Strain-Versus-Dislocation Model for Understanding the Heteroepitaxial Growth of Nanowires

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Supplemental Material

S1. Strain energy of ZnO nanowire on GaN substrate

To calculate the strain energy of the nanowire on GaN, following derivations are applied:

$$u_r(r,\theta,z) = Br\exp(\frac{-z}{2\alpha R})$$
$$u_\theta(r,\theta,z) = 0$$
$$u_z(r,\theta,z) = (Pr+QR)\exp(\frac{-z}{2\alpha R})$$

We have:

$$\varepsilon_{rr} = \frac{\partial u_r}{\partial r} = B\exp(\frac{-z}{2\alpha R})$$
$$\varepsilon_{\theta\theta} = \frac{u_r}{r} + \frac{1}{r}\frac{\partial u_\theta}{\partial \theta} = B\exp(\frac{-z}{2\alpha R})$$
$$\varepsilon_{zz} = \frac{\partial u_z}{\partial z} = -\frac{Pr+QR}{2\alpha R}\exp(\frac{-z}{2\alpha R})$$
$$\varepsilon_{rz} = \frac{1}{2}(\frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r}) = \frac{-Pr+2QR\alpha}{4\alpha R}\exp(\frac{-z}{2\alpha R})$$
$$\varepsilon_{r\theta} = \frac{1}{2}(\frac{\partial u_\theta}{\partial r} + \frac{1}{r}\frac{\partial u_r}{\partial \theta} - \frac{u_\theta}{r}) = 0$$
$$\varepsilon_{z\theta} = \frac{1}{2}(\frac{\partial u_\theta}{\partial z} + \frac{1}{r}\frac{\partial u_z}{\partial \theta}) = 0$$

With Hooke's Law, one obtains:

$$[\sigma]=[C][\varepsilon]=\begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix}\begin{pmatrix} \varepsilon_{rr} \\ \varepsilon_{\theta\theta} \\ \varepsilon_{zz} \\ 2\varepsilon_{\theta z} \\ 2\varepsilon_{zr} \\ 2\varepsilon_{r\theta} \end{pmatrix}$$

Then we get the strain energy density:

$$e(r,\theta,z)=\frac{1}{2}\sigma_{ij}\varepsilon_{ij}=[\frac{1}{2}C_{11}B^2+\frac{3}{2}C_{12}B^2+\frac{C_{33}Q^2}{8\alpha^2}-\frac{C_{13}BQ}{\alpha}+\frac{1}{2}C_{44}P^2+(\frac{C_{33}P^2}{8\alpha^2R^2}+\frac{C_{44}B^2}{8\alpha^2R^2})r^2$$
$$+(\frac{C_{33}PQ}{8\alpha^2R}-\frac{C_{13}BP}{\alpha R}-\frac{C_{44}BP}{2\alpha R})r]\exp(\frac{-z}{\alpha R})$$

Integrate the strain energy density in the cylindrical nanowire, we have:

$$E_C=\int_0^H\int_0^{2\pi}\int_0^R e(r,\theta,z)rdrd\theta dz=\frac{\pi R^3}{96\alpha}[(48C_{11}B^2+144C_{12}B^2+48C_{44}P^2)\alpha^2+(-96C_{13}BQ$$
$$-64C_{13}BP-32C_{44}BP)\alpha+12C_{33}Q^2+8C_{33}PQ+6C_{33}P^2+6C_{44}B^2][1-\exp(\frac{-H}{\alpha R})]$$

Assume the substrate is rigid along the radial direction, we have:

$$E_C=\frac{\pi R^3}{96\alpha}[(48C_{11}f^2+144C_{12}f^2+48C_{44}P^2)\alpha^2-(96C_{13}fQ+64C_{13}fP+32C_{44}fP)\alpha+12C_{33}Q^2$$
$$+8C_{33}PQ+6C_{33}P^2+6C_{44}f^2][1-\exp(\frac{-H}{\alpha R})]$$

To minimize *E*, the 'fminsearch' function in MatLab was applied with three variables. Then we have the strain energy of the ZnO nanowire grown on GaN:

$$E_C^*=E_{min}$$

For instance, for a ZnO nanowire with radius 25 nm and length 5 nm, E_C^* was calculated to be 5.5 × 10 $^{-16}$ *J*, where *α, P* and Q were determined to be 0.2737, 0.0117 and 0.0071, respectively.

S2. Shear modulus of ZnO nanowire

Shear modulus *G* is obtained by following expression:

$$B=\frac{(C_{11}+C_{12})C_{33}-2C_{13}^2}{C_{11}+C_{12}+2C_{33}-4C_{13}};E=3B(1-2\nu);\nu=\frac{C_{13}}{C_{11}+C_{12}};G=\frac{E}{2(1+\nu)}$$

S3. Strain Energy of ZnO nanowire on sapphire substrates

Cartesian coordinate is applied in this calculation considering a tetragonal wire is assumed. The following displacement fields are assumed:

$$u_x(x,y,z) = A$$
$$u_y(x,y,z) = By\exp(\frac{-z}{2\alpha T})$$
$$u_z(x,y,z) = (Py+QT)\exp(\frac{-z}{2\alpha T})$$

By applying the same method we use for nanowire on GaN, we get the expression of non-minimized strain energy:

$$E_C = \frac{2T^3}{12\alpha}(12C_{11}f^2\alpha^2 - 12C_{13}fQ\alpha + 3C_{33}Q^2 + 12C_{44}P^2\alpha^2 + 4C_{33}P^2 + 4C_{44}f^2 + 6C_{33}PQ$$
$$-12C_{13}fP\alpha - 12C_{44}fP\alpha)[1-\exp(\frac{-H}{\alpha T})]$$

In the calculation of the strain energy, we only considered the 20% lattice mismatch between $(11\bar{2}0)_{ZnO}$ and $(0001)_{Al2O3}$. The strain from lattice mismatch between $(1\bar{1}00)_{ZnO}$ and $(1\bar{1}00)_{Al2O3}$ was simply ignored due to the likelihood of insignificant strains. This simplification also generated a conservative result of the strain energy, which has been shown to be high enough to be overcome by any possible energy of dislocated systems.

Here, *2T* is defined as 40 nm. If the length of the NW is 5 nm, E_C^* was calculated to be 2.2×10^{-14} *J*, where *α, P* and Q were determined to be 0.9236, 0.0726 and 0.0970, respectively.

S4. Strain energy of ZnO nanofin on GaN and Sapphire

Since we considered both ZnO nanofin on GaN along GaN $[1\bar{1}00]$ direction and ZnO nanofin on sapphire along sapphire $[1\bar{1}00]$ direction are strain free, the same derivation process was used. The displacements fields were assumed as followings:

$$u_x(x,y,z) = A$$
$$u_y(x,y,z) = By\exp(\frac{-z}{2\alpha T})$$
$$u_z(x,y,z) = (Py+QT)\exp(\frac{-z}{2\alpha T})$$

Similar process as the ZnO nanowire on sapphire, we have:

$$E_C = \frac{WT^2}{12\alpha}(12C_{11}f^2\alpha^2 - 12C_{13}fQ\alpha + 3C_{33}Q^2 + 12C_{44}P^2\alpha^2 + 4C_{33}P^2 + 4C_{44}f^2 + 6C_{33}PQ - 12C_{13}fP\alpha$$
$$-12C_{44}fP\alpha)[1-\exp(\frac{-H}{\alpha T})]$$

For ZnO nanofin on GaN substrate, by assuming *2T* as 50 nm, width as unit and height as 5 nm, E_C^* was calculated to be 8.3×10^{-9} *J*, where *α, P* and Q were determined to be 1.0539, 0.0075 and 0.0136, respectively.

For ZnO nanofin on sapphire substrate, *2T* was defined as 40 nm and width was unit. If the height of the ZnO nanofin on sapphire is only 5 nm, E_C^* is calculated to be 5.48×10^{-7} *J*, where *α, P* and Q are determined to be 0.9236, 0.0726 and 0.0970, respectively. In fact, at any thickness starting from 0.5 nm, E_C^* was found greater than E_D^*. Therefore, we concluded that the ZnO nanofin is energy unfavorable structure on sapphire substrate.