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KAKENHI 科研費

科学研究費助成事業　　研究成果報告書

平成　２９　年　　８　月　　８　日現在

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研究課題名（和文） 動的高分解能TEM観察によるナノスケールの光発電と光電子工学に関する研究

研究課題名（英文） Research on nanoscale photovoltaics and optoelectronics by dynamic high resolution TEM observations

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研究成果の概要（和文）：1.TEM内その場ナノ操作の実現：2本以上のナノワイヤーをナノの精度で操作しTEM内で接続することに成功し、かつナノ接合部の特性評価も行った。2.ZnOナノワイヤーの光-力-電気３連特性の発見：歪んだZnOナノワイヤーで光起電力スペクトルのピーク分離を発見し、これが光－力－電気特性が連動した現象であることを示した。理論計算から、ワイヤーの収縮側と圧縮側で電子構造が異なっていることに起因することがわかった。3.CdSナノワイヤーの光学応答の解析：電気と光の両プローブを導入することで、CdSナノワイヤーの光学特性を1本ずつ測定した結果、オン／オフ比は弾性変形を受けても変化しないことを明らかにした。

研究成果の概要（英文）：1. In situ TEM manipulation possibilities for “nanoarchitectonics”: We demonstrate precise manipulation of multiple nanowires with nanoscale accuracy and in situ TEM creation of hetero-junctions between them. Optoelectronic tests are carried out on them using light, introduced inside the TEM column through an optical fiber. 2. Opto-mechano-electrical tripling in ZnO nanowires: We observe that in situ bent ZnO nanowires exhibit an opto-mechano-electrical tripling phenomenon, due to the electronic structure changes in the expanded/compressed regions of the wire, in excellent agreement with theoretical simulations. 3. Statistically analyzed photoresponse of elastically bent CdS nanowires: Using in situ electrical probing and light illumination, we measure the optoelectronic features of individual CdS nanowires under elastic bending, while visualizing deformation features. Our statistical analysis shows that the ON/OFF ratios of the wires do not change due to bending deformation.

研究分野： In-situ transmission electron microscopy

キーワード： TEM　optoelectronics　nanomaterials

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１．研究開始当初の背景

These days, the fast development of Transmission Electron Microscopy (TEM) is pushing boundaries for nanomaterial observations at an unprecedented high spatial resolution, down to 60 pm. The advances in sampling techniques, lens aberration correction and spectroscopic analysis allow for the complete understanding of various materials' atomic structures and spatially-resolved chemical compositions. However, common TEM techniques have not had access to nanomaterial electrical, mechanical, optical and thermal properties which may be advantageous for future applications, such as flexible electronics, optoelectronics, etc. Thus it is crucial to find a way to manipulate, contact, and in situ probe a nanomaterial in order to reveal its peculiar functionality. For example, in order to understand light-matter interactions, electrical and optoelectronic properties of semiconducting nanomaterials and their heterostructures, it is essential to perform challenging optoelectronic tests under various manipulations inside a high-resolution TEM. The beauty and power of the state-of-the-art in situ TEM experiments stem from a fact that any functional property may be measured under full control of the nanomaterial's atomic structure, its deformation and chemistry and allow for the unambiguous establishment of a clear structure-property relationship. And this is the "Holy Grail" of the whole Materials Science field. However, this task is never as simple as handling and building toy bricks, especially inside a TEM. Throughout this project we were able to successfully perform diverse in situ TEM probing experiments on a wide range of nanomaterials, which will be used as part of flexible electronic and optoelectronic devices.

２．研究の目的

In situ studies on nanomaterials toward optoelectronics, electronics and energy conversion are required by society. Our purpose was to take this challenge and to analyze the dynamics of these building blocks, as well as their heterostructures, and to provide detailed knowledge for advanced applications.

３．研究の方法

We explored new experimental methods and engineering details, including *in situ* TEM setups and methodologies.

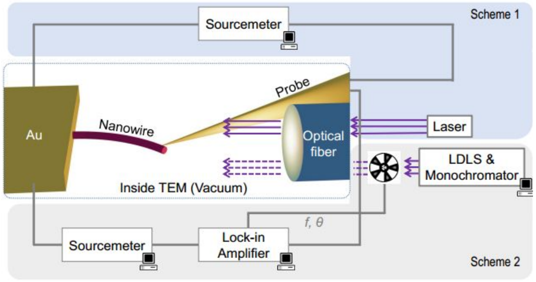

Fig. 1. Schematic of the experimental setup used for photocurrent I-V measurements (Scheme 1, upper part), and for photocurrent spectroscopy (Scheme 2, lower part).

As illustrated in Fig. 1, the system is equipped with an optical fiber protruded through the TEM specimen holder connected to a piezo-tube, inside the pole piece of the microscope. A metallic probe with a tip radius ranging from 50 nm to several micrometers was aligned to the axis of the optical fiber core at a distance of ~0.5 mm. Probing, imaging and diffraction studies were conducted by using an energy-filtered 300 kV JEM-3100FEF high-resolution TEM, under high vacuum (10^{-5} Pa) at room temperature.

４．研究成果

***In situ* TEM manipulation possibilities for**

“nanoarchitectonics”

On-demand precise manipulation of two or more individual nanowires with nanoscale accuracy and *in situ* TEM creation of axial hetero-architectures using them has never been attempted before. Building of such junctions and their *in situ* optoelectronic probing would be highly innovative with respect to the overall “nanoarchitectonics” standpoint and would allow uncovering novel physical phenomena.[5]

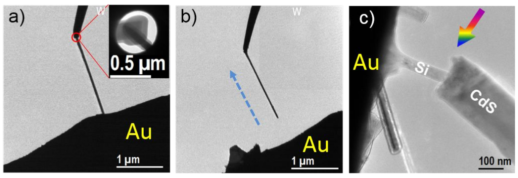

Fig. 2. TEM images representing fabrication of an axial CdS/p-Si nanowire junction under delicate manipulation in TEM. (a) First step: Making a physical contact with an individual CdS nanowire and soldering the tip and the wire under focused electron beam irradiation. (b) Second step: Pulling out the nanowire from the Au support; (c) Third step: Connecting CdS nanowire to the individual B-doped Si nanowire.

Thus, CdS nanowires and B-doped Si nanowires are chosen by us as building blocks. Then, we demonstrate a delicate and precise nanomanipulation technique for creating new axial nanowire architectures inside HRTEM. Finally, straightforward electrical and optoelectronic tests are carried out on them using a variable wavelength light, introduced inside the TEM column through an optical fiber. Importantly, the experiments allow for simultaneous control over the crystallography and chemistry of the two constituents and the interface between them, before, during and after probing, and under ultrahigh spatial resolution only achievable with HRTEM. The tests directly reveal clear photosensing properties of the junctions. They possess selective sensitivity to purple and blue lights rather than to the light of larger wavelengths. Furthermore, they exhibit a photocurrent saturation effect. This suggests that such junctions are practical for detection of the light intensity; they do not require large energy consumption and operate in a stable way even under sudden voltage pulses.

In summary, an *in situ* HRTEM technique allowing for a direct fabrication of individual axial nanowire junctions has been demonstrated. *In tandem* structural characterizations and optoelectronic measurements uncovered the photosensing performance of the single-crystalline axial CdS/p-Si nanowire junctions. These exhibit excellent selectivity toward the yellow range of light wavelengths. They also possess a peculiar photocurrent saturation effect, which could be smartly employed in low consumption light intensity sensing and integrated tunable voltage-driven applications. The presented technique provides a strong motivation toward establishing new operational principles of single crystal nanomaterial devices. It is also expected that the near-field scanning technique could be easily applied to this system for a further detailed study of nanoscale optoelectronic phenomena.

Opto-mechano-electrical tripling in ZnO nanowires probed by photocurrent spectroscopy in HRTEM

The built-in optical *in situ* HRTEM system combines two important features: scanning tunneling microscopy (STM) probing paired with modulated light illumination, see Fig. 1. The *in situ* bent ZnO nanowires exhibit an interesting opto-mechano-electrical tripling phenomenon, *i.e.* the photocurrent spectra at around 3.3 eV exhibits a split in bent nanowires. This reflects

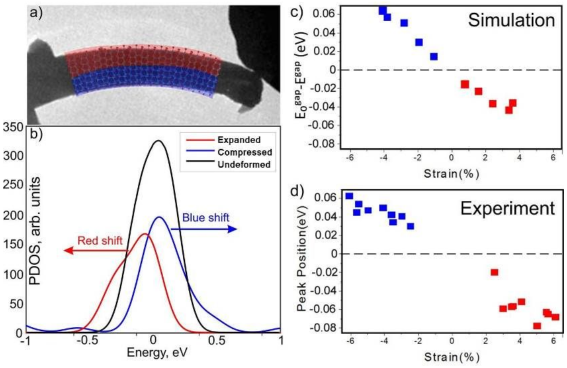

Fig. 3 (a) Simulated geometry of a bent ZnO nanowire in comparison with the experimental TEM image. (b) PDOS of expanded (red) and compressed (blue) sides of the bent ZnO nanowire. Black curve denotes the total DOS for the undeformed nanowire as a whole. (c) DFTB simuilations, and (d) experimental results of the ZnO wire band gap under bending deformation.

the electronic structure changes in the expanded/compressed regions of the wire.

In this work, we discuss on the *in situ* photocurrent spectroscopy. We present the first ever report on opto-mechano-electrical tripling phenomenon uncovered under *in situ* TEM. By comparing photocurrent spectra of individual ZnO nanowires under bending, the splitting of photocurrent spectra is documented. The photocurrent peak shifts directly follow the bending strains. The red and blue shifts of ZnO photocurrent peaks under bending are confirmed to be due to the splitting of levels in the valence band. DFTB simulations are in excellent agreement with the experimental results. The discovered splitting effect provides valuable information for flexible optoelectronics and piezo-phototronics. For example, this may be employed for strain tuned wavelength-division multiplexing and MEMS devices, and for flexible optoelectronics where photocurrent splitting should be avoided.

Statistically analyzed photoresponse of elastically bent CdS nanowires probed by light-compatible *in situ* high-resolution TEM

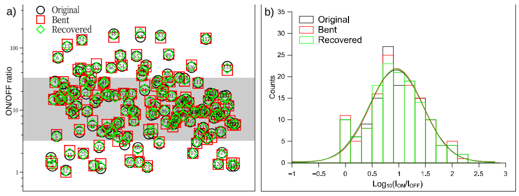

Fig. 4. Statistical distribution of the measured ON/OFF (photocurrent/dark current) ratios for 139 bending/recovery experiments undertaken on individual CdS nanowires. (a) ON/OFF ratio scatter; a gray region, where the majority of cases was documented, is marked as a guide to the eye. (b) Statistical analysis of the data in (a); the lines represent Gaussian fits to the 3 histograms.

In this work, we describe pioneering photocurrent measurements on elastically bent CdS nanowires inside HRTEM. Using in-tandem *in situ* electrical probing and light illumination, we trace the optoelectronic features of individual wires under elastic bending, while at the same time visualize all deformation features with ultimately high spatial resolution. In the first part of this work, the photocurrents measured under nanowire bending are discussed, as shown in Fig. 4. In order to achieve a reliable and stable physical contact, the probe was slightly pressed towards the nanowire. The probe was then moved, resulting in strain. The nanowire was then recovered to its original state by retracting the probe. For each state, I-V measurements were performed in both dark and illuminated conditions. Numerous experiments were performed for a comprehensive statistical analysis. The statistical information from ON/OFF ratios was thoroughly analyzed. Although the values vary from case to case, caused by probing-induced contact changes, the

ON/OFF ratios are rather stable for each individual case. The statistical distribution of the ON/OFF values confirms this trend on a wider scale, and also allows for the estimation of an average value of around 10. The results of stable ON/OFF ratios are most common; however, some data shows deviations. The reason is that our setup has only two electrodes and the contact resistance becomes an uncertainty. The effects of this variable are however absorbed by the detailed statistical analysis. The independent nature of this variable with respect to the resistance of the nanowire itself allows for the contributions to be separated, enabling us to observe the effects which are due to the intrinsic nature of the sample.

In the second part of the work, spectroscopy information is presented. The photocurrent spectroscopy results are displayed before and during bending with a 1.1% elastic strain, as shown in Fig. 5. The nanowire photocurrent cut-off wavelength has a 7.3 nm red shift upon bending: in the initial state, the edge wavelength is 521.8 nm; under bending, this value increases to 529.1 nm. More wires were tested; these show similar red-shifts for the cut-off wavelength. Overall, for 1.68%, 0.75%, 1.59%, 1.21% and 3.36% strains, 1.2 nm, 5.4 nm, -0.6 nm, 0.7 nm and 5.5 nm shifts were recorded. Thus we obtain an average red shift value of 3.3±2.9 nm; although there is some deviation in the data, it shows that the effect is not limited to individual cases. The cut-off value of the photocurrent spectra is related to band structure, which determines the near-band-edge emission (NBE) of the material.

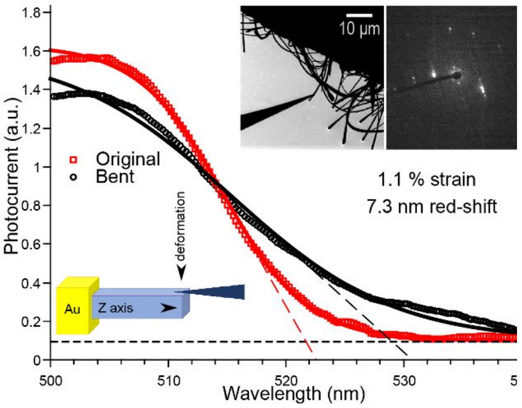

Fig. 5. Photocurrent spectroscopy measurements performed on a representative individual CdS nanowire. The insets present a low-magnification TEM image and a corresponding SAED pattern from the wire of interest.

In summary, we successfully performed pioneering photocurrent measurements for elastically bent CdS nanowires inside HRTEM. All nanostructures reveal very close photocurrent-to-dark current ratios (ON/OFF ratios) in original, bent and recovered states, with an average value of approximately 10. Photocurrent spectroscopy of several examples shows red shifts of the order of several nanometers for the photocurrent cut-off wavelength. Our experiments reveal a variety of bending-induced effects for individual nanowires, while showing that from a statistical point of view the nanowires display common features in their response to deformation, making them suitable for future flexible optoelectronic applications.

５．主な発表論文等

（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計　４件）

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〔図書〕（計 0 件）

〔産業財産権〕
○出願状況（計 0 件）
○取得状況（計 0 件）

〔その他〕
ホームページ等
http://www.nims.go.jp/nanotube/

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