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Atom-By-Atom Distance Measurements

Knowledge of the precise position of atom columns provides access to measuring global and local lattice parameters, strain analysis, and quantitative investigation of lattice changes near defects, interfaces, and secondary phases.

Introduction

Tailoring device performance now requires strict control of materials behavior at the atomic scale. The need for such localized control has necessitated new breakthroughs in characterization to be able to understand the structure at an atom-by-atom basis. Aberration corrected scanning transmission electron microscopy (AC-STEM) has enabled the analysis of atomic structure and composition to become routine. One area that has remained challenging to study at the atomic scale is precise atomic spacing or strain measurements. In this application note, we show the possibility to extract distance information at an atom-column to atom-column basis with picometer level precision. We demonstrate how atom columns can be identified and their positions fit. Knowledge of the precise position of atom columns provides access to measuring global and local lattice parameters, strain analysis, and quantitative investigation of lattice changes near defects, interfaces, and secondary phases.

Discussion

Figure 1 shows a frame averaged HAADF STEM image of quantum wells in a GaN-based LED. The thin bright layers are InGaN, while the dim, thicker layers are nominally pure GaN. The heterostructure is viewed down the a-plane [11$\bar{2}$0] zone axis from which the (0001) and (1$\bar{1}$00) interplanar spacings are readily measurable. The digitally magnified inset shows one way these values can be measured directly from the image. The red circle lies on an example atom column, and red lines point to four neighboring atom columns (white X marks) that form a rectangle around the center atom column. The white lines between indicated neighbors show

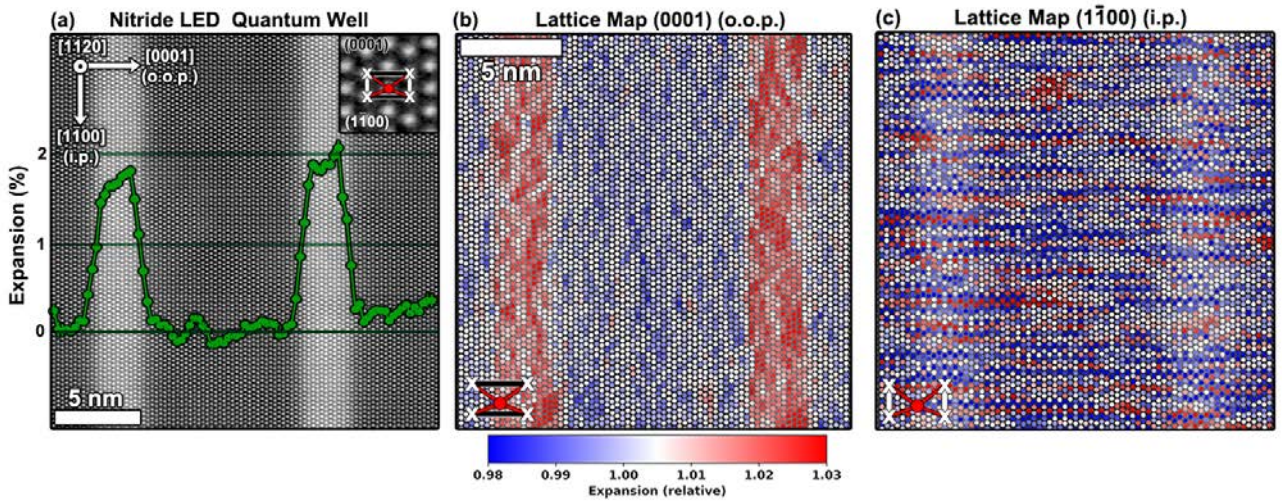

Figure 1: (a) Frame averaged HAADF STEM image including a portion of the quantum well region in a nitride-based light emitting diode. Relevant inter-planar spacings and indicated by the magnified inset. The out-of-plane lattice expansion is overlaid on the HAADF image in green. (b-c) show the out-of-plane and in-plane atom column distance maps respectively.

($1\bar{1}00$) plane spacings around the center site, while the black lines show the (0001) plane spacings. The (0001) corresponds directly to the c-axis [0001] lattice parameter which is nominally ~5.185 Å for pure GaN.

Direct measurement of lattice parameters in these and similar systems can provide useful information regarding composition, strain, and presence of non-uniform structural features like defects. All these features can influence LED efficiency and the emission properties of the device. For nitride-based semiconductors, the lattice parameters scale with alloying accordingly to Vegard's law. Provided growth is pseudomorphic (i.e. the layers are coherently strained to each other with little-to-no relaxation), the alloy composition of a layer can be inferred from the out-of-plane lattice parameters. The structure in Figure 1 is analyzed using atom column distance mapping to generate the mean (0001) spacings surrounding each site. These values at each site are then normalized by the (0001) mean values measured across a large area of the unstrained GaN lattice in between the InxGa1-xN layers. This analysis provides access to mapping of lattice expansion and contraction across the heterostructure as seen in Figure 1. The InxGa1-xN layers in Figure 1a show marked expansion to values of ~1.02 with respect to GaN, which corresponds to an increase in out-of-plane c-axis lattice parameter by about 2 %. By contrast, the in-plane map (Figure 1c) shows no strong features that correlate to the presence of the InxGa1-xN layers. This unchanged in-plane parameter confirms that these layers are not relaxing from the GaN layers which indicates that the growth remains within the pseudomorphic regime. As an alternative way of visualizing the data, the lattice expansion in the c-direction is also plotted as an overlay on the original STEM image in Figure 1a. Using this visualization, it shows the expansion in the growth direction correlates directly to the intensity, composition, observed in the STEM image.

A HAADF STEM image of a LSMO thin film is shown in Fig. 2b. The image was acquired by summing multiple rapidly-acquired image frames that were aligned via cross-correlation. Frame averaging for improving signal-to-noise ratio while decreasing sample drift related distortions. The left side of the image shows LSMO adopting its standard perovskite structure (see structure inset in Fig. 2b) where the bright atom columns are (La,Sr) containing A-sites (Z = 57, 38) and the dim are B-site containing Mn columns (Z = 25). Towards the right of the image, the structure visibly changes and appears darker on every other plane of Mn sites (see red arrows in Fig. 2b). This strongly suggests that either a phase

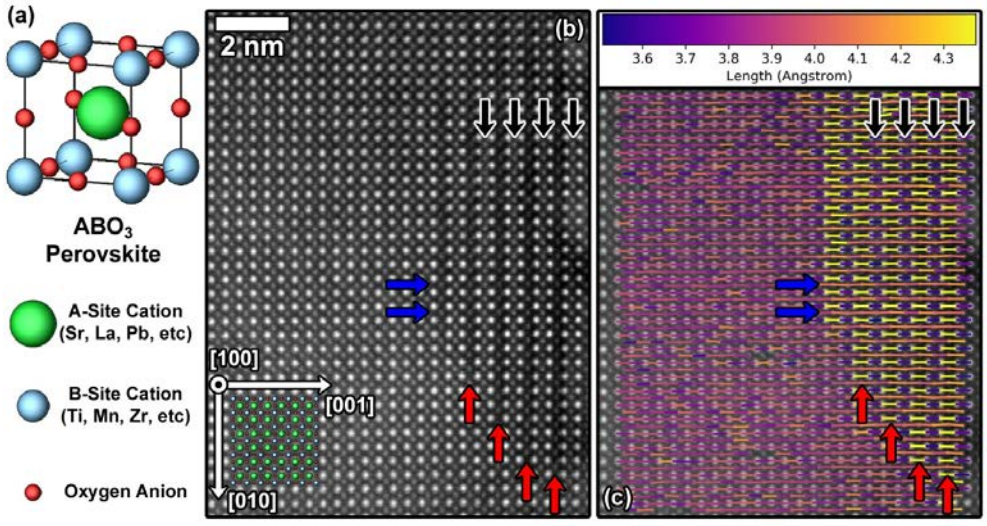

Figure 2: (a) Structural schematic of the ABO3 perovskite. (b) A HAADF STEM image of LSMO exhibiting a transition between the standard perovskite structure and a secondary phase (red arrows indicate ordered columns of darker B-sites in the secondary phase portion). (c) "Lattice mapping" displays quantitative spacing information that elucidates the structure of the secondary phase: A-sites in the secondary phase oscillate between large (~ 4.4 – 4.5 Å, red arrows) and small (~ 3.6 Å, black arrows) [001] spacings, while the B-site [001] increases from ~3.9 Å of perovskite LSMO to ~ 4.0 – 4.1 Å (blue arrows). Note the colorscale is clipped to the mean ± 2σ.

change or a composition change (or both) is occurring in this region. Atomic scale metrology by mapping the distances between atom columns can provide greater insight into the quantitative changes that are occurring in this region.

Fig. 2c shows (La,Sr)-(La,Sr) and Mn-Mn [001] lattice spacings drawn on the image by fitting each atom column position and measuring the distances between atoms in the [001]. The pixel size was calibrated from the uniform pseudo-cubic LSMO region of the image, assuming the [001] = 3.88 Å. In the perovskite-like LSMO, the parameter is uniformly around ~ 3.88 Å indicating only small-scale variations are present in the pseudo-cubic region. On the other hand, the lattice map reveals that the [001] measured between (La,Sr)-sites in the secondary phase portion oscillates considerably between large and small values, respectively, as indicated by red and black arrows in Fig. 2c. The large spacings correlate to [001] measurements between (La,Sr)-sites that span (001) planes containing dim Mn-sites. The Mn-sites do not exhibit a similar trend of oscillatory spacing along the [001]; instead, the spacings are rather uniform though slightly expanded (see blue arrows).

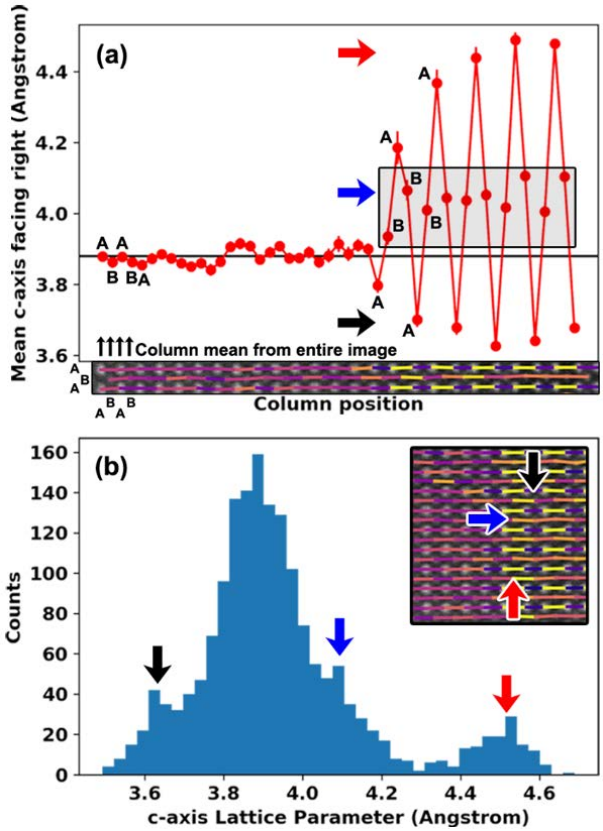

Figure 3: (a) Plot showing the mean [001] value for each A/B-site plane of atoms in Fig. 1c (error bars show ± the standard error of the mean). The points are equally spaced along the position-axis but are displayed above a section of the lattice map for comparison. Some data points are displayed with A/B-site labels to show trends of the separate sites. The black horizontal line shows 3.88 Å. (b) Histogram of all [001] spacings from Fig. 1c. In addition to the mean distribution at 3.88 Å, three sub-distributions form due to the small (black arrow) and large (red arrow) A-site [001] spacings in the secondary phase, as well as due to the rather uniformly expanded B-sites (blue arrow) in the secondary phase portion of the image.

These measurements can be averaged along certain planes to show mean values along the growth direction. In the case of the present image, most of the lattice parameter variation across the image appears to occur left-to-right. Fig. 3a shows an integrated line profile of the mean [001] (i.e. right facing) measurements for each plane of atom columns of Fig 2c. The points are displayed with an equal spacing along the x-axis and are roughly aligned to a sub-slice of Fig. 1c for visual comparison. The lattice parameter deviates from its mean value (~ 3.88 Å) in the normal region to form three distinct distributions in the secondary phase region (see Fig. 3a). In the secondary phase region, the (La,Sr) A-sites split into large spacings (~ 4.4 – 4.5 Å, see red arrow) and small spacings (~ 3.6 – 3.7 Å, see black arrow) that oscillate around the Mn B-site spacings that are more uniformly distributed (~ 4.0 – 4.1 Å, within the shaded rectangle next to the blue arrow). The onset of the lattice parameter changes appears gradual with smaller oscillations in the maxima near the interface. In fact, this likely arises because of steps near the interface which leads to a combining of matrix and secondary phase lattice parameters in that region.

Histograms can also be generated for various interplanar spacings. Fig. 3b shows a histogram of all the [001] measurements taken from the image in Fig. 2c. Aside from the primary distribution centered at ~ 3.9 Å, the three unique features of the secondary phase are evident. The large (red arrow) and small (black arrow) sub-distributions are visible to the sides of the main distribution. The expanded Mn-Mn sites [001] within the secondary phase also appear in the histogram as a subtle peak in the tail of the main distribution (blue arrow).

Conclusion

This direct atom column distance measurement between provides an extremely powerful way to measure information such as strain or phase transformations at the atomic scale. However, the technique is also very demanding from both data acquisition and image analysis sides. While typical images are acquired in under a minute and the data can often be analyzed and understood with the human eye almost instantly, each dataset for the distance mapping can require hours of work from proper image set up to refining atom column fitting. Further, based on the required signal to noise ratio and time required to fit every atom column, the structure must have large enough spacings between atoms so that the columns are well separated, typically above 1.5 Å, and the field of view should be limited to 20-30 nm per image. With that said, there are many cases where this technique can provide meaningful information that is well worth the effort. Further, through the combination of atom column distance mapping with atomic scale spectroscopy and imaging, it is now possible to have a more comprehensive understanding of the local structure than ever before. Contact us today to learn how AC-STEM can help with your next project.