasan Dweik
Department of Chemistry, Al-Quds University, East Jerusalem, Palestine

High sensitive non-contact tapping mode atomic force microscopy has been used to study the effect of Cu^{+2} doping on the nano-scale surface roughness of polyacrylamide replicas. The study was carried out by determining the root mean square roughness of the polymer surface as a function of doping concentration on glass substrates. Results show that doping with Cu^{+2} leads to the formation of multiscale features that increase in size and number with the doping concentration, which results in increasing the surface roughness.

Keywords: AFM, polymer replica, surface roughness

INTRODUCTION

Polymeric materials are widely used in replication technologies. The replication technologies such as polymer imprinting, casting, hot

Received 20 July 2007, in final form 30 July 2007.

The nanotechnology research laboratory at Al-Quds University, www.eng.alquds.edu/nrl, is supported by the German Research Foundation (DFG), French Academy of Sciences and French Ministry of Foreign Affairs.

Address correspondence to Mukhles Sowwan, The Nanotechnology Research Laboratory, Materials Engineering Department, Al-Quds University, East Jerusalem, Palestine. E-mail: msowwan@eng.alquds.edu, and Hasan Dweik, Department of Chemistry, Al-Quds University, East Jerusalem, Palestine. E-mail: hdweik@planet.edu

imposing, and injection molding are capable of reproducing microstructures over areas of many cm^2 at low cost. Examples of such microstructures produced in this way include compact discs (injection molding), holographic structures (hot embossing), and micro-optics gratings (casting) [1–4]. Generally, the properties of a replica system are strongly influenced by doping with metal ions. These properties include surface morphology and microstructure, electrical properties, surface chemistry, and mechanical properties. However, the surface of a polymeric replica system may have different chemical, physical, and mechanical properties from the bulk [5,6]. Thus, characterization of bulk material properties might not be sufficient for predicting performance. Consequently, techniques with high sensitivity to the surface physical and chemical properties are required. Atomic force microscopy (AFM) has emerged as a powerful technique to provide direct spatial mapping of surface topography and surface heterogeneity with nanometer resolution. Tapping mode AFM often reflects differences in the properties of individual components of heterogeneous materials, and is useful for compositional mapping in polymer blends, replicas, copolymers, and coatings [7–11]. Herein, we study the effect of Cu^{+2} doping on the nano-scale surface roughness of polyacrylamide thin replicas using contactless high sensitive tapping mode atomic force microscopy technique.

Materials

Polyacrylamide (PAam) with Mw 5,000,000 and copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), were purchased from Sigma-Aldrich Co. and used as received. All solutions were prepared in triple-distilled water. Mica sheet (V-5 grade) substrates were purchased from SPI suppliers Co, USA. Glass microscopic slides were purchased from Paul Marienfeld GmbH & Co, Germany.

EXPERIMENTAL

Polyacrylamide Doping with Cu^{+2} Metal Ions

Polyacrylamide complexation with Cu^{+2} ions was characterized by the spectroscopic techniques of FTIR, UV-vis, and DSC and reported previously [12].

Preparation of the Polymer Replicas

The polymer replicas were prepared in the following way. A droplet of 5 μL of liquid pre-polymer were deposited on a pre-cleaned glass

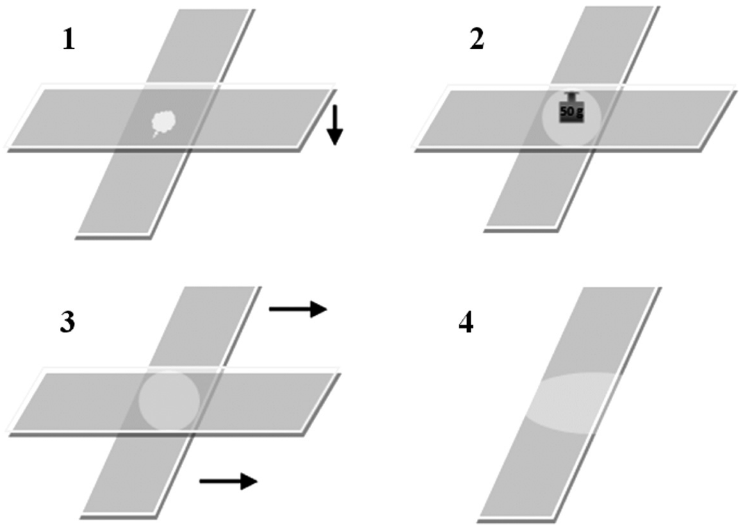

FIGURE 1 Schematic presentation of the polymer replica preparation procedure. **1**. A droplet of 5 μL of liquid pre-polymer were deposited on a pre-cleaned glass substrate surface. **2**. The substrate and a freshly cleaved mica sheet were pressed (0.5 N/cm^2) together for one minute. **3**. Sliding the mica sheet horizontally away from the glass surface with a constant speed of 0.5 cm/sec. **4**. Polymer replica on glass substrate.

substrate surface. Afterwards, the substrate and a freshly cleaved mica sheet were pressed (0.5 N/cm^2) together for a minute, followed by sliding the mica sheet horizontally away from the glass surface with a constant speed of 0.5 cm/sec, see Figure 1. The prepared replica on the glass substrate was dried in an oven at 35°C overnight. As a result, thin polymer layers of approximately 5 μm thickness, as estimated from the volume of the droplet and the surface area of the compressed polymer (diameter = 2.5 cm), were formed between the two surfaces.

Measurements

A scanning atomic force microscope and software designed by Nanotech Electronica Company (Madrid, Spain) was used for the surface roughness investigation [13]. A SiN tip with a resonance frequency in the range 190–325 KHz and force constant in the range of 5.5–22.5 N/m with tip diameter 10 nm was used as the AFM probe. Tips were purchased from NT-MDT Company (Russia). A set of five frames of equal sizes of certain scale was taken from different areas of each sample surface, and five different samples were tested. The root mean square (RMS) roughness of each frame size was the average of twenty-five measurements.

RESULTS AND DISCUSSION

AFM Measurements of Mica and Glass

A tapping mode AFM measurement with frame sizes of 2.5 μm, 2 μm, 1.5 μm, 1 μm, 600 nm, and 200 nm of freshly cleaved mica and cleaned glass were acquired. Figures 2a and 2b show AFM images with a 2.0 μm frame size (2.0 μm × 2.0 μm scanning area) for mica and glass, respectively. The corresponding roughness histograms are shown in

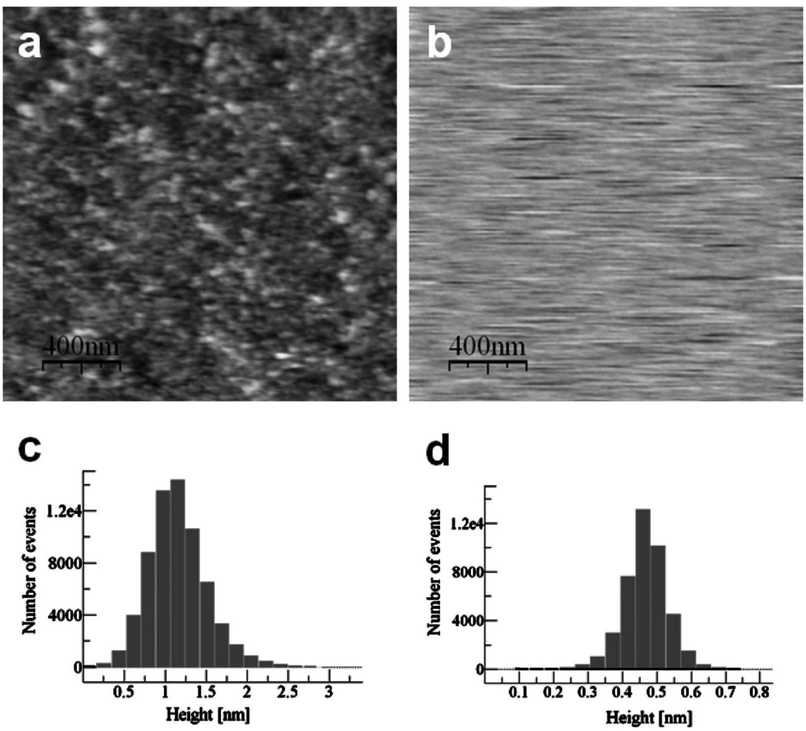

FIGURE 2 AFM topography images and roughness histograms (2μm × 2μm scanning area). **(a)** AFM topography image of glass surface. **(b)** AFM topography image of mica surface. **(c)** Roughness histogram of glass surface. **(d)** Roughness histogram of mica surface.

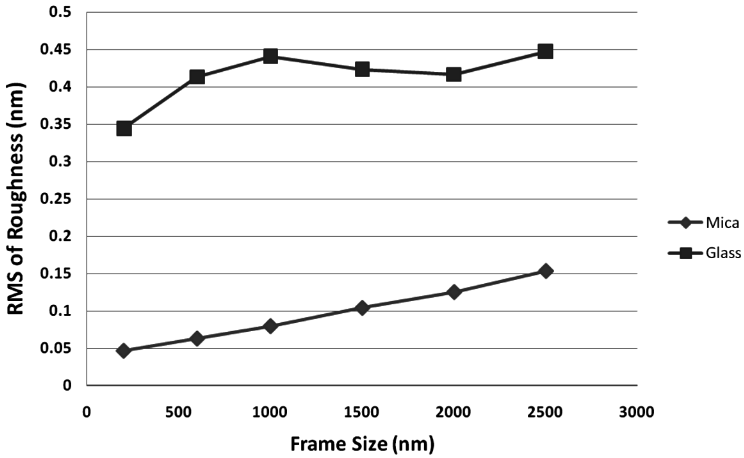

FIGURE 3 RMS roughness of mica and glass surface as a function of frame size.

Figures 2c and 2d respectively. The root mean square roughness as a function of frame size of the two kinds of materials are shown in Figure 3. The results show that there is negligible dependence on the frame size in the range 0.2–2.5 μm and the freshly cleaved mica is smoother than glass.

AFM Measurement of Cu^{+2}-Polyacrylamide Replica on Glass Substrates

AFM images with frame sizes of 2.5 μm, 2 μm, 1.5 μm, 1 μm, 600 nm, and 200 nm of polyacrylamide replica doped with Cu^{+2} with concentrations 0, 2.5, 5, 7.5, 10 and 15% (wt/wt) were acquired. Doping with Cu^{+2} leads to the formation of large-scale features; their number and size increase with increased doping concentration. Figure 4 (a–f) are AFM topography images of polyacrylamide doped with Cu^{+2} at different concentrations, on fixed frame size (1.5 μm).

The RMS roughness as a function of concentration for fixed frame sizes is shown in Figure 5. The RMS roughness as a function of frame size for fixed concentrations is shown in Figure 6. Results show that the surface roughness of the undoped polymer film is independent of the frame size. When increasing the Cu^{+2} concentration, the surface roughness increases but is still independent of the frame size up to 10% Cu^{+2} doping concentration. When the Cu^{+2} concentration is increased beyond 10% up to 15% for example, the surface roughness increases and becomes strongly dependent on the frame size.

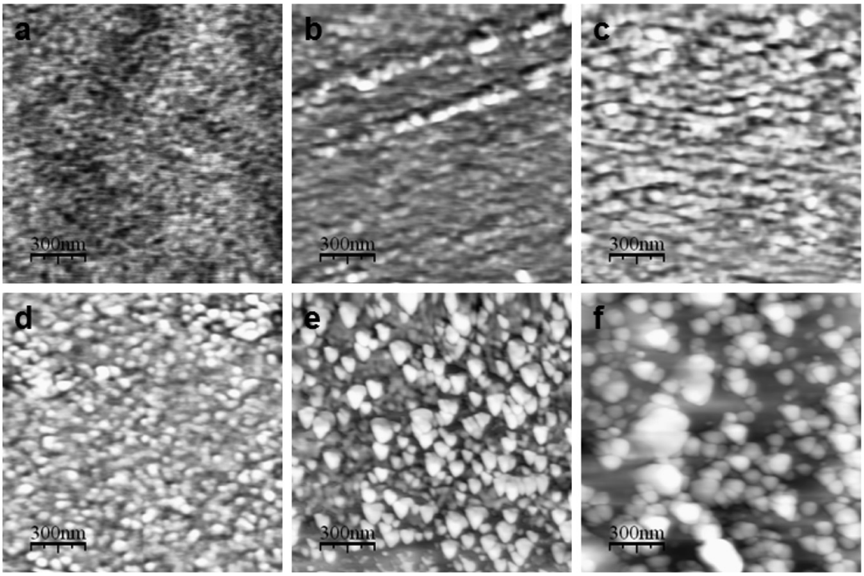

FIGURE 4 (a–f) AFM topography image polyacrylamide doped with Cu^{+2} at different concentrations (wt/wt), (**a**) 0%, (**b**) 2.5%, (**c**) 5%, (**d**) 7.5%, (**e**) 10% and (**f**) 15% at 1.5 μm frame size.

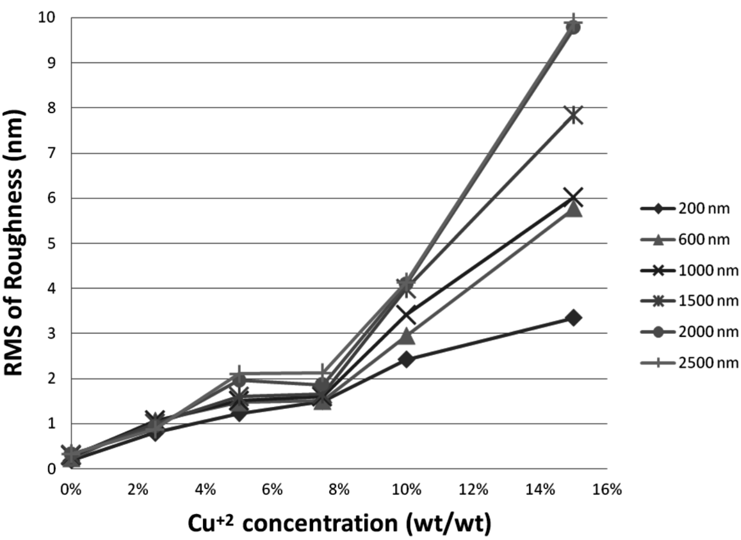

FIGURE 5 RMS roughness of polyacrylamide doped with Cu^{+2} as a function of doping concentration at fixed frame sizes.

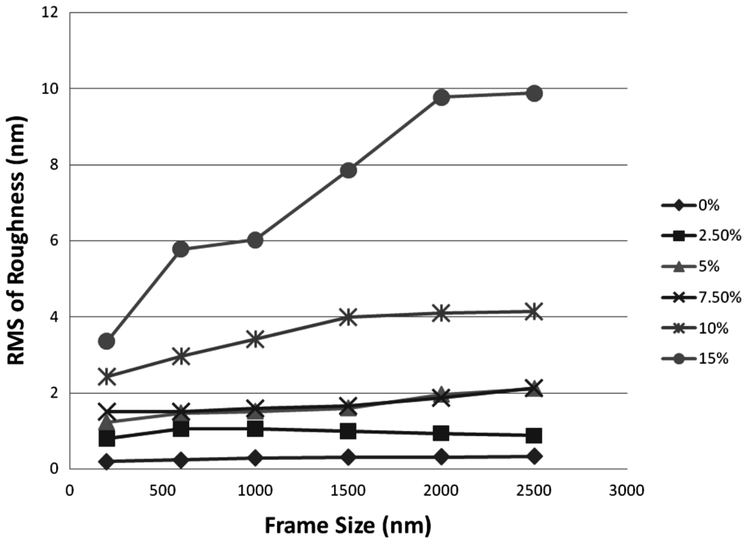

FIGURE 6 RMS roughness of polyacrylamide doped with Cu^{+2} as a function of frame size at fixed concentrations.

CONCLUSIONS

AFM investigation of polymer replica surfaces on glass substrate showed that the undoped polyacrylamide film successfully replicated the smooth mica sheet surface. When doped with Cu^{+2}, all polyacrylamide-prepared surfaces tend to have a multiscale relief structure. The main component of this structure is a low-scale Gaussian roughness. But there are various large-scale features, their size and number increase as a function of doping concentration and hence increase the root-mean-square roughness.

REFERENCES

[1] Jaszewski, R. W., Schift, H., Gobrecht, J., and Smith, P., *Microelectronic Eng.* **41/42**, 575 (1998).
[2] Chou, S. Y., Krauss, P. R., and Renstrom P., *J. Appl. Phys. Lett.* **67**, 3114 (1995).
[3] Gale, M. T. (1997). In *Micro-Optics: Elements, Systems and Applications*. H. P. Herzig, Ed., Taylor and Francis, London, pp. 153–177.
[4] Hannan, W. J., Flory, R. E., Lurie, M., and Ryan, R. J., *J. SMPTE* **82**, 905–915 (1973).
[5] Ebbens, S. J. and Badyal, J. P. S., *Langmuir* **17**, 4050 (2001).
[6] Chen, X., McGurk, S. L., Davies, M. C., Roberts, C. J., Shakesheff, K. M., Tendler, S. J., and Williams, P. M., *Macromolecules* **31**, 2278 (1998).

[7] Cleveland, J. P., Anczykowski, B., Schmid, A. E., and Elings, V. B., *Appl. Phys. Lett.* **72**, 2623 (1998).
[8] Raghavan, D., Gu, X., Nguyen, T., Vanlandingham, M. R., and Karim, A., *Macromolecules* **33**, 2573 (2000).
[9] Raghavan, D., Gu, X., Nguyen, T., and Vanlandingham, M. R., *J. Polym. Sci. Polym Phys.* **39**, 1460 (2001).
[10] Gu, X., Raghavan, D., Nguyen, T., and Vanlandingham, M. R., *Polymer Degradation and Stability* **74**, 139 (2001).
[11] Bar, G., Thomann, Y., Brandsch, R., and Cantow, H. J., *Langmuir* **13**, 807 (1997).
[12] Dweik, H., Sultan, W., Sowwan, M., and Makharza, S., *Intern. J. of Polymeric Mater.* accepted for publication.
[13] Horcas, I., Fernandez, R., Gomez-Rodriguez, J. M., Colchero, J., Gomez-Herrero, J., and Baro, A. M., *Rev. Sci. Instrum.* **78**, 013705 (2007).