Sub-Ångstrom Imaging of the six-membered rings in Si_3N_4 by C_s-corrected HRTEM

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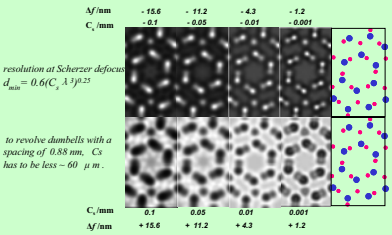
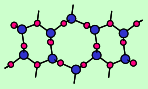
I. Image calculations with different C_s along Si_3N_4 [000-1]

I-A. C_s required to resolve the Si-N dumbbells in Si_3N_4



Atomic model of β - Si_3N_4

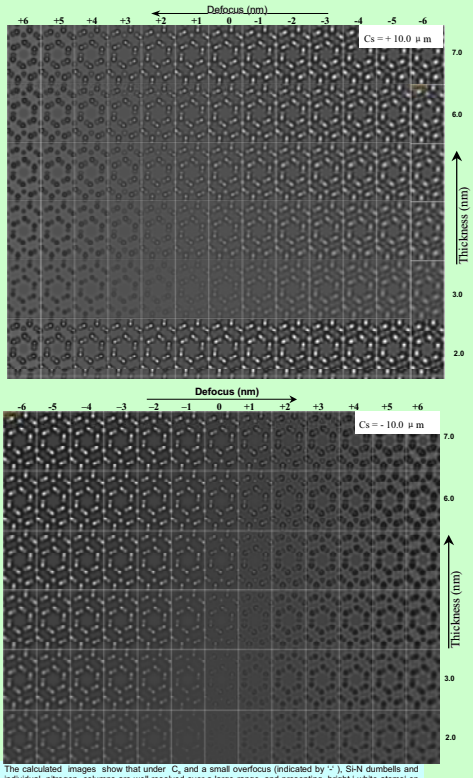


Si and N atom arrangements in dumbbells of the six-membered ring are counter-clockwise.

Lattice constants:
a=b= 7.608(5), c= 2.911(1). Hexagonal (P 6$_3$/m, No.176)

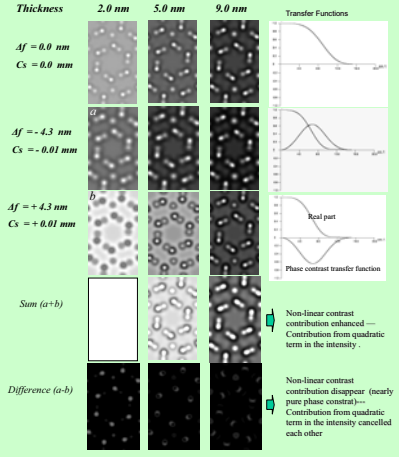
Ref. Wild, S; et al., Special Ceramics (1972), 5, 385-395.

I-B. Image calculation under the symmetrical C_s and defocus



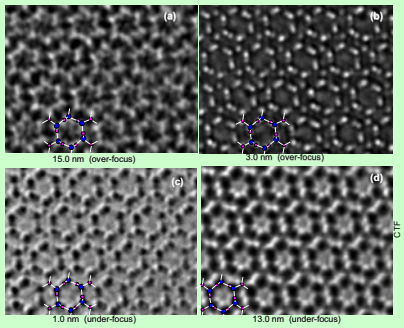
The calculated images show that under C_s and a small overfocus (indicated by '-'), Si-N dumbells and individual nitrogen columns are well resolved over a large range, and presenting bright ' white atoms' on dark background. Asymetrical image contrast demonstrates the non-linear contributions.

I-C. Understanding of image contrast in a C_s –corrected HRTEM



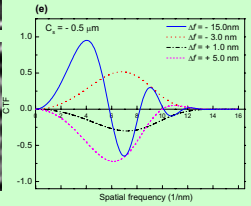
II. Experimental HRTEM images along Si_3N_4 [000-1] with a different C_s

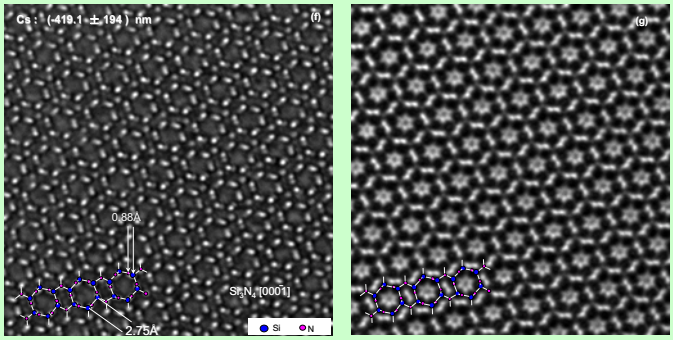
II-A. HRTEM image along Si_3N_4 [000-1] with small negative C_s



HRTEM Experimental conditions

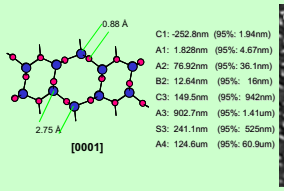
A2: 2.629nm / -100.2deg (95%: 7.49nm)
B2 : 2.26nm / +117.1deg (95%: 3.78nm)
C3 : -419.1nm (95%: 194nm)
A3: 44.27nm / +89.7deg (95%: 239nm)
S3: 112.9nm / +172.2deg (95%: 90.4nm)
A4: 3.036um / +48.4deg (95%: 8.42um)



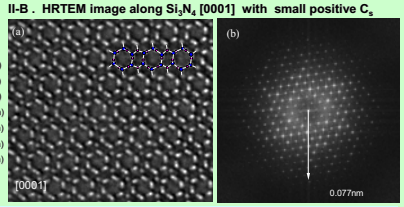


The images were taken at 1.4 Mx magnification at a sampling rate of 0.013 nm/ pixel. The focus step is 0.3nm. Compared with calculated images the thickness is found to be in the range of 2.0 ~ 4.5 nm. Closely looking at the images, the Si-N dumbells and single N columns are clearly resolved. From over-focus (-3.0 nm) to underfocus (+1.0 nm), the image contasts vary from bright 'white-atoms' (b) into 'dark atoms' (c), however, point resolution is almost the same as revealed by CTF (e), therefore, the Si-N dumbells are still resolved in 'dark-atom' image (c).

II-B. HRTEM image along Si_3N_4 [0001] with small positive C_s

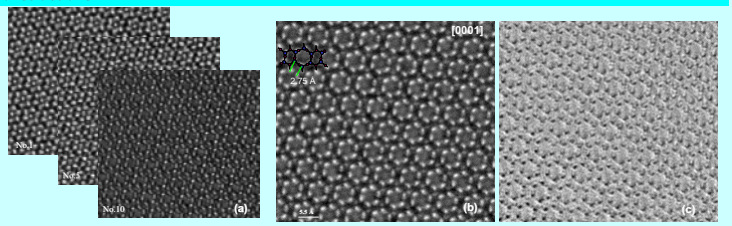


C1: -252.8nm (95%: 1.94nm)
A1: 1.828nm (95%: 4.67nm)
A2: 76.92nm (95%: 36.1nm)
B2: 12.64nm (95%: 16nm)
C3: 149.5nm (95%: 942nm)
A3: 902.7nm (95%: 1.41um)
S3: 241.1nm (95%: 525nm)
A4: 124.6um (95%: 60.9um)

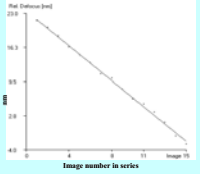


(a) The image was taken at 620 k magnification, corresponding to a sampling rate of 0.029 nm/ pixel. Close examination reveals a different orientation relative to the above one. (b) Fourier components of the structural image extend into the sub-ångstrom region as indicted by arrow.

III. Imaging of six-membered rings in Si_3N_4 by a combination of Cs-corrected HRTEM and focus-series reconstructions

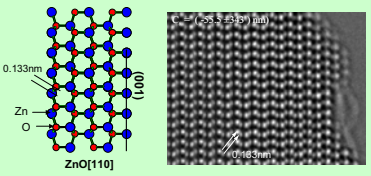


(a) Three experimental images in a through-focus series. Viewing direction along [0001], the defocus are 21.6 nm (No.1), 14.7 nm (No.5), 6.1 nm (No.10), respectively. All images were acquired at 620k, corresponding to a sampling rate of 0.029 nm/ pixel. (b) Reconstructed phase image, showing a crystal structure of Si_3N_4, atomic model superimposed. (c) Reconstructed amplitude image. Compared with the above experimental image (Fig.II), Si-N dumbells seem not well resovled, which has to be clarified!



Defoci measured for individual micrographs from the through-focus series of image in (a).Value of average focal step size (linear fit): -1.72 +/- 0.02 nm.

IV ZnO atomic structure with Oxygen sublattice



Direct determination of polarity possible by Cs-corrected HRTEM !

Acknowledgement: We thank Professor H. Rose for very fruitful discussions on image contrasts in C_s- corrected HRTEM.