Nanometre resolution using high-resolution scanning electron microscopy corroborated by atomic force microscopy

Sam M. Stevens,[ab] Pablo Cubillas,[a] Kjell Jansson,[b] Osamu Terasaki,[b] Michael W. Anderson,*[a] Paul A. Wright[c] and María Castro[c]

Received (in Cambridge, UK) 14th March 2008, Accepted 7th May 2008
First published as an Advance Article on the web 26th June 2008
DOI: 10.1039/b804440f

The resolving power of high-resolution scanning electron microscopy was judged using topographical height data from atomic force microscopy in order to assess the technique as a tool for understanding nanoporous crystal growth.

Microscopy is a crucial tool in the arsenal of the crystal-growth chemist. According to the resolution available access is gained to different types of information. For crystals of substantial size relative to the wavelength of light, average morphology is readily obtained with optical microscopy. However, in the study of crystal growth much finer detail is often required. The early stages of crystallisation necessarily deal with small, sub-micron crystals. But, further, the intricacies of the molecular processes involved can only be revealed by observation at the nanometre scale. Atomic force microscopy (AFM) is usually the method of choice for observing these fine topographic details on crystal surfaces with the technique amenable to operation under solution as well as in air. AFM, while yielding phenomenal vertical resolution at the ångstrom scale is, however, a rather slow and laborious technique and not suitable to all crystal surfaces. Consequently, there is the perennial microscopist's problem that observation may be focussed on curiosities rather than average features. There is an urgent need, therefore, for a fast, robust technique for scanning large numbers of crystals whilst retaining the nanometre-scale resolution. Here we report substantial progress in the deployment of *high-resolution* scanning electron microscopy (HRSEM) to solve this problem. We demonstrate, by careful *ibidem* ("in the same place," *i.e.* same crystal, same coordinate) measurement by HRSEM and AFM of nanometre features on the surface of a zeotype crystal, STA-7, and the aluminosilicate, zeolite A, the vertical resolution that may be obtained on important nanoporous crystals.

Scanning electron microscopy (SEM) has long been used as a method for observing the surface morphology of crystals. The interaction of an electron with a crystal also yields a broader range of information such as compositional information as a quantifiable spectrum or contrast image by detecting backscattered electrons and characteristic X-rays, respectively. Topographic contrast, generated by the detection of secondary electrons ejected near the specimen surface, provides an image that is interpreted by the user as a magnified image of the specimen source.

The ability to navigate efficiently around a sample surface coupled with the large available range of magnification, rapid acquisition of images at TV-scan speeds and ease of operation of a SEM makes observation of a crystal population size, shape and distribution readily achievable for the overwhelming majority of crystal systems.[1]

With the advent of HRSEM, where nanometre features may now be observed,[2] the goal for combining all the advantages of SEM mentioned above with a vertical resolution comparable to AFM is close. In this work we observe the surfaces of nanoporous crystals related to zeolites. These materials are electrically insulating making study by electron microscopy particularly challenging as this results in charging of the specimen and thus a loss of surface detail. The most common approach to deal with this problem has been to sputter crystals with metal particles which increase the secondary electron yield and reduce charging effects.[3] However, such particles are of the same magnitude in size as the features to be observed.[4] New SEMs with reduced aberration coefficients and more sensitive electron detection systems allow for lower accelerating voltages to be used, thus eliminating the need for surface sputtering. This combined with the incorporation of field emission electron sources into SEMs (FE SEMs) had led to HRSEM of insulating materials being possible. HRSEM applied to zeolites is a technique still in its infancy and reports have shown the observation of the appearance of terraces on a zeolite surface.[2,5] In the current work we take this a step further by measuring the vertical resolution through *ibidem* HRSEM/AFM measurements and show that individual terraces on a crystal are distinguishable using HRSEM.

Ibidem measurements have been performed before; SEM with integrated AFM has been done, however, HRSEM is not yet possible in this configuration owing either to the presence of water vapour in the system as the SEM is 'environmental' in nature[6] or because the SEM creates contamination on the material surface and thus causes problems between surface and AFM probe tip.[7] *Ex situ* measurements have also been performed, but never to the same degree of resolution or applied to nanometre surface growth features.[8]

[a] *Centre for Nanoporous Materials, School of Chemistry, The University of Manchester, Chemistry Building, Oxford Road, Manchester, UK M13 9PL. E-mail: sammichaelstevens@mac.com; Fax: +44 161 275 4598; Tel: +44 161 306 4527*
[b] *Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden. Fax: +46 8 16 3118; Tel: +46 8 16 2379*
[c] *School of Chemistry, University of St. Andrews, Purdie Building, North Haugh, St. Andrews, Fife, UK KY16 9ST. Fax: +44 133 446 3808; Tel: +44 133 446 3793*

 This journal is © The Royal Society of Chemistry 2008

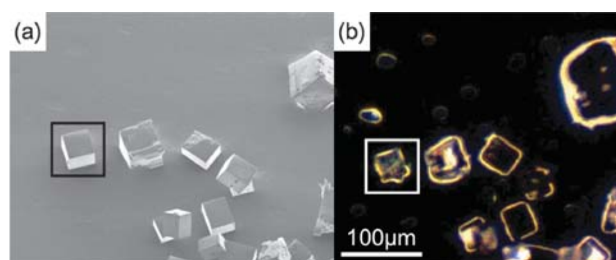

Fig. 1 Optical image (b) used to locate the particular crystal (highlighted with box) with AFM for *ibidem* measurements that has been located with SEM (a).

STA-7, an aluminophosphate zeotype with the framework code **SAV**,[9] was synthesised according to the co-templating method recently reported[10] giving single crystals with tetragonal morphology and dimensions of 30 µm. Molar, chemical composition of the SAPO crystals was 24Al : 7.2Si : 16.8P : 96O. HRSEM images were taken on a JEOL JSM-7000F which has a quoted nominal lateral resolution of 3.0 nm at 1 kV. The crystals were embedded in a conducting adhesive, and were left uncoated. After imaging in the HRSEM the crystals were transported using the same sample support into a Nano-wizard atomic force microscope (JPK Instruments A.G.). The same crystal was identified by optical microscopy and scanned in tapping mode using a high aspect ratio tip with a nominal tip-radius of <10 nm (Fig. 1).

AFM and HRSEM imaging of STA-7 crystals reveal the presence of multiple growth spirals on the {100} and {001} faces. Fig. 2 shows *ibidem* HRSEM and AFM images (a to e) of a growth spiral on the {001} face of an STA-7 crystal. It is noteworthy that the images are both in proportion with one another and only a simple change in the image size and aspect ratio of the HRSEM image was required to produce the resulting figure. Alteration of the HRSEM in preference to the AFM image was performed because in the AFM there is little angle between the surface tip and tip axis but in HRSEM the crystal surface is at an angle to both the secondary electron detector and optical axis of the microscope and thus an element of perspective in the resultant image is expected. The overall shape of the spiral, as well as numerous terraces, are clearly visible in the HRSEM image (Fig. 2a and b). Whilst the degree of overlap and level of detail is remarkable, the centre of the spiral is not resolved as the comparison with the AFM deflection image (Fig. 2c) indicates. Cross sections taken from the AFM height images of STA-7 show that the heights

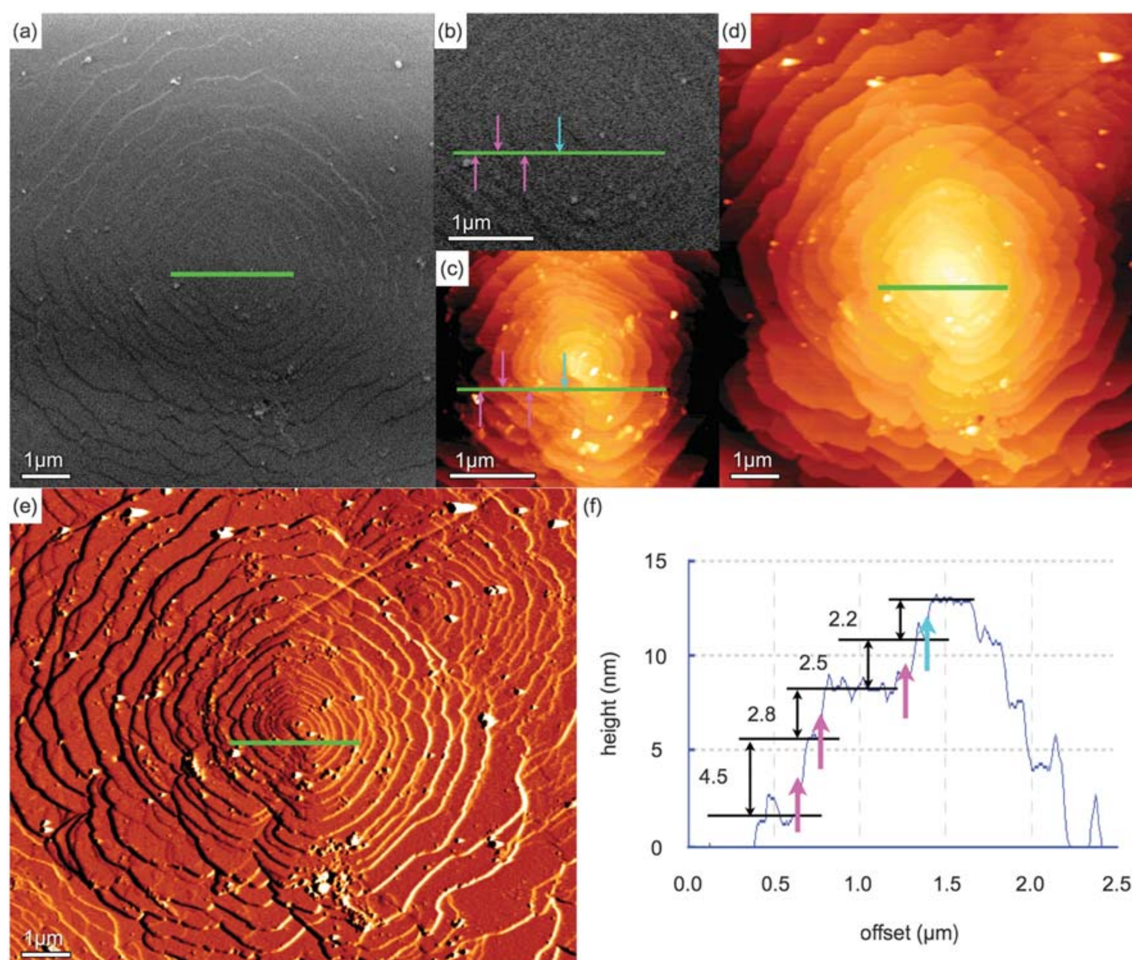

Fig. 2 *Ibidem* high-resolution scanning electron microscopy (a,b) and atomic force microscopy (height c,d, error e, and cross section, f) measurements on STA-7. (b) and (c) show magnified images of the central spiral region where the resolution of the HRSEM reaches its limit. Green lines represent the AFM cross-section (f) showing heights of terraces measured by AFM and visible in the HRSEM.

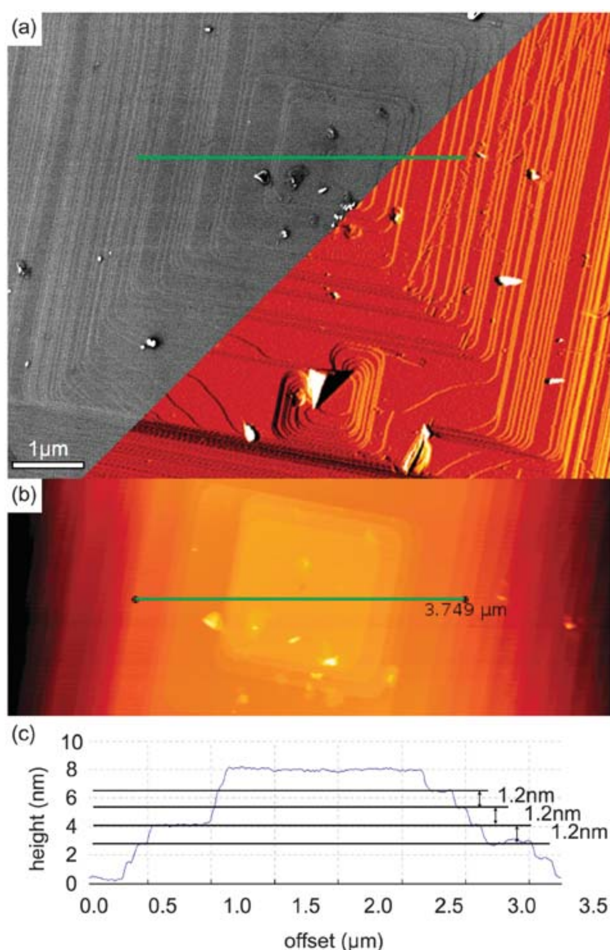

Fig. 3 *Ibidem* high-resolution scanning electron microscopy and atomic force microscopy measurements on zeolite A: (a) split-screen HRSEM/AFM deflection image of (100) surface; (b) AFM height image with region chosen for cross-section (shown with green line); (c) cross section showing 1.2 nm terraces.

of the spiral terraces decrease towards the centre of each spiral with a minimum height of 0.9 nm. The range of terrace heights is caused by the coalescence of multiple terraces into a larger terrace which is why all terrace heights observed were in multiples of 0.9 nm. The HRSEM was able to observe larger terraces but unable to observe the smallest terraces located towards the centre of each spiral where the resolving limit of the HRSEM had been reached.

Fig. 3 shows a similar study on the aluminosilicate zeolite A synthesized by the Charnell method,[11] with a molar ratio $1Na_2O : 1Al_2O_3 : 2SiO_2 : xH_2O$. Both the AFM and the HRSEM (performed on a JSM-7401F with a quoted lateral resolution of 1.5 nm at 1 kV) show extremely well-defined terraces with a consistent step height of 1.2 nm. Consequently, on this crystal the vertical resolution is approaching 1 nm. There are a number of differences between STA-7 and zeolite A which might give rise to this substantially improved vertical resolution in zeolite A over STA-7. The chemical make-up of the two structures is different which may result in different charging effects. Also, in zeolite A the terraces are somewhat further apart and the edges are rectilinear rather than round. We suggest that as well as a high resolving power of the microscope, the nature of nanometre steps as surface protrusions are therefore susceptible to an increased emission of secondary electrons known as the edge effect,[12] and here it is being positively exploited to illuminate surface topography and other important features.

In conclusion, we have demonstrated that it is possible to achieve near nanometre vertical resolution of topological features on the surfaces of nanoporous crystals. The resolution is sufficient to observe signature features of fundamental growth processes.

We wish to thank The Knut and Alice Wallenberg Foundation, EC Marie-Curie Research Training Networks 'INDENS' (MRTRN-CT-2002-005503) and the EPSRC and ExxonMobil Research and Engineering for financial support and L. Itzel Meza for the LTA sample.

Notes and references

1 A. Kuperman, S. Nadimi, S. Oliver, G. A. Ozin, J. M. Garces and M. M. Olken, *Nature*, 1993, **365**, 239–242; X. Yang, D. Albrecht and J. Caro, *Microporous Mesoporous Mater.*, 2006, **90**, 53–61.
2 T. Wakihara, Y. Sasaki, H. Kato, Y. Ikuhara and T. Okubo, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3416–3418.
3 S. Bazzana, S. Dumrul, J. Warzywoda and A. Sacco, Jr, *Microporous Mesoporous Mater.*, 2006, **92**, 165–172.
4 I. Stokroos, D. Kalicharan, J. J. L. Van Der Want and W. L. Jongebloed, *J. Microsc.*, 1998, **198 pt.1**, 79–89.
5 S. Bazzana, S. Dumrul, J. Warzywoda, L. Hsiao, L. Klass, M. Knapp, J. A. Rains, E. M. Stein, M. J. Sullivan, C. M. West, J. Y. Woo and A. Sacco, Jr, *Stud. Surf. Sci. Catal.*, 2002, **142A**, 117–124.
6 I. Joachimsthalter, R. Heiderhoff and L. J. Balk, *Meas. Sci. Technol.*, 2003, **14**(1), 87–96.
7 K. Fukushima, S. Kawai, D. Saya and H. Kawakatsu, *Rev. Sci. Instrum.*, 2002, **73**(7), 2647–2650.
8 A. G. Bitterman, S. Jacobi, L. F. Chi, H. Fuchs and R. Reichelt, *Langmuir*, 2001, **17**, 1872–1877; T. Vijaykumar, N. S. John and G. U. Kulkarni, *Solid State Sci.*, 2005, **7**, 1475–1476.
9 P. A. Wright, M. J. Maple, A. M. Z. Slawin, V. Parinec, R. A. Aitken, S. Welsch and P. A. Cox, *J. Chem. Soc., Dalton Trans.*, 2000, 1243–1248.
10 M. Castro, R. Garcia, S. J. Warrender, A. M. Z. Slawin, P. A. Wright, P. A. Cox, A. Fecant, C. Mellot-Draznieks and N. Bats, *Chem. Commun.*, 2007, 3470–3472.
11 J. F. Charnell, *J. Cryst. Growth*, 1971, **8**, 291–294.
12 L. Reimer, *Image Formation in Low-Voltage Scanning Electron Microscopy*, SPIE – The International Society for Optical Engineering, Bellingham, Washington, USA, 1993.

 This journal is © The Royal Society of Chemistry 2008