Large-angle illumination STEM: toward three-dimensional atom-by-atom imaging

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To fully understand and control materials and their properties, it is of critical importance to determine their atomic structures in all three dimensions. Recent revolutionary advances in electron optics – the inventions of geometric and chromatic aberration correctors as well as electron source monochromators – have provided fertile ground for performing optical depth sectioning at atomic-scale dimensions. In this study we theoretically demonstrate the imaging of top/sub-surface atomic structures and identify the depth of single dopants, single vacancies and the other point defects within materials by large-angle illumination scanning transmission electron microscopy (LAI-STEM). The proposed method also allows us to measure specimen properties such as thickness or three-dimensional surface morphology using observations from a single crystallographic orientation.

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1. Introduction

The main factors limiting the illumination angle and therefore the resolution in a modern STEM are the aberrations of the electron lenses. The Scherzer theorem implies that spherical and chromatic aberrations are unavoidable in round lenses, with the result that aberration correctors, consisting of non-round elements are needed [1,2]. Modern aberration correctors are based on either quadrupoles and octupoles [3] or round lenses and hexapoles [4]. The development of STEM imaging theory and aberration correction in electron microscopy both owe a great deal to the work of Prof. Rose [5-8]. Following the realization by Beck that two sextupoles (hexapoles) could be used to correct spherical aberration, it was found that the problem with early designs was that they would make higher-order aberrations worse [4,9]. Prof. Rose's ingenious solution, of including a round lens doublet between the two hexapoles, is widely used today [7].

Following the successful implementation of geometric aberration correctors in electron microscopy [10,11], the spatial resolution has dramatically improved and atomic column-by-column imaging and spectroscopy have been accomplished in the last decade. Subsequently, the sub-Ångstrom electron probe has become a versatile tool and has solved a variety of problems in materials science and condensed matter physics [12]. The currently-achievable spatial resolution – less than half an Ångstrom in STEM [13,14] – might be sufficient to directly determine the atomic and electronic structures of some materials [15], but this resolution is valid only in the lateral two-dimensions and the width of the point spread function along the axial direction, the 'depth of field', is still several nanometers [16,17]. To push the boundaries of electron microscopy and perform 'atom-by-atom' imaging and spectroscopy of three-

dimensional materials, it is necessary to improve the resolution limit along the depth dimension by an order of magnitude.

In moving towards three-dimensional atomic-resolution imaging, one promising approach is optical depth sectioning by annular dark-field scanning transmission electron microscopy (ADF-STEM) [18]. Other notable approaches include scanning confocal electron microscopy [19], hollow-cone illumination [20], or exploiting the channeling conditions [21].

According to general optics [16,22], the depth resolution d_α can be expressed by analogy to the Rayleigh criterion for lateral resolution, by placing two point objects one behind the other such that one at the position of the first minimum in the intensity distribution of the other, when a clear dip is seen between the two points as focus is changed. Then

$$d_\alpha = 2 \left(\frac{\lambda}{\alpha^2} \right), \quad (1)$$

where α is the illumination semi-angle (illumination aperture size) and λ is the electron wavelength. Figure 1 shows the depth of field as a function of α at acceleration voltages of 100, 200, and 300 kV. Even given a fifth-order geometric aberration corrected microscope, the optimum illumination semi-angle is 30 mrad at 200 kV [23] and the expected depth of field is 55 Å at the best, which is far from atom-by-atom analysis along the depth. Though an Ångstrom-depth resolution would be our ultimate goal, such a high resolving power may not be necessary for most materials research. For example, the interatomic spacing in a simple perovskite-type structure is about 4 Å, and hence a depth resolution of several Ångstroms would be adequate to determine the locations of single dopants [24,25], surface atomic structures [26,27], and the morphology of embedded dopant-clusters in three dimensions [28,29]. As shown in Fig. 1, one can achieve a depth of field of 4 Å by

implementing a 100 mrad illumination semi-angle at 300 kV, which would be sufficient for three-dimensional, atom-by-atom imaging. Recently, Sawada et al. developed a new DELTA-type aberration corrector that allows the flat phase area of the Ronchigram to reach up to 71 mrad at 60 kV [30,31]. Therefore, given continued technological progress, 100 mrad illumination at 300 kV could be feasible in future.

In this study we theoretically explore the possibility of three-dimensional atom-by-atom optical depth sectioning by large-angle illumination STEM (LAI-STEM). Via image simulations, we explore three different applications of LAI-STEM: measurement of 1) specimen thickness, 2) surface atomic structure, and 3) the depth-location of point defects within a bulk material.

2. Chromatic aberration and the depth of field

The resolution obtainable from a practical STEM probe, in both the lateral and depth directions, is limited by both coherent and incoherent contributions. The coherent contributions include geometric aberrations of the illumination system and diffraction due to the illumination semi-angle (α). The incoherent contributions come from the finite electron source size, the energy spread of the source (ΔE), and the chromatic aberrations of the illumination system. The focus spread along the depth direction due to incoherent contributions can be written as [32]

$$d_c = C_c \sqrt{\left(\frac{\Delta E}{E}\right)^2 + \left(\frac{\Delta H}{H}\right)^2 + \left(\frac{2\Delta I}{I}\right)^2} \sim C_c \left(\frac{\Delta E}{E}\right), \quad (2)$$

where ΔE , ΔH , ΔI are the energy spread of the electron source, the instability of the acceleration voltage and the objective lens current. The latter two terms containing ΔH and ΔI can, at least in principle, be kept small enough to be neglected. A typical d_c

is estimated to be 17 Å for $C_c = 1.1$ mm and $\Delta f = 0.3$ eV at 200 kV [23]. The total probe spread along the depth can be formulated by a combination of Eq. (1) and (2),

$$d_t = \sqrt{(d_\alpha)^2 + (d_c)^2}, \quad (3)$$

so even if very large-angle illumination is used, the depth of field is still ultimately limited by chromatic aberrations. However, recent progress in a chromatic aberration correctors ($C_c < 10$ μm) [30,32] and electron source monochromators ($\Delta f < 30$ meV) [33,34] means that the focus spread along the depth can be sufficiently reduced that d_c should approach the Ångstrom level. Therefore, in the following, we assume a perfectly monochromated and geometric-aberration-free electron source and study the impact of just the illumination angle α on the depth of field.

To estimate the probe spread along the depth, we calculated the probe intensity in a vacuum as a function of defocus with specific illumination angles. Fig. 2 shows the cross-section of the calculated probe intensity as a function of defocus, where the conditions are (a) $\alpha = 30$ mrad at 200 kV (representative of a current microscope), (b) $\alpha = 60$ mrad at 300 kV, and (c) $\alpha = 100$ mrad at 300 kV (representative of potential future capabilities), summarized in Table 1. In the following, we will use these three conditions for our image simulations. At Gaussian focus ($\Delta f = 0$), the probe waist is steadily squeezed in the lateral dimension with increasing illumination angles, improving the lateral spatial resolution up to Feynman's dream of 0.1 Å (with 100 mrad illumination) [35], although, in practice of course, serious problems such as the finite source size of the gun or thermal magnetic noise from metal components [36] will still need to be overcome to achieve such a resolution. From Fig. 1 we can see that the probe spread along the depth also quickly decreases by the use of large-angle illumination, a feature which is mirrored by the probe intensity profiles along the optical axis (X-X' direction) of Fig. 2(d): the full

width of half maximum (FWHM) is (a) 24 Å, (b) 7 Å, (c) 2 Å, respectively. This is striking because larger-angle illuminations can open the way to perform optical depth sectioning in a similar manner to confocal optical microscopy, but providing depth-resolution of a few Ångstroms.

3. Measurement of specimen thickness

The image simulations were performed using a multislice algorithm with the frozen phonon model [37], using the TEMSIM package [38]. The frozen phonon model is usually adequate for STEM image simulation although the limitations of this method can sometimes be significant [39]. For wurtzite-type aluminum nitride (w -AlN), a 1024×1024 pixel mesh was used for a supercell of $16.2 \text{ Å} \times 14.9 \text{ Å}$, and 20 frozen phonon configurations with an Einstein model were averaged per pixel. Debye-Waller factors for Al and N atoms are obtained from the literature [40]. We used geometric and chromatic aberration-free conditions but the effective source size was considered by convoluting a simulated image with a Gaussian source size (FWHM): (a) 0.6 Å for 30 mrad [25], (b) 0.3 Å for 60 mrad and (c) 0.18 Å for 100 mrad. We have checked higher inner angles for ADF simulations, but found no significant improvement in spatial resolution. Therefore we used relatively low inner angles for ADF imaging to get more signal.

We define underfocus as positive (the probe is focused into a specimen), and $\Delta f = 0$ corresponds to the probe focused on the entrance surface of a specimen. Figures 3(a) – (c) show simulated ADF STEM images of 12.4 nm thick w -AlN viewed along the $[11\bar{2}0]$ direction (1 nm focal step), for illumination semi-angles of (a) 30 mrad, (b) 60 mrad, and (c) 100 mrad and a range of defocus values. In a current microscope of Fig. 3(a) the image contrast is maximized at $\Delta f \sim 2 \text{ nm}$, and strong contrast is still obtained even if the probe is focused out of the specimen. For the

large-angle illumination cases, the depth of field is significantly reduced and atoms can be imaged only when the probe is focused within the specimen, as is most evident with the $\alpha = 100$ mrad for the 300 kV case. It follows then that ADF STEM images obtained under such conditions show a sharp change in contrast as the focus is moved from outside the specimen to inside (and vice versa), and it may therefore be possible to measure the thickness of the specimen by measuring such changes (not by counting all the atoms, but by looking at the ADF intensity with depth). In order to measure the specimen thickness in this way, we use the standard deviation of the images. The results are plotted in Fig. 3(d), where we have normalized the profiles by dividing by the maximum. As one might expect qualitatively from the images in Fig. 3(a), the normalized standard deviation obtained from the small-angle illumination varies slowly across the specimen, and it is difficult to measure the specimen thickness accurately. However, the profiles in LAI-STEM show steep variations at the entrance/exit-surfaces of the specimen, and hence we can evaluate a specimen thickness by measuring a series of images at different defocus values. In the case of $\alpha = 100$ mrad, we have an accuracy of one-unit-cell ($< \pm 5$ Å) for the measurement of specimen thickness which is much higher accuracy than that of the electron energy loss spectrum (EELS) log-ratio method [41] and does not require the use of an additional detector to determine the thickness. Our method can *separately* determine the atomic steps on both top- and bottom-surfaces, and therefore it could be applicable to reconstruct three-dimensional morphology with atomic precision by acquiring focal-series LAI-STEM images.

4. Imaging the atomic structure of a surface reconstruction

Interest in surface science is rapidly increasing to encompass a broad range of applications where understanding the atomic structure of the surface is key to controlling physical or chemical properties. The reconstructed atomic structure on a clean Si (001) specimen was analyzed by low-energy electron diffraction, revealing that the surface has a double-spaced lattice [42]. Several decades later the atomic structure of the Si (001) surface was imaged by scanning tunnelling microscopy [43]. To date, the atomic structure of surfaces in plan-view experiments has been extensively investigated by scanning probe microscopy. However, since electron microscopy has been limited to a depth of field of several nanometers, it has almost no access to the surface atomic structure in real space, except for projected surface structures (cross-section views) [26,44]. LAI-STEM allows us to investigate surface atomic structures in plan-view owing to the higher depth-resolution. To confirm the versatility of LAI-STEM, we have tested the imaging of the Si (001) $p(2\times 1)$ surface atomic structure, where the surface structure model was calculated by first-principles calculation (see Appendix A).

Figures 4(a) and (b) show the relaxed atomic structure of the Si (001) surface, viewed along the [100] and [001] directions (cross-section and plan views) for a specimen thickness of 2.2 nm. The green, red and blue balls in the model denote Si atoms located at the top- and sub-surface layers and the bulk respectively, and the semi-transparent balls are located at the bottom surface layers. Figures 4(c)-(e) show focal-series simulated images viewed along the [001] direction of Si (plan-view), with illumination semi-angles of (c) 30 mrad, (d) 60 mrad and (e) 100 mrad. For the small-angle illumination, it is difficult to identify the locations of top/sub-surface Si atoms, although faint comet-shape contrast along the arrows appears at the overfocus

conditions ($\Delta f = -10 \text{ \AA}$). For the case of 60 mrad illumination, the top surface Si atoms can be recognized as new bright-dot contrast features slightly shifted from the bulk Si atom position (shown by arrowheads). These top surface Si atoms are observed at the Gaussian focus as well as at a small defocus either side of the entrance surface ($\Delta f = -5, 0, +5 \text{ \AA}$) because the probe spread in depth is larger than the interatomic distance (see Fig. 2(b)). For 100 mrad illumination, the depth-resolution is improved to the point that the top surface Si atoms can be recognized as distinct bright dots in the image at Gaussian focus. Owing to the annular-shape probe at the slightly defocussed conditions of $\Delta f = -5$ or $+5 \text{ \AA}$, the top surface Si atoms can be imaged as volcano-shape contrast at these defocus values. The same effect can be seen for the bulk Si atomic columns at $\Delta f = 0$, which is more evident from the dip in the ADF line profile shown in Fig. 4(f). [Although the model specimen is extremely thin, it may be possible to determine the entrance surface reconstructed structure even in slightly thicker samples because of the reduced channeling effect for large illumination angles.](#)

The sub-surface Si atoms (red) in Fig. 4(b) show $0.1 \text{ \AA}$ lateral shift from the bulk Si atoms along the $[010]$ direction, which is difficult to detect even by the use of 60 mrad illumination. However, for 100 mrad illumination, the sub-surface Si atoms are imaged at their true locations, confirmed by the ADF intensity profile. Figures 4(f) and (g) show ADF intensity profiles for $\alpha = 100 \text{ mrad}$ with $\Delta f = -5, 0, +5 \text{ \AA}$ obtained from X-X'' and Y''-Y' directions as marked in Fig. 4(b), where the location of X is the top-surface, Y' is the sub-surface and X'' and Y'' are in the bulk. At the overfocus condition in Fig. 4(g) ($\Delta f = -5 \text{ \AA}$, green line), the sub-surface Si atoms show a volcano-shape contrast profile (Y'). The visibility of these atoms is enhanced by increasing the defocus to the Gaussian focus, where sharp peaks are observed.

Increasing the defocus further to underfocus, the peak position shifts from the sub-surface position Y' to the bulk position Y'' at the underfocus conditions, suggesting that we can identify sub-surface atomic structures by optimizing the focus condition. Accordingly, we could reconstruct multi-layer surface atomic structures, with not only the atom locations but also relative atomic number (Z-contrast) by focal-series LAI-STEM imaging, and perhaps also elemental identification by EELS. This would be an advantage over scanning probe microscopy that cannot directly identify the chemical species of surface atoms [45].

5. Three-dimensional point defect imaging

To understand materials' properties, it is important to determine the three-dimensional spatial distribution of point defects in the structure such as vacancies, interstitial sites, antisite defects, impurities and their complexes. Recently we have developed depth-sensitive dopant imaging with atomic precision, combining quantitative image analysis with accurate image simulations [25,46]. Our previous method requires extensive image simulations, but LAI-STEM is able to directly determine the depth-location of a point defect without image simulations.

To investigate the depth sensitivity of LAI-STEM, we have chosen to study a Ce-doped w -AlN system [47] and the defect structure model that was used is shown in Fig. 5(a). S_j , I_j , and V_j ($j = 1 \dots 3$) stand for Ce substitutional point defects at the Al site, Ce interstitial site and Al vacancy site respectively, with depth locations of 2.2 nm, 3.4 nm and 7.8 nm, for $j = 1, 2$ and 3 respectively. The thickness of the specimen was 12.4 nm or 80 atoms per column. A typical simulated image of the defect structure is shown in Fig. 5(b), where the calculation condition is $\alpha = 30$ mrad and Δf

= 5 nm at 200 kV. Although there is no point defect at 5 nm depth, all the Ce dopants of S_j and I_j appear with brighter contrast, which would make it difficult to experimentally determine the depth location of those point defects without simulations.

Figure 5(c) shows focal-series simulated images with the model of Fig. 5(a), and the calculated condition is $\alpha = 100$ mrad at 300 kV. In contrast to the current microscope of Fig. 5(b), LAI-STEM can highlight the dopant defects only when the probe is defocused close to the dopant-depth. ADF contrast of the S_2 defect (3.4 nm) at $\Delta f = 3$ nm is much brighter than that of $\Delta f = 4$ nm, suggesting that the depth resolution of the dopant is better than ± 5 Å. Although the depth resolution of LAI-STEM does not reach down to atomic dimensions, it could be practically useful to determine the depth location with a unit cell precision (± 1 u.c.).

Figure 6(a) shows ADF intensity of $S_{1,3}$ substitutional defects as functions of defocus and illumination angle ($\alpha = 30, 60, 100$ mrad), where the $S_{1,3}$ defect has two substitutional Ce atoms in the Al column at the depth of 2.2 nm and 7.8 nm. In a current microscope, the Z-contrast intensity at the $S_{1,3}$ column is bright in all the focal-series images and it is difficult to determine the depth locations of the dopants, and whether it is two dopants or a single, even heavier atom. Whereas, in LAI-STEM imaging, two distinct Z-contrast intensities peaks appear at $\Delta f = 2$ and 8 nm in the cases of 60 and 100 mrad illuminations, and we can directly determine the depth location of dopants with atomic precision. Moreover we can count the number of both constituent Al atoms and Ce dopants in a single atomic column.

Similar results can be seen in I_3 interstitial defect shown in Fig. 6(b). Although the interstitial Ce atom can be imaged with $\alpha = 30$ mrad, we may not correctly measure the Ce depth location from Z-contrast intensity without simulations. In fact,

the maximum Z-contrast intensity (or standard deviation) is at $\Delta f \sim 6$ nm but the actual Ce atom depth location is 7.8 nm. However, in LAI-STEM imaging, the I_3 interstitial defect can be visualized as bright-dot contrast at $\Delta f = 8$ nm. While 60 mrad illumination may be enough to identify the depth location of a dopant with atomic precision, larger-angle illumination would be useful for determining atomic depth positions with higher accuracy.

Figure 6(c) shows focal-series simulated images obtained from the column consisting of a V_1 vacancy defect (2.2 nm). For 30 and 60 mrad illuminations, no significant Z-contrast intensity changes were observed in these images of $\Delta f = 2$ nm. However, for 100 mrad illumination, faint but distinct Z-contrast reduction at the Al column can be seen only in the image of $\Delta f = 2$ nm. Z-contrast reduction related to the V_1 defect is more evident in Fig. 6(d) of the standard deviation profile: the intensity abruptly reduces at $\Delta f = 2$ nm, which is observed only with 100 mrad illumination. We note that the roughness of the curve in Fig. 6(d), compared with Fig. 3(d), originates from the nearby S_3 defect (overlapping a ring-shape contrast). A similar result is obtained for the V_3 defect (7.8 nm) and the profile is shown in Fig. 6(e). Even for such a deep location of the Al vacancy, we can observe a distinct Z-contrast contrast reduction at $\Delta f = 8$ nm ($\alpha = 100$ mrad). Although experimentally, the signal-to-noise ratio would affect the detectability, in principle LAI-STEM is able to identify the depth-location of a single vacancy embedded within a material.

6. Concluding remarks

We have theoretically investigated the possibility of optical depth sectioning with atomic-precision by means of LAI-STEM imaging. For atomic depth-resolution, one requires a larger illumination angle of more than 60 mrad and therefore further

developments of higher order geometric and chromatic aberration correctors are desirable. LAI-STEM imaging shows great potential for determining surface atomic structures, three-dimensional atomistic morphology and the depth-location of single dopants, single vacancies and the other point defects within bulk materials. Moreover, it may also be possible to perform depth-sensitive spectroscopy such as electron-energy loss spectroscopy or energy dispersive X-ray spectroscopy at atomic-dimensions. Although we have not considered signal to noise issues, or the effects of residual geometric or chromatic aberrations, we hope that these examples may stimulate more research in the direction of depth resolution, and that Prof. Rose will design new aberration correction schemes for this purpose. Ultimately, it may be possible to extract three-dimensional structural information from amorphous materials and nanophase metals and ceramics by reconstructing from layer-by-layer focal-series images with a single axis of observation, which will open the way toward three-dimensional materials characterization with atomic precision.

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Appendix A. First-principles calculations for Si (001) reconstructed surface structure

The calculation of the Si (001) surface with 2×1 reconstruction was performed using the projector augmented-wave method [48] and the Perdew-Burke-Ernzerhof generalized gradient approximation [48-50] as implemented in the VASP code [51-53]. A 36-atom supercell composed of 18 layer ($22.6 \text{ \AA}$)-thick slabs separated by approximately the same amount of vacuum and $4\times 6\times 1$ k points were used. After atomic relaxation, the lattice constant was scaled to the experimental value ($5.431 \text{ \AA}$).

Fig. 1. Depth resolution as a function of illumination semi-angle at accelerating voltages of 100, 200, 300 kV.

Fig. 2. Probe intensity profiles (cross-section) as a function of defocus with illumination semi-angles and accelerating voltages of (a) $\alpha = 30$ mrad at 200 kV, (b) $\alpha = 60$ mrad at 300 kV, (c) $\alpha = 100$ mrad at 300 kV. The scale bar in (a) is 1 Å. (d) The intensity profile along the defocus (X-X' direction in (b)).

	α (mrad)	β (mrad)	E (kV)
(a)	30	60 - 400	200
(b)	60	80 - 400	300
(c)	100	120 - 400	300

Table 1. The three calculation conditions for illumination semi-angle (α), detector semi-angle (β), and accelerating voltage (E) .

Fig. 3. Focus-series simulated ADF STEM images of *w*-AlN (12.4 nm thick) viewed along the $[11\bar{2}0]$ direction with illumination angles of (a) $\alpha = 30$ mrad, $\beta_{det} = 60 - 400$ mrad (200 kV), (b) $\alpha = 60$ mrad, $\beta_{det} = 80 - 400$ mrad (300 kV), (c) $\alpha = 100$ mrad, $\beta_{det} = 120 - 400$ mrad (300 kV). The defocus range is -6 to 16 nm with 1 nm step and the probe ($\Delta f = 0$) is focused on the entrance surface. The normalized standard deviation of the images is plotted in (d). The structure model of *w*-AlN is inset in (d), where the red and blue balls are Al and N atoms respectively.

Fig. 4 The relaxed Si (001) surface atomic structure viewed along the (a) [100] and (b) [001] directions. The green-, red- and blue-colored Si atoms are positioned at top- and sub-surface layers and the bulk, respectively. Focal-series ADF STEM images of the Si (001) surface with (c) $\alpha = 30$ mrad at 200 kV, (d) $\alpha = 60$ mrad at 300 kV and (e) $\alpha = 100$ mrad at 300 kV. The focus range is -10 to 35 Å with 5 Å steps. The scale bar in (e) is 2 Å. Z-contrast intensity profiles obtained from the (f) X-X' and (g) Y''-Y' regions shown in (b) for the 100 mrad illumination with $\Delta f = -5, 0, +5$ Å.

Fig. 5 (a) Point defect structure model of Ce-doped w-AlN viewed along the $[11\bar{2}0]$ direction. S_j , I_j , and V_j ($j = 1...3$) stand for Ce substitutional point defects of Ce at the Al site, Ce interstitial site and Al vacancy site respectively, with depth locations of 2.2 nm, 3.4 nm and 7.8 nm, for $j = 1, 2$ and 3 respectively. (b) Simulated image of the defect structure with $\alpha = 30$ mrad, $\Delta f = 5$ nm at 200 kV. The scale is $3 \text{ \AA}$. (c) Focal-series ADF-STEM images with $\alpha = 100$ mrad at 300 kV. The focus ranges from 0 to 11 nm with 1 nm steps.

Fig. 6 Focal-series ADF-STEM images obtained from the (a) $S_{1,3}$, (b) I_3 , and (c) V_1 point defects. The top, middle and bottom rows of each panel correspond to 30 mrad, 60 mrad and 100 mrad illumination semi-angles, respectively. The standard deviations of the images are plotted as a function of defocus for (d) V_1 and (e) V_3 defects.

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