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Manipulation of low temperature grown ZnO rigid structures via Atomic Force Microscope

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Abstract

In this work, we present the manipulation of zinc oxide microrods grown through aqueous chemical growth method via atomic force microscopy (AFM). The synthesized rods are found to strongly adhere to the silicon substrate, thus allowing for a raster AFM scan to be obtained. During manipulation, the oscillating cantilever is brought near the rod while the z-scanner feedback is disabled, until its oscillation amplitude reached 1-5% of the initial value. The rods are moved to desired locations which were verified by the imaging capability of AFM. In line with this, the motion of the cantilever followed a drawn path as was done in AFM lithography. In this way, the manipulation forces can be measured and analyzed. In terms of applications, the AFM manipulation technique could enable the fabrication of sophisticated zinc oxide based micro- and nano-devices, which would be of potential use in the fields of atomic-scale and nanostructure-based device integrations.

Keywords

Zinc Oxide, Microstructures/Microrods, Aqueous Chemical Growth, AFM Manipulation

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Introduction

Over the years, the utilization of controlled manipulation methods became increasingly popular as in opens a wide range of possibilities in the construction of novel atomic-scale devices and materials. Among these, the atomic force microscopy (AFM) [1]-[3], by virtue of its nanometer resolution and usability at room temperature, has found significant applications in the manipulation of metal and semiconductors nanoparticles [4]-[5], carbon nanotubes [6], and biological specimens [7]-[8]. In addition, AFM manipulation could also be used in constructing electrical contacts as in the case of carbon nanotubes [6].

One of potential nanomaterials important in the growing field of micro and nanoelectronicsis zinc oxide (ZnO). Manipulation of ZnO nanostructures makes it possible to encapsulate and characterize individual properties of the material. This could pave the way for improvements in the fields of medicine and biotechnology, where controlled manipulation could be used in studying cell adhesion and for the assembly and fabrication of nanosensors [9]-[10].

The AFM is a tip-based device that allows different forms of imaging: topography, phase contrast, and force spectroscopy, among others. For nanoparticles characterization, AFM has been utilized to measure piezoelectric voltages of ZnOnanorods by straining one end of the rod [11]-[12]. In a similar manner, deformation of nanobelts and nanobows has been achieved in measurement of forces [9]. However, up to this point, there has been no quantitative measurement that has been undertaken in order to analyze the involved mechanisms in the AFM manipulation of ZnO rods.

In this work, we fabricated ZnOnanorods using the aqueous chemical growth (ACG) technique at normal atmospheric pressure and low temperature without any catalyst. The synthesized ZnOnanorods were successfully imaged and manipulated via AFM. We then described two ways to manipulate ZnO structures and discussed the concepts involved during manipulation. Lastly, we gave an estimate of the magnitude of the force between the substrate and ZnO rod. With these, it is aimed to demonstrate a semicontact mode-based AFM manipulation method, with good repeatability and measurable parameters.

Experimental Details

The synthesis of ZnO rods was carried out via the ACG method with the following steps. Equimolars of ($Zn(CH_3COOH)_2 \cdot 2H_2O$: HMT;$C_6H_{12}N_4$) were dissolved in 80 mL distilled water. The Si(100) substrate was placed inside the solution, and was heat-treated. Solutions are covered with aluminum foil and heated at 95^{o}C for several minutes using a programmable temperature controller hotplate. Substrate with synthesized ZnO structures was removed, rinsed with DI water for several times, and annealed at 500^{o}C for 20 minutes.

As a preparation to the manipulation process, the rods were dispersed on a clean Si substrate and air dried for at least 24 hours, through sonication in acetone. Manipulation of ZnO rods was done using NT-MDT Solver Pro-M Atomic Force Microscope operating in the semi-contact mode configuration, and employing a piezoscanner with a maximum range of 100 x 100 μm^2 along the X and Y and 10 µm along Z. It is equipped with capacitive displacement sensors with feedback on each axis to reduce the drift and nonlinearity. A NGS-01 gold-coated silicon probes tip was used during image scan and manipulation. The normal and torsional force constants of the cantilevers are, respectively, 0.783N/m and $1.325X10^{-10}$ Nm measured using the technique developed by Sader et al.[13]. An AFM image was first obtained to know the location of the ZnOnanorods to be manipulated. In the first process of manual manipulation, the feedback system of the AFM was turned off, and the scanner was withdrawn from the substrate. The amplitude of oscillation of the scanner length was extended at around 5% of its free oscillation. This procedure would imply that a stronger force is applied to the cantilever compared when doing AFM imaging. The scanner is then moved in X and Y directions to displace the ZnOnanorods.

Furthermore, manipulation of ZnOnanorods can be done using lithography mode of the AFM. The feedback gain of the AFM was set to 0.001 in order to prevent the system to detect possible change in topography immediately. This was done for the system to perform manipulation. The vector lithography mode was used during the manipulation process. Vector lithography allows us to create a pattern of points and lines for the system to follow and used a frequency of 0.03 Hz. During the displacement of the tip towards the starting point of the pattern, the default set point value during the system approach was used. And during lithography (mode used to manipulate the ZnOnanorods), a set point value of 0.01 - 0.5 nA was used. These values are optimized to ensure successful manipulation of ZnOnanorods.

Results and Discussion

The ZnOnanorods were successfully synthesized using ACG on Si substrates. Figure 1 shows the SEM images of synthesized ZnO. It is observed that the synthesized ZnOnanorods have a cleavage in the middle, which could possibly indicate that ZnO rods nucleated from the middle, and continued to grow on both sides. The length and diameter of ZnOnanorods ranges from 4.47 to 6.79 μm and 0.44 to 1.18 μm, respectively. Figure 2 shows the XRD spectra of the as synthesized ZnOnanorods. Crystal orientation seen at (100), (101) and (110) shows that the as grown ZnO structures have hexagonal-wurtzite crystal structure (in accordance with JCPDS-36-1451). The computed lattice parameters *a* and *c* for the ZnOnanorods are 3.23 Å and 5.10 Å, respectively. No significant peaks from other phases or chemicals that may be due to impurities were observed.

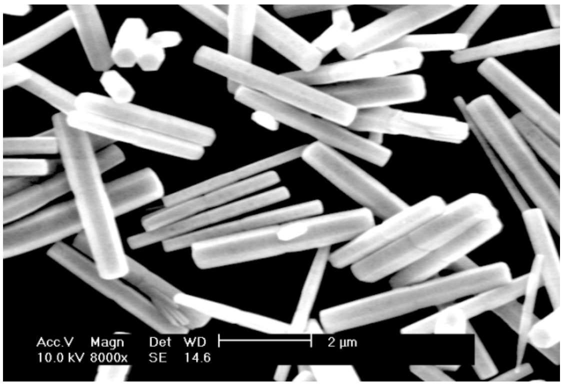

Figure 1: SEM image of the as grown ZnOnanorods on Si (100).

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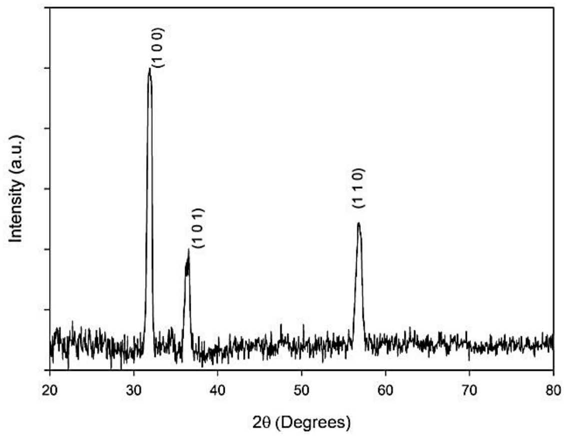


Figure 2: XRD spectra of the as grown ZnO showing peaks at (100), (101) and (110).

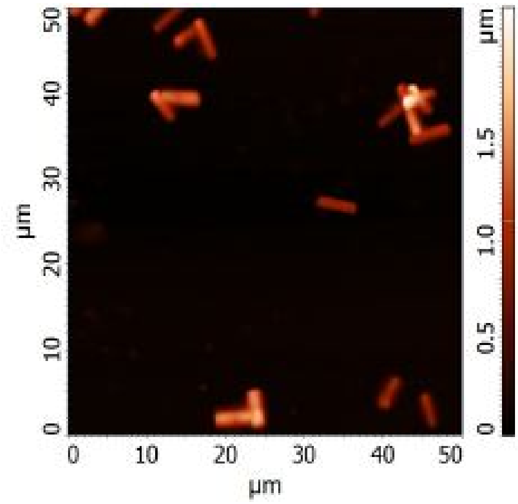
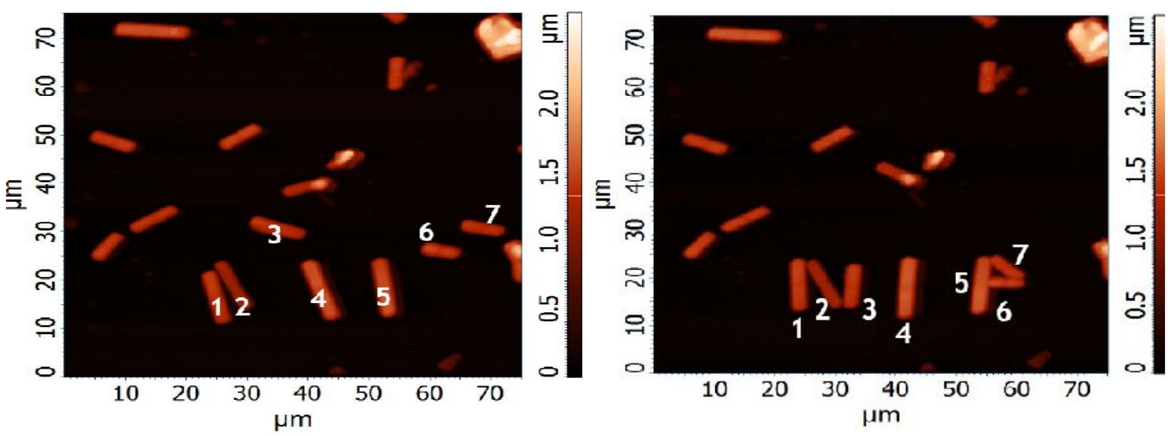


Figure 3: AFM image of the dispersed Zno rods on Si(100) done in semicontact mode.



(a) (b)

Figure 4:Screen snap shots of the(a) before and (b) after performing vector lithography to manipulate ZnOnanorod.

A semicontact mode AFM image of dispersed ZnO rods on Si(100) substrate is shown in Figure 3. It can be noted that the obtained image is relatively discernible, which is related to the stronger adhesion of the rods to the substrate compared to the forces applied by the tip along the X fast scan direction. As such, the rods can be held in place firmly during the raster scan. In comparison, it was found that for as-grown annealed samples grown by ACG method, as well as carbothermal reduction at 900°C sprinkled on Si substrate [14] did not show the same discernible image as Figure 3. This could be explained by the weak adhesion of the rods on the substrate, displacing the rods along the substrate during scanning. Furthermore the heat treatments could have dried the surface of the substrate, thus limiting the interaction of the rods with the substrate. Thus, it is noted that suspension of the rods in acetone is necessary for the rods to achieved good adhesion with the substrate. Going back to Figure 3, the blurred edges observed for some rods specifically those at the lower part of the figure could be traced to slight movements such as rotation of the rods, or the interaction of the suspension layer with that of the tip.

Figure 4 shows ZnO rods configuration before (a) and after (b) AFM manipulation around a 100x100 μm^2 region. The manipulation process was carried out in semicontact mode, with the operator controlling the tip's path. Here, an initial scan is made, wherein the z-feedback system was disabled thereby automatically retracting the cantilever from the substrate. Then the probe is moved along the x and y directions in such a way that it is very near a rod. The oscillation amplitude of the cantilever was decreased to 1-5 % of the setpoint value during imaging. This was done by increasing the voltage across the z component of the piezo scanner. Afterwards, the rods are pushed to the desired location by the tip across the substrate. The AFM was switched back to semicontact imaging mode after the manipulation.

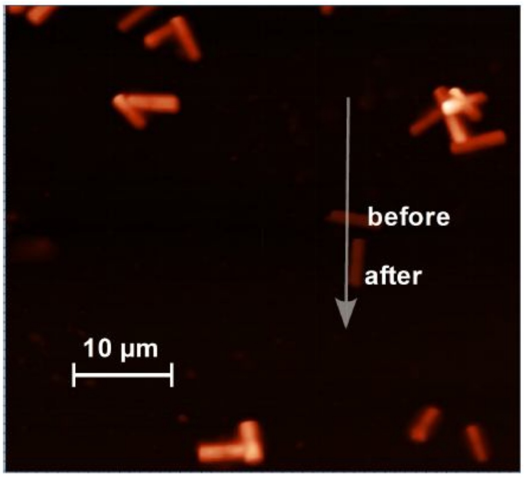


Figure 5:Semicontact mode lithography manipulation of ZnO rods. The before and after manipulation images are superimposed. The arrow points to the path of the tip and cantilever during manipulation process. It should be noted that the initial position of the rod is also shown in Figure 2.

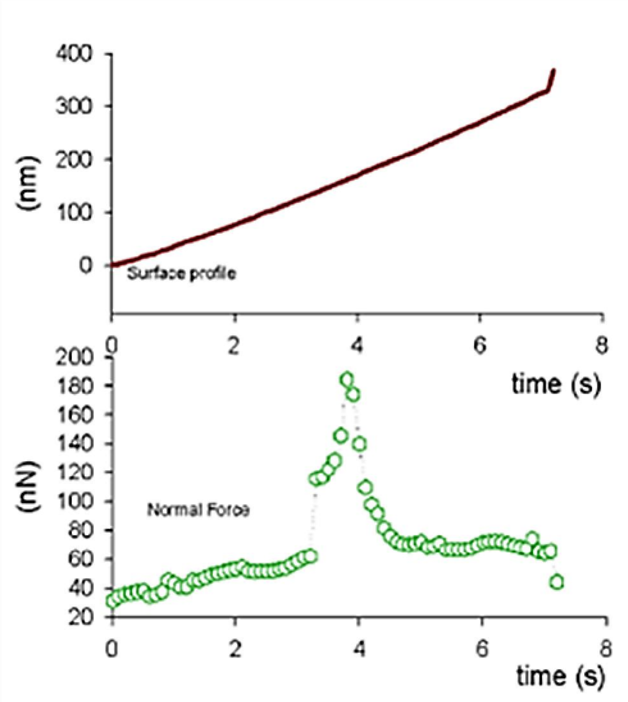


Figure 6: Surface topography (top plot) of the path shown in Figure 4 and the normal force (bottom plot) measured during lithographic manipulation.

Manipulation via the semicontact mode vector lithography was done with a predrawn path for the tip, and the resulting superimposed images of before and after manipulation is shown in Figure 5. The feedback gain coefficient was set to the lowest possible values by closing the feedback loop for the z-scanner. By using this setting, a strong tip-substrate contact for most of the lithography line is maintained, and at the same time keeping the scanner from following the sharp topography of the rod.

One advantage of the lithographic technique is that the measurement of the force applied by the cantilever on the rod can be done through analysis of the cantilever deformation signal. As shown in Figure 5, the topography traces the tilted silicon substrate surface but no indication of the rod's profile. The rod was pushed by the tip parallel to the substrate plane in the entire duration of the manipulation. It can be seen that at the highest profile, there is a small hump, and the scanner slightly is able to respond to the rod's topography. The force versus time plot was obtained from the photodiode signals that correspond to normal cantilever bending. The calibration constants were derived from force-distance spectroscopy curves and from the cantilever normal spring constant. Lateral force signal is also collected during the manipulation process shown in Figure 5, but as was discussed in [15], it is difficult to account for the cross-talk between the normal bending of the cantilever and the lateral force signal measured by the photodiode. This is due to the fact that its order of magnitude is comparable to the lateral force change during the force-distance curve spectroscopy. The peak observed in Figure 6 signals the contact between AFM tip and rod. This peak appears to be a combination of two adjacent peaks, which could be deduced from factors affecting the force versus time profile. The rod's center has moved and has rotated by about 90 degrees. Another is that frictional force is applied between the tip and rod. Lastly, the frictional force between substrate and rod is not necessarily constant. The peak estimates an average shear force value of 70 nN.

A softer cantilever (CSG10, typical force constant of 0.11 N/m) was used, and it was found that the rods didn't move even during raster scanning in contact mode imaging. This implies that the manipulation process is possible only at specific range of applied forces. It is interesting to note that the rod can undergo several manipulation cycles and still adhere firmly to the substrate during image scanning. Furthermore, the rods are still intact even after being exposed in ambient atmosphere for seven days. It might be that the strong adhesion between the substrate and the rod could be attributed to water present in the suspension fluid that is strongly bound to ZnO rods, which has a dipole moment because of different edge terminations.

Conclusion

AFM semicontact mode based manipulation of ZnOnanorods was successfully done by manually controlling the system and by performing vector lithography. The applied shear force by the cantilever and the substrate on the rods was obtained via AFM. Realization of precise and controlled movement of ZnO rods promises potential application in optics and nano-electronics, as well as in nano-biotechnology. Consideration of interaction forces such as capillary, van der Waals and electrostatic forces between the nanoparticle and substrate should be noted well in the choice of appropriate cantilever properties and suspension material.

Acknowledgements

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References

[1] H.Xie and S. Régnier. Journal of Micromechanics andMicroengineering 19 075009(2009)

[2] S. Decossas, L. Patrone, A.M. Bonnot, F. Commin, M. Derivaz, A.Barski and J. Chevrier. Surface Science 543 57–62 (2003)

[3] P.M. Letvyn, O.Y. Olikh, O.S. Lytvyn, O.M. Dyachyns'ka, and I.V. Prokopenko.Semiconductor Physics, Quantum Electronics & Optoelectronics 13 1 36-42 (2010)

[4] T. Junno,K. Deppert, L. Montelius, and L. Samuelson, Applied Physics Letters 66 3627 (1995)

[5] H.-F. Zhang, C.-M. Wang, E. C. Buck and L.-S. Wang. Nano Letters 3 577 (2003)

[6] Y. Kashiwase, T. Ikeda, T. Oya and T. Ogino. Applied Surface Science 254 7897(2008)

e-ISSN: 2321-1814, ISBN (Print): 978-1-62951-780-3

[7] D. Fotiadis, S. Scheuring, S.A. Müller, A. Engel, D. J. Müller. Micron 33 385 (2002)

[8] R. M. Henderson and H. Oberleithner. American Journal of Physiology-Renal Physiology 278 F689 (2000)

[9] J. Lee, B.S. Kang, B. Hicks, T.F. Chancellor, B.H. Chu, H.-T. Wang, B.G. Keselowsky, F. Ren and T.P. Lele. Biomaterials 29 3743–3749 (2008)

[10] B.H. Chu, J. Lee, C.Y. Chang, P. Jiang, Y. Tseng, S.J. Pearton, A. Gupte, T. Lele, F. Ren. Applied Surface Science 255 8309 - 8312 (2009)

[11] M.-H. Zhao, Z.-L. Wang and S. X. Mao.Nano Letters4 587 (2004)

[12] J. Song, J. Zhou, and Z. L. Wang.Nano Letters 6 1656 (2006)

[13] C.P. Green, H. Lioe, J.P. Cleveland, R. Proksch, P. Mulvaney, J.E. Sader. Review of Scientific Instrumuments 75 1988 -1996 (2004)

[14] E.R. Magdaluyo, I.H.J. Arellano, A.K.G. Tapia, R.V. Sarmago, L.M. Payawan, Advanced Materials Research31 92 (2007)

[15] M. Munz, Journal of Physics D: Applied Physics43 063001 (2010)