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Growth direction determination of a single RuO$_2$ nanowire by polarized Raman spectroscopy

Myung Hwa Kim,[1,2] Jeong Min Baik,[2,3] Seung Joon Lee,[2] Hae-Young Shin,[1,4] Jaeyeon Lee,[1] Seokhyun Yoon,[1,4] Galen D. Stucky,[2,a)] Martin Moskovits,[2,a)] and Alec M. Wodtke[2,a)]

[1]*Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Republic of Korea*
[2]*Department of Chemistry and Biochemistry, University of California at Santa Barbara, Santa Barbara, California 93106, USA*
[3]*School of Mechanical and Advanced Materials Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 689-805, Republic of Korea*
[4]*Department of Physics, Ewha Womans University, Seoul 120-750, Republic of Korea*

The dependence of band intensities in the Raman spectrum of individual single-crystal ruthenium dioxide (RuO$_2$) nanowires on the angle between the plane of polarization of the exciting (and collected) light and the long axis of the nanowire, is shown to be a simple, complementary technique to high resolution transmission electron microscopy (HRTEM) for determining nanowire growth direction. We show that excellent agreement exists between what is observed and what is predicted for the polarization angle dependence of the intensities of the nanowires' E_g (525 cm^{-1}) and the B_{2g} (714 cm^{-1}) Raman bands, only by assuming that the nanowires grow along the (001) crystallographic direction, as confirmed by HRTEM. © *2010 American Institute of Physics*. [doi:10.1063/1.3435475]

Metal oxide quasi-one-dimensional (1D) nanostructured materials are currently of great interest as building blocks in optoelectronic devices, devices for alternative energy applications, and as heterogeneous catalysts (among others) owing to the modification of their chemical, mechanical, electrical, and optical properties from those of the bulk.[1–4] Because of its high electrical conductivity, chemical stability, and excellent diffusion barrier properties, nanostructured ruthenium dioxide (RuO$_2$) is a promising candidate as an electrode material in electrochemical devices and field-emission displays. It also has potential as a catalyst due to its chemical properties.[5,6]

The physicochemical properties of quasi-1D nanostructures depend on their composition, crystal structure, and growth direction and means to determine these properties are essential for constructing nanodevices, in particular, and for understanding nanostructures, in general. X-ray diffraction is widely used to determine crystal structure; however, it is difficult to apply to single nanostructure. High-resolution transmission electron microscopy (TEM) and electron diffraction have been used very effectively to determine the structure of nano-objects, and specifically nanowires (NWs), down to atomic dimensions, thereby allowing their growth direction(s) to be determined. However, TEM measurements are not routine in all laboratories and require special sample preparation.

A routine and rapid method for growth direction determinations would be useful. One such facile technique is Raman spectroscopy, which has been used broadly in studying nanomaterials to measure, for example, the phonon structure of single semiconductor NWs from which properties such as the crystal structure, phonon spectrum,

chemical composition, and electronic states can often be determined.[7–11]

Polarized Raman measurements have also been carried out on single NWs unambiguously identifying the NW's growth direction and comparing the results with those obtained using electron diffraction.[12–16] As with electron microscopy, Raman spectroscopy can be used as a real-time probe under a broad range of experimental conditions. In this letter, we report the use of polarized Raman scattering as a rapid and reliable method for determining the growth direction of a single RuO$_2$ NW.

RuO$_2$ NWs were grown on a 200-nm-silica-covered Si(001) wafer, by vapor transport at 650 °C and atmospheric pressure, without catalyst as has been recently reported.[17] Specifically, NW growth was carried out in a three zone horizontal quartz tube furnace, 2.5 cm in diameter and 122 cm long. 10 mg of fine meshed RuO$_2$ (99.9%, Aldrich) powder was loaded at the center of a 10 cm long quartz boat without further purification. The quartz boat and its RuO$_2$ charge were cleansed of impurities by first placing it at the center of the quartz tube furnace and heating it to 950–1000 °C under He (99.999%) carrier gas flowing for ~10 min at a gas flow rate of 300 SCCM (SCCM denotes cubic centimeter per minute at STP). The source was then maintained at temperature for an additional 3 h. Following this procedure the (cleaned) Si substrate, was introduced into the furnace at a point approximately ~15 cm downstream of the RuO$_2$ powder source, where the temperature was ~650 °C, and gas consisting of high purity He (99.999%, 300 SCCM) and O$_2$ (99.9%, 10 SCCM) flowed for 3 h. The furnace was then allowed to cool to room temperature under flowing He.

The product collected on the Si/SiO$_2$ substrate was characterized by scanning electron microscopy (SEM) and micro Raman spectroscopy. RuO$_2$ NWs were also imaged by HR-TEM (FEI Titan TEM/STEM at 300 kV) at room temperature. Samples for TEM imaging were prepared by simply

[a)]Authors to whom correspondence should be addressed. Electronic addresses: stucky@chem.ucsb.edu, mmoskovits@ltsc.ucsb.edu, and wodtke@chem.ucsb.edu.
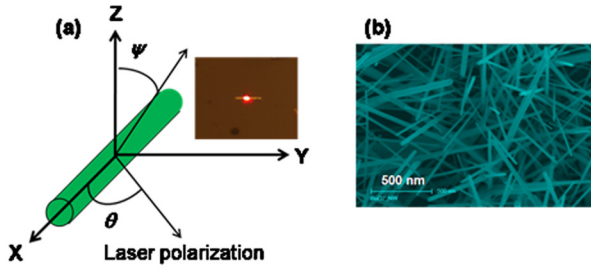
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FIG. 1. (Color online) (a) The coordination of the polarization dependence Raman scattering experiment for a single RuO$_2$ NW with respect to the incident and scattered light. (b) SEM image of as-grown RuO$_2$ NWs on a Si (100) substrate.

touching the NW-covered substrate to a TEM grid, thereby transferring some of NWs to the grid.

Polarization dependent Raman scattering measurements were carried out on well spaced single RuO$_2$ NWs transferred to a Pyrex glass slide. Raman spectra were recorded in the backscattering configuration using a confocal microscope (Renishaw InVia System), using a $100 \times (0.9$ NA) microscope objective, which both focused the laser beam (~ 1 μm) and collected the backscattered light. Raman spectra were excited with 632.8 nm He–Ne laser light. Low powers were used to ensure that the NWs did not decompose by localized laser heating. Optimal results were obtained with 0.57 mW laser power and 200 s integration times. Polarization-dependent Raman spectra were measured by rotating a half-wave plate in 10° increments, changing the angle, θ, between the electric vector of the incident light and the long axis of a NW as described in Ref. 13 and shown in Fig. 1(a).

SEM images of the as-grown RuO$_2$ NWs [Fig. 1(b)] indicate two shape categories: characterized by polyhedral or rectangular cross sections and each with well defined facets. The NWs used in the polarized Raman studies had lateral dimensions in the range 80–100 nm and approximately 10 μm in lengths as determined by SEM and TEM. Energy dispersive x-ray analysis indicated the NW to be composed of Ru and O only.

RuO$_2$ is known to have the tetragonal rutile structure with the space group D_{4h}^{14}-$P4/mmm$, and two molecular units per primitive cell, with lattice constants $a = b = 4.4931$ and $c = 3.1064$ (JCPDS No.88-0322).[18] Group theory predicts that its Raman active modes belong to the A_{1g}, B_{1g}, B_{2g}, and E_g, representations. Figure 2 shows a series of polarization-direction-dependent Raman spectra of a single RuO$_2$ NW as
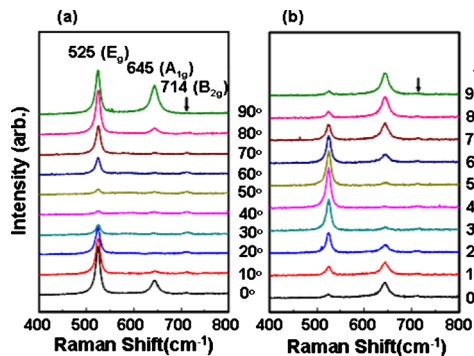

FIG. 2. (Color online) A series of Raman spectra of a single RuO$_2$ NW as a function of the angle ($0° \leq \theta \leq 90°$) in parallel ($\parallel$) (a) and perpendicular ($\perp$) (b) polarization configurations.
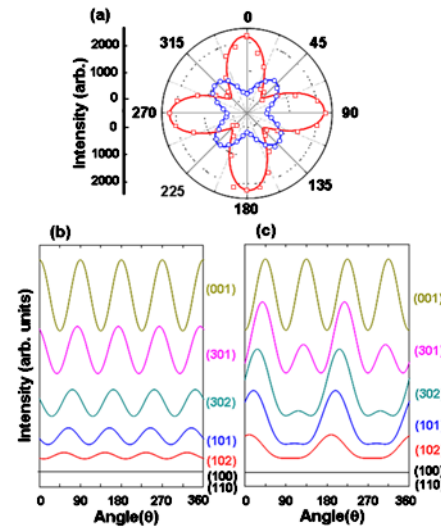

FIG. 3. (Color online) (a) Polar plots of polarization dependent Raman intensities of the E_g band at 525 cm^{-1} for parallel (rectangular) ($\parallel$) and perpendicular (circle) ($\perp$) polarization configurations. Two different solid curves represent fitting results to the data with the calculated Raman intensities in the (001) growth direction. (b) and (c) The calculated Raman intensity of the E_g mode with respect to various growth directions for parallel (b) ($\parallel$) and perpendicular (c) ($\perp$) polarization configurations.

a function of the angle between the polarization vector and the wire's principle axis, for the parallel ($\parallel$) and perpendicular ($\perp$) polarization configurations (i.e., respectively, with the incident and collection polarization coincident and at right angles to each other).

The Raman bands at 525 cm^{-1}, 645 cm^{-1}, and 714 cm^{-1} have previously been assigned to the first order E_g, A_{1g}, and B_{2g} phonon bands of rutile RuO$_2$, respectively.[19] Our measured band frequencies correspond closely to those observed with bulk samples; moreover, the full width at half-maximum of the 525 cm^{-1} E_g phonon mode at (11 cm^{-1}) is close to the value reported for the bulk single crystal, implying high crystalline quality for our NWs.[19] The B_{1g} mode—a soft phonon mode in the phase transition—is not observed in our measurements, due to the very small cross section of our NWs.[18]

The intensities of the E_g and A_{1g} phonon modes show pronounced polarization sensitivity (Fig. 2); however, the polarization-induced intensity variations in the 714 cm^{-1}, B_{2g} phonon mode cannot be determined with confidence on account of its low intensity. The dependence of the intensity of the E_g (525 cm^{-1}) as a function of polarization direction (θ) is shown as a polar plot in Fig. 3(a), for the parallel ($\parallel$) (shown in red), and perpendicular ($\perp$) (shown in blue) measurements. Each polar curve is fourfold symmetric for $0 \leq \theta \leq 2\pi$, and the parallel ($\parallel$) and perpendicular ($\perp$) polar curves are rotated by $\theta = \pi/4$ with respect to each other. The first maximum for the parallel ($\parallel$) polarization occurs at 0°, while the first maximum for the perpendicular ($\perp$) polarization occurs at 45°.

The Raman intensities for the various phonon bands in a single crystal can be calculated from the Raman tensor and taking account of the crystal symmetry using the following equation:

$$I_j \approx |\hat{e}_s \cdot \overleftrightarrow{R}_j \cdot \hat{e}_l|^2, \tag{1}$$

where $\overleftrightarrow{R}_j$ is the Raman tensor and $\hat{e}_l$ and $\hat{e}_s$ the unit vectors along the incident (l) and scattered (s) directions,

respectively.[13] Using the Raman tensors representing the respective phonon modes for rutile RuO_2, the polarization dependence of the intensity of the E_g band was computed by assuming the NW's long axis (i.e., its growth direction) corresponds to various crystalline directions. The results are summarized in Figs. 3(b) and 3(c).

The variation in the expected pattern of the predicted θ-dependence of the Raman intensities suggest that, provided that the quality of the Raman spectra and the crystallinity of the NW are sufficient, the growth direction can be unequivocally determined from the measured polarization angle dependencies using only the two, parallel and perpendicular, intensity components of the E_g Raman band. It is obvious even by inspection that our measurements suggest that this particular NW grew in the (001) direction. Note that the (100) and (110) growth directions are immediately excluded as here the E_g modes are forbidden.

To see this more quantitatively, consider the solid lines in Fig. 3(a), which are computed polarization-dependent Raman intensity variations for the E_g Raman band (525 cm^{-1}), assuming the (001) growth directions. The measured Raman intensities can be fitted to the computed curves by scaling the calculated intensities and included a nonzero baseline. The fit is excellent.

All of the RuO_2 NWs measured in this study were found to have the (001) growth direction, consistent with previous reports.[6,20] The nonzero observed intensities of the measured Raman scatterings at the minima are likely due to crystalline nonidealities, not least of which is the NW's nanoscale size, which requires a formal breakdown of translational symmetry. Some polarization mixing due to the focused nature of the incident laser beam also contributes.[16]

We also find that the Raman intensity measured with the electric field vector oriented perpendicular to the NW's long axis is approximately 2.5 times smaller than that with the electric field vector oriented the parallel to the NW's long axis. This is likely due to the nanosize of the wire whose effect would be greatest when exciting modes in its short direction.[15,16] One notes in passing that although the Raman intensity of the B_{2g} band is weak so that the detailed polarization angle dependence of its intensity is not as reliable as that for the E_g mode, its lack of polarization angle dependences is what is expected for a RuO_2 NW grown along the (001) direction.

Likewise, as previously reported,[21] the polarization angle dependence of the A_{1g} band has a number of complexities associated with arising from its very great sensitivity to small changes in the relative values of the polarizability tensor, that it is less reliable than the E_g mode (of the rutile structure) in determining growth direction.

TEM and HRTEM imaging, and SAED measurements (Fig. 4) confirm our conclusion based on Raman measurements that the RuO_2 NWs grow along the (001) direction. Figure 4(a) shows in greater detail the polyhedral cross section of the NW studied, with its 80 nm diagonal cross-sectional dimension. Interestingly, the sharp facets seen at the tip of the NW imply that these low-index facets are the low surface energy surfaces in the growth process.

In summary, we show that excellent agreement exists between what is observed and what is predicted for the polarization angle dependence of the intensities of the NWs' E_g (525 cm^{-1}) and the B_{2g} (714 cm^{-1}) Raman bands, only by
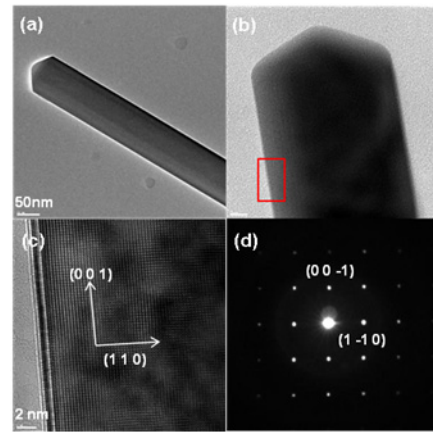

FIG. 4. (Color online) High resolution TEM images of an individual RuO_2 NWs and the corresponding electron diffraction pattern recorded along the (110) zone axis and lattice image.

assuming that the NWs grow along the (001) crystallographic direction, as confirmed by HRTEM. This illustrates the broader contention that polarized Raman measurements can often identify unequivocally the growth direction of single-crystal NWs, as a rapid *in situ* alternative to HRTEM.

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