Raman scattering characterization of well-aligned RuO$_2$ nanocrystals grown on sapphire substrates

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Abstract. Raman scattering (RS) spectroscopy is a popular measurement technique that uses inelastic scattering of monochromatic light to study vibrational characteristics of a material system. A typical application of RS is for material structure determination. This paper describes the application of RS for the characterization of the preferable growth direction of well-aligned nanocrystals (NCs) deposited on sapphire substrates. The results indicate that RS could become a powerful technique for the quick determination of the NCs orientation. The redshifts and asymmetric linewidth broadening of the Raman features of RuO$_2$ NCs are analysed by a modified spatial correlation (MSC) model, which includes the factor of stress-induced shift. The usefulness of experimental RS together with the MSC model analysis as a nondestructive structural and residual stress characterization technique for NCs has been demonstrated.

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1. Introduction

A wide range of nanosized oxide materials are currently the focus of intensive research owing to their potential use in nanodevice fabrication [1, 2]. Among the numerous oxides, the electrically conducting RuO$_2$ belongs to the family of transition-metal dioxide compounds with a rutile structure [3]. The attractive properties of RuO$_2$ have been extensively studied for several applications, such as thick film resistors [4, 5], electrode material for electrochemical devices [6, 7], an electrode in ferroelectric random-access memory [8], and an electrochemical capacitor for energy storage [9, 10]. Owing to their high chemical stability and high aspect ratio, RuO$_2$ nanocrystals (NCs) have been demonstrated to be a candidate material for vacuum microelectronic devices [11, 12].

Moreover, the vibrational properties of nanosized systems are interesting from a fundamental point of view because of the changes related to the spatially confined grain size effects. The structure of their grain boundaries has been rather controversial, and their properties give a non-consistent picture that appears to depend upon which experimental technique is being used [13]. Therefore, it is very important to understand and clarify the nature of the physical properties of nanocrystalline materials.

In this article, we report the Raman scattering (RS) characterization of RuO$_2$ NCs deposited on sapphire (SA) substrates with different orientations via reactive radio frequency magnetron sputtering (RFMS). Combined with x-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and modified spatial correlation (MSC) model calculations, RS is used to extract orientations and residual stress information of well-aligned RuO$_2$ NCs deposited on SA substrates. The usefulness of RS as a nondestructive structural and residual stress characterization technique for NCs will be demonstrated.

2. Experimental

The RuO$_2$ NCs were deposited on SA substrates with different orientations (SA(012), SA(110), SA(001), and SA(100)) via RFMS. The sputtering target was a 1-inch Ru (99.95%) metal. The reactive sputtering was carried out in a mixture of argon (11 sccm) and oxygen (1 sccm) gases. O$_2$ was introduced over the substrate into the sputtering chamber with Ar atmosphere. A working pressure of 7.5 mbar, radio frequency generator power of 65 W, substrate temperature of 200°C and a 180 min deposition time were used in the experiment.
The morphology of the RuO$_2$ NCs was studied with a JEOL-JSM6500F FESEM. XRD patterns taken on a Rigaku RTP300RC x-ray diffractometer equipped with a Cu K$_\alpha$ radiation source and a Ni filter were used to examine the crystallographic characteristics of the NCs over a large area of the surface. RS spectroscopy was used to extract nanostructural information of the RuO$_2$ NCs. Raman spectra were recorded at room temperature utilizing the back-scattering mode on a Renishaw in Via micro-Raman system with 1800 grooves mm$^{-1}$ grating and an optical microscope with a 50× objective. The same microscope was used to collect the signal in a backscattering geometry. The Ar-ion laser beam of the 514.5 nm excitation line with a power about 1.5 mW was focused on a spot size $\sim5\,\mu$m in diameter. Prior to the measurement, the system was calibrated by means of the 520 cm$^{-1}$ Raman peak of a polycrystalline Si.

3. Results and discussion

RuO$_2$ has the tetragonal rutile structure [14] belonging to the space group $D_{4h}^{14}$ with two RuO$_2$ molecules per unit cell as shown in figure 1. The cations are located at sites with $D_{2h}$ symmetry and the anions occupy sites with $C_{2v}$ symmetry. The Ru-ions are surrounded by six oxygen ions at the corners of a slightly distorted octahedron, while the three Ru-ions coordinating each oxygen ions lie in a plane at the corners of a nearly equilateral triangle. According to the factor group analysis, there are fifteen optical phonon modes with the irreducible representation as given in [15]. Only three modes are Raman active in the range of measurements (400–800 cm$^{-1}$) with symmetries $E_g$, $A_{1g}$, and $B_{2g}$, where the first is a doublet and the last two are singlets [15]. Corresponding to each Raman-active mode, there is a scattering tensor $\alpha$ having a distinctive symmetry. The forms of these tensors in materials of $D_{4h}^{14}$ space group are [16]:

$$\alpha(E_g) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & e \\ 0 & e & 0 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix},$$
To examine experimentally a given component $\alpha_{ij}$, the geometry is arranged such that the incident light is polarized in the ‘$i$’ direction while only the scattered light of ‘$j$’ polarization is observed.

A classification of the observed Raman-active modes for (101), (100) and (001) planes of RuO$_2$ may be accomplished as follows. We adopt the following notation for the various axes used in this experiment: $x = (100)$, $y = (010)$, $z = (001)$ and $x' = \frac{1}{\sqrt{2}}(\overline{1}0\overline{1})$, $y' = (001)$, $z' = \frac{1}{\sqrt{2}}(110)$. Since it is impossible to identify the direction in the experiment for NCs, we assume that the Raman signal is the average signal from all possible geometries. The expressions for the relative Raman intensities correlating to various $|\alpha_{ij}|^2$ for the (101), (100) and (001) planes in the backscattering configuration are listed in table 1. The results show that $E_g$, $A_{1g}$ and $B_{2g}$ modes are allowed for the polarization configurations for scattering from the (101) plane. The $B_{2g}$ and $E_g$ modes are forbidden for all configurations from (100) and (001) planes, respectively.

The spatial correlation (SC) model of Richter et al [17] extended by Fauchet and Campbell [18] was exploited for analysing the Raman-active modes of RuO$_2$ NCs. The main assumption is that the phonons in nanosized systems can be confined in space by crystallite boundaries or surface disorders. Consequently, this confinement causes an uncertainty in the wave vector of the phonons and results in a red shift and asymmetric broadening of the Raman features. The intensity of the first-order Raman spectrum, $I(\omega)$, is given by [18]:

$$I(\omega) \approx \int \frac{d^3q |C(0, \mathbf{q})|^2}{[\omega - \omega(\mathbf{q})]^2 + (\Gamma/2)^2},$$

where $\omega(\mathbf{q})$ is the phonon dispersion curve, $\Gamma$ is the natural linewidth and $C(0, \mathbf{q})$ is the Fourier coefficient of the phonon confinement function. The relaxation of the $\mathbf{q} = 0$ selection rule due to phonon confinement in a NC has been taken into account. Using the Gaussian confinement function and considering the column shaped crystal, the Fourier coefficient $|C(0, \mathbf{q})|^2$ can be written as follows [18]:

$$|C(0, q_1, q_2)|^2 \approx e^{-q_1^2L_1^2/16\sigma^2} e^{-q_2^2L_2^2/16\sigma^2} \left[1 - erf\left(\frac{i q_2 L_2}{\sqrt{32\pi}}\right)\right]^2,$$

where $L_1$ and $L_2$ are, respectively, the diameter and length of the RuO$_2$ NCs. For the dispersion relation, $\omega(q)$, we took the analytical model relationship based on a one-dimensional linear-chain model [19]:

$$\omega(q)^2 = A + \{A^2 - B [1 - \cos(\pi q)]\}^{1/2},$$

where $A = 1.396 \times 10^5$ cm$^{-2}$ and $B = 7.39 \times 10^9$ cm$^{-4}$ (for RuO$_2$ single crystal) are related to the atomic masses of the constituent atoms and the force constant between the nearest neighbour planes. To avoid any speculation of the measured Raman modes positions we used freshly grown RuO$_2$ single crystal by the chemical transport method [20] to determine the main signals of the Raman-active modes. The positions and the full width at half maximum (FWHM) of the $E_g$, $A_{1g}$ and $B_{2g}$ modes are listed in table 2. The RS spectrum of the single crystal reveals some discrepancies in identifying the $E_g$, $A_{1g}$ and $B_{2g}$ positions with the known values from the literature [21, 22].
Table 1. Relative Raman intensities of the $E_g$, $A_{1g}$ and $B_{2g}$ phonon modes for the various polarization configurations for RuO$_2$ NCs.

| Polarization configurations | Raman modes |
|-----------------------------|-------------|
|                            | $E_g$       | $A_{1g}$ | $B_{2g}$ |
| (101) plane                 |             |          |          |
| $\alpha_{x'x'}$            | $e^2$       | $1/4(a+b)^2$ | 0       |
|                           |             |          |          |
| $\alpha_{x'y'}$            | $1/2e^2$    | 0        | $1/2d^2$ |
| $\alpha_{y'y'}$            | 0           | $a^2$    | 0        |
| (100) plane                 |             |          |          |
| $\alpha_{zz}$              | 0           | $b^2$    | 0        |
| $\alpha_{zy}$              | $e^2$       | 0        | 0        |
| $\alpha_{yy}$              | 0           | $a^2$    | 0        |
| (001) plane                 |             |          |          |
| $\alpha_{xx}$              | 0           | $a^2$    | 0        |
| $\alpha_{xy}$              | 0           | $b^2$    | $a^2$   |
| $\alpha_{yy}$              | 0           | $a^2$    | 0        |

Table 2. The fitted peak positions and FWHM of the Raman-active modes of the RuO$_2$ single crystal and NCs deposited on different orientation of SA substrates. $\Delta \omega$ is the total red shift induced by the phonon confinement and residual stress effects.

| RuO$_2$ NCs grown by RFMS | Raman modes (cm$^{-1}$) | $\Delta \omega$(cm$^{-1}$) |
|---------------------------|-------------------------|-----------------------------|
|                           | $E_g$       | FWHM | $A_{1g}$ | FWHM | $B_{2g}$ | FWHM | $\Delta \omega_{\text{size}}$ | $\Delta \omega_{\text{stress}}$ |
| RuO$_2$ single crystal     | 526.0       | 10.9 | 644.0    | 16.5 | 714.0    | 13.6 | –                           | –                           |
| RuO$_2$(101)/SA(012)      | 519.7       | 21.0 | 638.0    | 36.9 | 707.7    | 27.6 | 4                           | 2                           |
| RuO$_2$(101)/SA(110)      | 520.2       | 21.8 | 637.8    | 37.9 | 707.9    | 25.6 | 4                           | 2                           |
| RuO$_2$(100)/SA(001)      | 518.1       | 24.2 | 635.8    | 40.2 | 705.8    | 28.3 | 4                           | 4                           |
| RuO$_2$(001)/SA(100)      | 520.0       | 20.6 | 638.0    | 39.1 | 708.1    | 26.6 | 4                           | 2                           |

Figures 2(a) and (b) show the FESEM images and the XRD pattern of the well-aligned RuO$_2$ NCs grown on SA(012) substrate. The results indicate that the self-assembled regularly tilted wedge-shaped rod-like NCs were grown with identical tilt angles from the normal to the substrate and all the RuO$_2$(101) planes are parallel to the SA(012) substrate. The first-order Raman spectrum of the single-direction tilted RuO$_2$(101) NRs deposited on SA(012) illustrated in figure 2(c) revealed three Raman modes, identified as $E_g$, $A_{1g}$ and $B_{2g}$ in the vicinity of the single crystal signals at 526 cm$^{-1}$, 644 cm$^{-1}$, 714 cm$^{-1}$, respectively. These results are consistent with the assignments given in table 1. The results of Raman scattering describe the qualitative trend of the peaks’ redshifts and asymmetric broadening of lineshape with a low-frequency tail when the size becomes nanometric.

The fitted peak positions and FWHM of the Raman modes for the RuO$_2$ NCs deposited on different SA substrates are shown in table 2. The shift in peak positions $\Delta \omega$ is a redshift in
Raman modes peak positions as compared with that of the single crystal. Our calculated results of the redshift for RuO$_2$(101) on a SA(012) sample using the SC model indicated a 4 cm$^{-1}$ redshift and an asymmetric broadening of 21 cm$^{-1}$ for the $E_g$ mode relating to the phonon confinement effect in NCs. To have a good agreement between SC model calculations and experimental data, we have to add an additional redshift of 2 cm$^{-1}$ to the SC model. We have assigned this shift to the residual stress effect induced by tensile strain which is consistent with the results previously reported by Rosenblum et al [22] about observation of blueshifts on the three strongest lines induced by hydrostatic pressure in a RuO$_2$ single crystal. This assignment leads to a modification of the theoretical modelling. The inclusion of the additional stress-induced redshift leads to a recalculation of the $A$ and $B$ constants for the analytical dispersion relation as given by equation (4). Our analysis gives $A = 1.41 \times 10^5$ cm$^{-2}$ and $B = 7.53 \times 10^9$ cm$^{-4}$.
for the series of RuO$_2$ NCs structures used in these experiments. Using the proposed MSC model we are able to determine the component of the residual stress-induced redshift and extract information on the nanometric size effect on the measured redshift of the Raman active modes. As shown in figure 2(c), the open circles indicate the theoretical calculations using the MSC model. The agreement of the experimental data for the phonon mode peaks and the calculated results with diameter $L_1 = 45$ nm is reasonably good. It should be noted that the diameters used as the correlation length in the MSC model are the average diameters estimated from the FESEM images.

Figures 3(a) and (b) are the FESEM images and the XRD pattern of high density and tilt-aligned RuO$_2$ NCs grown on SA(110) substrate. The FESEM images reveal that RuO$_2$ NCs, with unique symmetrically double-aligned directions, have a wedge-like rod structure with an
average diameter of about 45 nm. The corresponding XRD pattern indicates unique (101) planar deposition on SA(110) substrates. Figure 3(c) shows the Raman spectrum of the RuO$_2$(101) NCs on SA(110) and the fitting results (open circles) in the range of 400–800 cm$^{-1}$, in which three Raman modes, identified as $E_g$, $A_{1g}$ and $B_{2g}$ were observed. These results show good agreement with the assignments given in table 1. The analysis in the MSC model revealed 4 cm$^{-1}$ redshift and an asymmetric broadening of about 22 cm$^{-1}$ for the $E_g$ mode as a result of the phonon confinement effect and an additional 2 cm$^{-1}$ shift due to residual stress effects. The observation of $E_g$, $A_{1g}$ and $B_{2g}$ modes in the RS with the intensity of the $E_g$ peak much larger than the signal level of the $A_{1g}$ and $B_{2g}$ modes may be evidence of orientation of NCs in the (101) plane. From the experimental data analysed by the MSC model, the doubly tilted NCs (figure 3(a)) showed comparable intensities of $A_{1g}$ and $B_{2g}$ modes, whereas a single direction tilted NCs (figure 2(a)) showed higher intensity of the $B_{2g}$ peak in comparison with $A_{1g}$. Thus, the RS of NCs correlate well with the XRD patterns and could be a powerful technique for the quick determination of the NCs orientation.

Figures 4(a) and (b) are the FESEM images and the XRD pattern of mosaic-like structural RuO$_2$ NCs grown on SA(001) substrates. The FESEM images exhibit the elongated grains, aligned in three directions and intersecting at an angle of 120°, which are 10–15 nm in width and 30–100 nm in length. The XRD pattern reveals a preferential crystalline alignment of RuO$_2$ NCs along [100] for the sample deposited on SA(001). In figure 4(c) we show the Raman result of the RuO$_2$(100) NCs deposited on SA(001). Comparison of this figure with table 1 allows us to identify the allowed $E_g$ and $A_{1g}$ Raman modes. The weak intensity of the normally forbidden $B_{2g}$ mode as extracted by the MSC indicates good agreement with the theoretical prediction, as given in table 1. The additional redshift of 4 cm$^{-1}$ induced by a residual stress has been included in the MSC model for the adequate description of the 8.1 cm$^{-1}$ redshift of the $E_g$ mode peak (518.1 cm$^{-1}$, FWHM = 24.2 cm$^{-1}$) (see table 2).

Figures 5(a) and (b) show the FESEM images and the XRD pattern of the high-density vertical-aligned RuO$_2$ NCs grown on SA(100) substrate. The FESEM images reveal a rod-shaped geometry with sharp tips and an edge size of about 45 nm. The XRD pattern confirms the uniquely single-directional growth of RuO$_2$ NCs along [001] for the sample grown on SA(100). Figure 5(c) shows the Raman spectrum of the vertical-aligned RuO$_2$(001) NCs deposited on SA(100) and the fitting results (open circles) in the range of 400–800 cm$^{-1}$. The Raman spectrum revealed three Raman mode signals that are inconsistent with the allowed modes for the (001) plane (table 1). We observe the signal of the forbidden $E_g$ mode for this configuration with an intensity slightly less than that of the $A_{1g}$ and $B_{2g}$ modes. The occurrence of the normally forbidden $E_g$ mode might indicate observation of the scattering from other planes of the NCs as evidenced from the pyramidal tips of the NRs (see figure 5(a)) and/or from the strain induced Raman tensor which may break down the selection rules. The soft $E_g$ signal may be evidence of the rod-like vertical aligned RuO$_2$ NCs with (001) orientation.

As shown in table 2, the values of the red shift extracted by MSC analysis, which describe the trend of peaks’ redshifts and asymmetric lineshape broadening when the sizes become nanometric, are similar for all samples and are about 4 cm$^{-1}$ (edge size of NCs are about 45 nm). The redshift related to residual stress exhibits different values for different NCs samples. The samples grown with the minimal mismatch (grown on SA(012), SA(110) and SA(100)) exhibit a minimal additional red shift of about 2 cm$^{-1}$ and for higher mismatch (SA(001)) the value is about 4 cm$^{-1}$.
Figure 4. (a) The FESEM images (typical 30° perspective view and cross-sectional view), (b) XRD patterns and (c) Raman spectrum (solid line) and the theoretical results of analysis of the line shape using a MSC model (open circles) of the RuO$_2$(100) NCs deposited on SA(001).

4. Summary

The micro-RS spectra of RuO$_2$(101), RuO$_2$(100) and RuO$_2$(001) NCs grown on SA(012) and SA(110), SA(001) and SA(100) substrates by RFMS have been analysed. The results reveal three major Raman-active modes, identified as $E_g$, $B_{2g}$ and $A_{1g}$, respectively, in the range of 400–800 cm$^{-1}$. The RS intensity of some modes is shown to be dependent on planes of NCs and follows the selection rules reasonably well. Thus, the RS of NCs correlate well with the XRD patterns and could be a powerful technique for the quick determination of the NCs orientation. We also show that the MSC model can account for the measured redshift of the Raman active modes due to nanometric size and residual stress effects. The first component in the MSC analysis corresponds to a nanometric size effect and leads to an asymmetric broadening of the redshifted...
Figure 5. The FESEM images (typical 30° perspective view and cross-sectional view), (b) XRD patterns and (c) Raman spectrum (solid line) and the theoretical results of analysis of the line shape using a MSC model (open circles) of the vertical aligned RuO$_2$ (001) NCs deposited on SA(100).

Raman mode, while the second component relates to residual stress induced redshift which depends on the lattice mismatch between the RuO$_2$ NCs and the substrates. The usefulness of experimental RS together with the MSC model analysis as a nondestructive structural and residual stress characterization technique for NCs has been demonstrated.

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References

[1] Xia Y, Yang P, Sun Y, Wu Y, Mayers B, Gates B, Yin Y, Kim F and Yan H 2003 Adv. Mater. 15 353
[2] Rao C N R and Govindaraj A 2005 Nanotubes and Nanowires (London: Royal Society of Chemistry)
[3] Mattheiss L F 1976 Phys. Rev. B 13 2433
[4] Dziedzic A and Golonka L J 1988 J. Mater. Sci. 23 3151
[5] Khanna P K, Bhatnagar S K and Sisodia M L 1988 J. Phys. D: Appl. Phys. 21 1796
[6] Ferro S and de Battisti A 2002 J. Phys. Chem. B 106 2249
[7] Kuhn A T and Mortimer C J 1973 J. Electrochem. Soc. 120 231
[8] Bai G R, Tsu I F, Wang A, Foster C M, Murray C E and Dravid V P 1998 Appl. Phys. Lett. 72 1572
[9] Hu C C, Chen W C and Chang K H 2004 J. Electrochem. Soc. 151 A281
[10] Ke Y F, Tsai D S and Huang Y S 2005 J. Mater. Chem. 15 2122
[11] Hsieh C S, Tsai D S, Chen R S and Huang Y S 2004 Appl. Phys. Lett. 85 3860
[12] Hsieh C S, Wang G, Tsai D S, Chen R S and Huang Y S 2005 Nanotechnology 16 1885
[13] Kosacki I, Suzuki T, Anderson H U and Colomban P 2002 Solid State Ion. 149 99
[14] Xu J H, Jarlborg T and Freeman A J 1989 Phys. Rev. B 40 7939
[15] Loudon R 1964 Adv. Phys. 13 423
[16] Loudon R 1963 Proc. Phys. Soc. 82 393
[17] Richter H, Wang Z P and Ley L 1981 Solid State Commun. 39 625
[18] Campbell I H and Fauchet P M 1986 Solid State Commun. 58 739
[19] Kittel C 1996 Introduction to Solid State Physics 7th edn (New York: Wiley) p 106
[20] Huang Y S, Park H L and Pollak F H 1982 Mater. Res. Bull. 17 1305
[21] Huang Y S and Pollak F H 1982 Solid State Commun. 43 921
[22] Rosenblum S S, Weber W H and Chamberland B L 1997 Phys. Rev. B 56 529

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