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Nanospectroscopic investigation of individual free-standing semiconductor nanowires using nanoprobe-cathodoluminescence techniques

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Abstract

Single-crystalline free-standing nanowires are attractive as novel electronic materials since they bear giant strain (uniaxial $\varepsilon_{zz} \sim 10^{-1}$), larger than bulk crystals ($\varepsilon_{zz} \sim 10^{-3}$) or heteroepitaxial thin-films (biaxial $\varepsilon_{xx} \sim 10^{-2}$). However, there has been no technique to evaluate a strain-response of bandgap (bandgap deformation potential) or to characterize the local carrier concentrations within a single nanowire, which bottlenecked the strain-engineering and precise control of their electronic properties. This talk introduces the development of nanoprobe-cathodoluminescence system: SEM-cathodoluminescence nanospectroscopy with *in-situ* nanomanipulator, which is applied to ZnO free-standing nanowires (1) for the evaluation of the uniaxial bandgap deformation potential and (2) for the measurement of local carrier concentration within a single nanowire. These novel techniques pave the way for the strain-engineered nanoelectronics using well-defined bottom-up materials.

1. Introduction

Strain-engineering of the semiconductor band-edge structure is a major approach to realize advanced electronics, such as field-effect transistors (FETs) with enhanced carrier mobilities, laser diodes with reduced lasing threshold and gain, and wavelength tuning of optoelectronic devices, such as light-emitting diodes, photodiodes, and solar-cells. Therein, parameters on semiconductor band-edge structures, such as bandgap $E_g(\varepsilon_{ij})$ $(i, j = x, y, z)$ and carrier effective mass $m_{kl}(\varepsilon_{ij})$ $(i, j, k, l = x, y, z)$, are tuned by the strain ε_{ij} which are applicable up to the fracture strain ε_{ijF} of the material. Recent progress on the crystal growth technique offers us single-crystalline free-standing nanowires (NWs) of various semiconductors with high crystallinities. Since these NWs have fracture strain (uniaxial $\varepsilon_{zzF} \sim 10^{-1}$) larger than bulk crystals (uniaxial $\varepsilon_{zz} \sim 10^{-3}$) or heteroepitaxial thin-films (biaxial $\varepsilon_{xx} \sim 10^{-2}$), they are potential materials for advanced strain-engineered electronics.

However, these NWs faced two bottle-necks. First, in contrast to bandgap deformation potentials under hydrostatic pressure a_P, there have been a significant disagreement among literature values of those under uniaxial stress ($a_{zz} = dE_g/d\varepsilon_{zz}$), which makes difficult to design the strain-engineering of electronic properties. Second, NWs grown by bottom-up route commonly have non-uniform electronic properties which makes difficult to control the device properties. This is because NWs experience anisotropic crystal growths with different impurity incorporation rates which then forms growth sectors with different impurity concentrations within each NW. This issue is bottle-necking due to the lack of measurement technique for local carrier concentrations at high spatial resolution and high sensitivity available for semiconducting free-standing NWs.

In this work, nanoprobe-cathodoluminescence (Nanoprobe-CL) system is developed and applied to individual ZnO free-standing nanowires (1) for the evaluation of the uniaxial bandgap deformation potential ($a_{zz} = dE_g/d\varepsilon_{zz}$) and the fracture strain (ε_{zzF}) and (2) for the measurement of local carrier concentration within a single semiconducting NW.

2. Experimental

Sample preparation

Free-standing ZnO nanowires with controlled diameters ranging from 0.1 μm to 1 μm are grown homoepitaxially on single-crystalline ZnO(0001) substrate using precursor aqueous solution growth technique in combination with electron beam lithography of growth windows.[1,2]

Nanoprobe-CL system

Nanoprobe-CL system is developed based on low-temperature (10-300 K) SEM-CL nanospectroscope with *in-situ* nanomanipulator, where this nanomanipulator enables sampling, stress-loading tests, and electrical probing of an individual single-crystalline free-standing NWs *in-situ*.[1-3]

3. Results and Discussion

Figure 1(a) illustrates a measurement principle of the a_{zz} of a single-crystalline free-standing NW.[1] An apex of the NW is deflected by the metal nanoprobe indenter. Based on the Euler-Bernoulli beam theory, nominal uniaxial strain ε_{zzN} and plastic uniaxial strain ε_{zzP} at arbitrary position P on the NW are evaluated by the SEM image analyses of the deflected NWs deformed quasi-elastically and elastic uniaxial strain at P is then calculated by $\varepsilon_{zzE} = \varepsilon_{zzN} - \varepsilon_{zzP}$. Simultaneously, an optical bandgap E_g at arbitrary position P is also characterized by the CL nanospectroscopy of photons emitted by the band-edge radiative carrier recombinations. A fracture strain ε_{zzF} of each NW is also evaluated by SEM observation of its fracture during the bending deformation test. An application of above technique to ZnO free-standing NWs with diameters of 150 nm yields $a_{zz} = dE_g/d\varepsilon_{zzE} = -1.7$ eV and $\varepsilon_{zzF} = 0.04$. We found that our a_{zz} values obtained and those reported

in several literatures are fully explained by the surface-elasticity of the NW as well as the surface sensitivity of the measurement. This technique determines the bandgap deformation potentials more accurately than existing techniques and demonstrate the robustness of single-crystalline free-standing NWs.

Local carrier concentration within a ZnO NW with a diameter of about 1 μm is characterized by CL nanospectroscopy.[2] While the ZnO (0001):+*c* top-plane of the ZnO NW exhibited the band-edge CL emission energy of 3.28 eV, the ZnO (1-100):*m* side-planes exhibited redshifted CL emission energy of about 3.20 eV. Temperature-dependent CL nanospectroscopy in combination with Raman spectroscopy, x-ray photoemission spectroscopy, and electrical measurement of a single NW attributed this redshift to the band-tailing or bandgap shrinkage due to the residual carriers generated from unintentional hydrogen donors at high concentrations (n = 2.8×10^{17} cm^{-3} at +*c* top-plane and $n = 2.8\times10^{17}$ cm^{-3} at *m* side-planes). Figure 1(b) shows the cross-sectional CL nanospectroscopy of an individual ZnO NW. ZnO free-standing NW is micro-sampled using the micromanipulator with a sharp metal nanoprobe and its axial and basal cross-sections are fabricated using focused ion beam (FIB) with controlled incident angles. Monochromatic near-band-edge CL image of ZnO NW cross-sections visualized two distinct regions within a single ZnO NW at spatial resolution better than 60 nm, with different photon energies and intensities of CL emission, which are attributed to the axial (+*c*) and lateral (*m*) growth sectors with different residual carrier concentrations. Thus, this technique visualize carrier concentration map of arbitrary NW cross-section at high resolution and high sensitivity.

4. Conclusions

Nanoprobe-CL technique enables us to visualize carrier concentration map within a single NW at high resolution and high sensitivity and to evaluate uniaxial bandgap deformation potentials and its fracture strain accurately. These novel techniques pave the way for the strain-engineered nanoelectronics using well-defined bottom-up materials.

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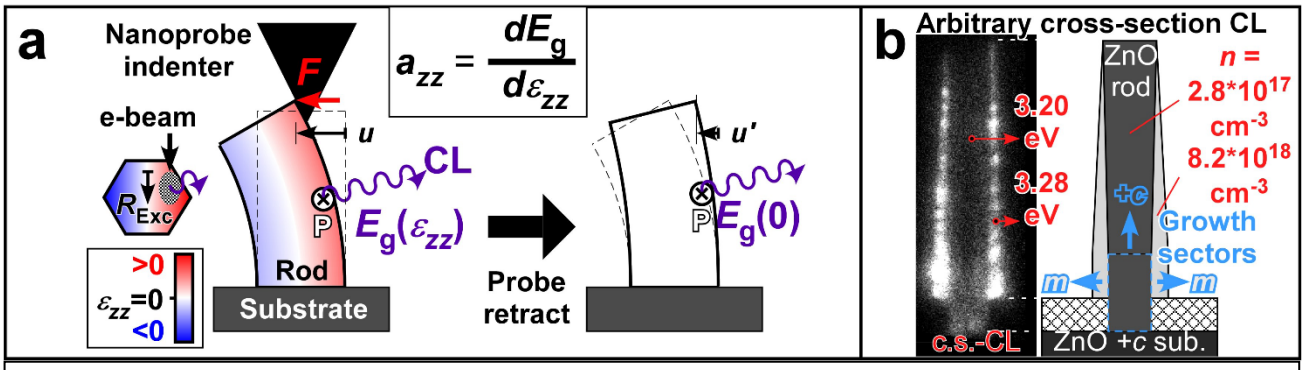

Fig. 1
(a) Nanoprobe-CL technique for determining ZnO nanorod plastic deformation and uniaxial ZnO band-gap deformation potential a_{zz}. Reprinted with permission from [1]. Copyright (2015) Americal Chemical Society.
(b) Nanoprobe-CL technique for imaging ZnO nanorod growth sectors with different carrier concentrations n at axial cross-section. Reprinted from Ref. [2].