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Polymorphic transformation of dense ZnO nanoparticles: Implications for chair/boat-type Peierls distortions of AB semiconductor

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I. INTRODUCTION

Peierls distortions refer to the configurational instabilities associated with a half-filled band of a solid, originally documented for one-dimensional1 and later two- and three-dimensional structures such as AB semiconductor.2 Upon symmetric structure distortion for coordination number to change, such as from 6 to 4 for rock salt (denoted as R) to wurtzite (denoted as W) transition, the energy gap is opened.2 While the exact nature of the motion of individual atoms is not well understood, Burdette has shown that much insight can be gained by using symmetry and modeling the R→W transition as a Peierls distortion.3,4 Tolbert and Alivisatos5 further proposed that such a transition in CdSe nanocrystals may involve so-called “chair-” and “boat” type Peierls distortions by deforming the {100}R into {001}W and {1120} plane, respectively. This scenario is in accord with acoustic shear modes consideration,6 although direct experimental evidence for this path yet to be found for analog material such as ZnO focused in this study.

Intrinsic W-ZnO is an n-type semiconductor with a wide direct band gap of 3.37 eV at a high exciton binding energy of 60 meV at ambient pressure7 for promising applications in the UV region.8 On the other hand, there is an indirect band gap of 2.45 eV at 13.5 GPa for R-type structure with octahedral coordination9 originally synthesized at ca. 10 GPa and room temperature.10 This high-pressure phase in the form of nanosize particles can be retained to ambient pressure due to a sluggish transition11,12 and therefore suitable for the present in situ observations of back transformation, upon electron irradiation at ambient condition, with emphasis on the following points: First, the specific crystallographic relationships of the polymorphs in support of the chair- and boat-type Peierls distortion path, respectively. Second, to rationalize such a lattice correspondence from the standpoint of lattice mismatch. Third, the effect of transformation strain of chair-type on the activation of boat-type distortion as the system goes from finite to bulk.

II. EXPERIMENT

The powdery W-ZnO statically compressed at 15 GPa and 550 K was quenched to ambient condition as R-ZnO particles ca. 12 nm in size according to x-ray diffraction and x-ray absorption spectroscopy.11 The compact polycrystals were pulverized by an alumina mortar and pestle, and then collected on copper grids overlaid with a carbon-coated collodion film for analytical electron microscopy study using a JEOL 3010 instrument at 300 keV and a beam current of 60 pA/cm2. Bright field image and selected area electron diffraction (SAED) patterns were used to identify the size distribution and phase identity of the ZnO particles. Lattice imaging coupled with two-dimensional Fourier transform and inverse transform were used to identify the crystallographic relationship defect microstructures due to back transformation of R-ZnO under the effect of electron irradiation at a time interval of 30 s.

III. RESULTS AND DISCUSSION

Transmission electron micrograph (TEM) showed that the pulverized sample consist of randomly oriented particles ca. 10 to 20 nm in size which are predominantly W-ZnO with well-developed {1010} surface [Fig. 1(a)]. SAED from
an area of about 0.8 \( \mu m^2 \) indicated that some particles survived decomposition as \( R-ZnO \) with characteristic (200) and (220) diffractions [Fig. 1(b)]. These relic particles were used for \textit{in situ} observations of the \( R \rightarrow W \) transformation upon electron dosage. An isolated and thin \( R-ZnO \) particle [Fig. 2(a)] typically underwent partial transformation into \( W-ZnO \) single domain within 1 min of electron irradiation. Fourier transform [Fig. 2(b)] showed the polymorphs followed the crystallographic relationship \((11\bar{1})_R//\langle011\rangle_W; [011]_R//\langle12\bar{3}\rangle_W\). The reconstructed image [Fig. 2(c)] further showed that the \{11\bar{1}\}_R planes are either parallel to \{011\}_W or \{10\bar{1}\}_W with a rather rough \( R/W \) interface. Dislocation glide on \{11\bar{1}\}_R planes caused interface migration toward \( -(1\bar{1}1)_R//\langle01\bar{1}\rangle_W \) when irradiated for a total of 2 min [Fig. 2(d)]. The semicoherent interface was decorated with nanometer-spaced edge dislocations having \{11\bar{1}\}_R half plane.

As for a typical \( R-ZnO \) particle surrounded by yet coalesced particles [Fig. 3(a)], two crystallographic relationships were developed subsequently. The Fourier transform and reconstructed image showed this intact \( R-ZnO \) in \{011\} zone axis [Fig. 3(b)]. Upon electron irradiation for a total of 6 min, two \( W \)-domains following \((11\bar{1})_R//\langle01\bar{1}\rangle_W; [011]_R//\langle12\bar{3}\rangle_W\) and \((1\bar{1}1)_R//\langle10\bar{1}\rangle_W; [01\bar{1}]_R//\langle011\rangle_W\) were developed from \( R-ZnO \) as indicated by Fourier transform [Fig. 3(c)] and reconstructed image [Fig. 3(d)] [Fig. 3(e)] further showed that the relic \( R-ZnO \) has well developed \{11\bar{1}\} faults before changing into \( W \)-structure. The two \( W \)-domains adjoined the \( R \)-relief with the same type \{11\bar{1}\}_R//\langle011\rangle_W \) interface, i.e., \((1\bar{1}1)_R//\langle01\bar{1}\rangle_W\) and \((1\bar{1}1)_R//\langle10\bar{1}\rangle_W\).
planes are also parallel to \{0\overline{1}1\}_{W} \), i.e., \(\overline{0111}_{W}\) and \((101)_{W}^{2}\) planes, across the interface. The \(R/W\) interface was found to migrate by dislocation (presumably with a Burgers vector of 1/2(110)) as for analog NaCl structure\(^{13}\) gliding on \(\{1\overline{1}1\}_{R}\) planes until completion of transformation estimated to be ca. 10 min of electron irradiation. The impinged \(W\)-domains then have \((101)_{W}^{1}\) and \((101)_{W}^{2}\) planes matched despite the migration of the domain boundary [Fig. 3(f) versus Fig. 3(d)].

The lattice correspondence observed in this study indicates deviation from the ideal case of \((001)_{R}^{1}/(0001)_{W}^{2}\); \((010)_{R}^{1}/(1\overline{2}10)_{W}^{2}\) [Fig. 4(a)]. Theoretically, chair-type Peierls distortion is about puckering of \((001)_{R}^{1}\) plane to become \((0001)_{W}^{2}\) plane, i.e., the middle two atoms of a 2\times3 rectangle \((001)_{R}^{1}\) plane [Fig. 4(b)] move apart and the plane puckers to produce a six membered ring chair-type structure in a wurtzite \((0001)_{W}^{2}\) plane [Fig. 4(b)].\(^{5}\) On the other hand, boat-type Peierls distortion refers to puckering of \((010)_{R}^{2}\) plane to become \((\overline{1}2\overline{1}0)_{W}^{2}\) plane [Fig. 4(c)] or alternatively \((100)_{R}^{1}\) plane to become \((2\overline{1}10)_{W}^{2}\) plane (refer to Fig. 15 of Ref. 5). The observed crystallographic relationships as compiled in the stereograms [Figs. 4(e) and 4(f)] showed that \((001)_{R}^{1}\) originally aligned with \((0001)_{W}^{2}\) became tilted for ca. 13° and 3° along the plane \((100)_{R}^{1}\) and \((2\overline{1}10)_{W}^{2}\) for the chair- and boat-type distortions, respectively. The latter may have a higher activation energy because of two-step puckering of orthogonal \((101)_{R}^{1}\) and \((100)_{R}^{1}\) planes, i.e., apparent tilting of \((001)_{R}^{1}\) along \((5\overline{3}0)_{W}^{2}\) determined by stereographic projection [Fig. 4(f)].

The specific Peierls distortion can be rationalized by
TABLE I. Lattice misfit for hypothetical and observed (hkl)_{R}/(hkl)_{W} match. The calculated d spacings of W-ZnO were based on the lattice parameters (a = 0.3250 nm, c = 0.5207 nm, space group P6_{3}mc) of synthetic sample at room pressure and temperature (Refs. 14 and 15) and those of R-ZnO were based on the lattice parameter (a = 0.4278 nm, space group Fm\overline{3}m) measured at room pressure and temperature (Ref. 11). The d spacings of R-ZnO in parenthesis were based on the lattice parameter (a = 0.4128 nm) measured at 15 GPa (Ref. 16). The hypothetical cases refer to Fig. 4(d) and real cases to Figs. 4(e) and 4(f).

<table>
<thead>
<tr>
<th>Lattice plane</th>
<th>d spacing (nm)</th>
<th>Misfit (%)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>123\n/111</td>
<td>0.0820/2.470 (0.238)</td>
<td>100.30/7.5</td>
<td>Fig. 4(d)</td>
</tr>
<tr>
<td>125\n/110</td>
<td>0.1060/3.030 (0.292)</td>
<td>96.30/9.5</td>
<td>Fig. 4(d)</td>
</tr>
<tr>
<td>127\n/010</td>
<td>0.1630/4.280 (0.413)</td>
<td>89.70/6.8</td>
<td>Fig. 4(d)</td>
</tr>
<tr>
<td>127\n/011</td>
<td>0.1190/3.030 (0.292)</td>
<td>87.20/8.4</td>
<td>Fig. 4(d)</td>
</tr>
<tr>
<td>101\n/2/101</td>
<td>0.1900/3.030 (0.292)</td>
<td>45.80/4.2</td>
<td>Fig. 4(d)</td>
</tr>
<tr>
<td>101\n/1/100</td>
<td>0.2810/4.280 (0.413)</td>
<td>41.50/3.8</td>
<td>Fig. 4(d)</td>
</tr>
<tr>
<td>100\n/001</td>
<td>0.5210/4.280 (0.413)</td>
<td>19.60/2.1</td>
<td>Fig. 4(d)</td>
</tr>
<tr>
<td>101\n/1\n1\n1\n1\n0\n0\n1\n1\n1\n1\n1\n1\n</td>
<td>0.2480/4.270 (0.238)</td>
<td>0.40/4.1</td>
<td>Fig. 4(e)</td>
</tr>
<tr>
<td>011\n/1/111</td>
<td>0.2480/4.270 (0.238)</td>
<td>0.40/4.1</td>
<td>Fig. 4(f)</td>
</tr>
</tbody>
</table>

The barrier to chair- and boat-type Peierls distortion is a function of the loss of octahedral bonding as the central atoms move apart, balanced against the gain in covalent sp^{3} bonds as the system approaches a tetrahedral geometry, with theoretical s electron density increase. Some finite barrier to transition may still exist at the phase transition pressure in view of nonzero shear mode frequency for analogous tetra-

### IV. CONCLUSIONS

We have experimentally characterized the Peierls distortion path for dense ZnO nanoparticles prepared by static compression. Electron irradiation caused back transformation of R structure to W structure, following preferential (111)_{R}/(0111)_{W}: [011]_{R}/[123]_{W} and then transformation strain induced (111)_{R}/(1011)_{W}: [011]_{R}/[1011]_{W}. The two relationships can be rationalized by specified extent of chair- and boat-type Peierls distortions accompanied with band gap opening and intermediate {111}_{R} slip for energetically favorable {111}_{R}/(0111)_{W} match. The present knowledge of transformation paths for dense ZnO nanoparticles may shed light on chair/boat-type Peierls distortions of AB semiconductor in general.

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