From phonon confinement to phonon splitting in flat single nanostructures: A case of VO$_2$@V$_2$O$_5$ core–shell nano-ribbons

B.W. Mwakikunga [a,b,*], M. Maaza [c], K.T. Hillie [a,d], C.J. Arendse [e], T. Malwela [a], E. Sideras-Haddad [f]

[a] DST/CSIR National Centre for Nano-Structured Materials, PO Box 395, Pretoria 0001, South Africa
[b] Department of Physics and Biochemical Sciences, The Polytechnic-University of Malawi, Private Bag 303, Chichiri, Blantyre 0003, Malawi
[c] Materials Research Group, iThemba LABS, P O Box 722, Somerset West 7129, Cape Town, South Africa
[d] Physics Department, University of the Free State, P.O. 339, Bloemfontein, South Africa
[e] Department of Physics, University of the Western Cape, Private Bag X17, Bellville 7535, South Africa
[f] School of Physics, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg, South Africa

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ABSTRACT

Raman spectroscopy of the VO$_x$ nano-ribbons is discussed in the framework of the Richter (1981) equation for optical phonon confinement (a) as modified for thin films by Fauchet and Campbell (1986), (b) as presented by Kim and co-workers for slabs, (c) as explained by Eklund's group for surface phonons and (d) our own modification based on the transformation from the spherical coordinates in the Richter equation to Cartesian coordinates; the latter being in keeping with the ribbon geometry. The change of coordinates also influences the profiles of the phonon dispersion curves. Phonon splitting is ascribed to the bi-layer and core–shell geometries of the ribbons and this is used to calculate the ratio of the V^{5+} to V^{4+} to the value of 0.54 ± 0.10. This is in perfect agreement with the V^{5+}/V$^{4+} \sim 54.60\%$ from X-ray photo-electron spectroscopy (XPS) measurements.

1. Introduction

Vanadium oxide (VO$_x$) is one of several transition-metal oxides that exhibit metal-to-insulator transition. The several main groups among the vanadium oxides are V$_n$O$_{2n-1}$ (e.g. V$_2$O$_3$, V$_7$O$_{13}$) [1], V$_n$O$_{2n+1}$ (e.g. V$_2$O$_5$, V$_6$O$_{13}$ and V$_3$O$_7$) [2,3], V$_n$O$_n$ (e.g. VO, V$_2$O$_2$) and V$_n$O$_{2n}$ [3]. Among the V$_n$O$_{2n}$ class, VO$_2$ is the most interesting because its transition temperature is close to room temperature ($T_c \sim 340$ K), and it displays $\sim 10^5$ decrease in resistivity as well as a large change in transparency in the infrared region. VO$_2$ is known to exist in four polymorphs (a) the most stable VO$_2$ rutile VO$_2$(R), (b) the metastable VO$_2$(M) with a slightly distorted rutile structure, (c) a tetragonal VO$_2$(A) and (d) the metastable VO$_2$(B) with a monoclinic structure [4].

VO$_2$ is thermo-chromic and can be used for window coatings to keep homes and buildings cool in summer and warm in winter, thereby saving electricity. VO$_2$ has been analysed by Raman spectroscopy [5]. This important material has been used in plasmonics [6] and ultrafast switches (since it shows a switching period of ~ 100 fs), holographic storage and recording industry [7] and protection from laser guided missiles in defence [8]. Raman spectra

of the CuO–V$_2$O$_5$–P$_2$O$_5$–CaO [9] glass system VO$_x$ [10], VO$_x$ supported on silica [13] have been presented. V$_2$O$_5$ finds applications in gas sensors [11], rechargeable vanadium batteries [11], vanadium superconducting SQUIDS [12] and hydrogen storage [14]. There have been some reports on Raman spectroscopy of VO$_2$ [5], and V$_2$O$_5$ [9,10,13,16] but, to our knowledge, none on the bi-layered |V$_2$O$_5$|VO$_2$| or VO$_2$@V$_2$O$_5$ core–shell nano-ribbons of a combination of these phases and let alone the phenomenon of phonon confinement, phonon splitting and electronic transport on these structure. Also it has been difficult to determine phonon dispersion relations for the vanadium oxides by calculation [17] and let alone by the traditional neutron scattering method [18]. Due to vanadium's large scattering cross-section of neutrons, cans made from it are used in holding samples in typical neutron scattering experiments. So, it is difficult to find published data on phonon dispersion curves and their equations by this method in vanadium or its oxides. Here we attempt this task by Raman scattering through phonon confinement in ultrathin ribbons.

2. Background theory on phonon confinement and phonon splitting

Among the spatial correlation models, the phonon confinement model by Richter et al. [19] has been the most employed in studying

* Corresponding author. Tel.: +27 12 841 3874; fax: +27 12 841 2229.
E-mail address: bmwakikunga@csir.co.za (B.W. Mwakikunga).

confined optical phonons in spherical structures due to spatial size effects. The so-called Richter equation is given by

$$I(\omega) = A_0 \int_{-\infty}^{\infty} \left[\frac{|C(0, \mathbf{q})|^2}{(\omega - \omega(\mathbf{q}))^2 + (\Gamma_0/2)^2} \right] d^3\mathbf{q} \qquad (1)$$

where A_0 is a pre-factor to be determined from experiment, $|C(0,\mathbf{q})|^2$ are Fourier coefficients that depend on the size of the particle that scatters the light and the phonon momentum, ω is the phonon wave-number, $\omega(\mathbf{q})$ is the phonon dispersion relation for the material in the particle and Γ_0 is the full width at half maximum of the phonon peak of the bulk material. The $C(0,\mathbf{q})$ signifies that apart from the zone centre phonon of momentum $q_0 = 0$, there exists other phonons whose momentum $q \neq 0$ but centred at q_0. Campbell and Fauchet [20,21] suggested that the Fourier coefficient $|C(0,\mathbf{q})|^2 d^3\mathbf{q}$ be given by $\exp(-\mathbf{q}^2 d^2/16\pi^2) d^3\mathbf{q}$. Their other achievement was their ability to extend the Richter model to other shapes of the micro-crystals such as what they called columnar (nano-rods, nano-wires) and also thin films. They argued that for thin films of thickness, τ, $|C(0,\mathbf{q})|^2$ should be equal to $\exp(-\mathbf{q}^2\tau^2/16\pi^2)|1 - \mathrm{erf}(i\tau/\sqrt{(32\pi)})|^2$.

Campbell and Fauchet admittedly saw very small significance in replacing the Gaussian with other size-distribution functions especially for spherical nano-crystals. Also the Fourier coefficients for thin films and columnar shapes make the Richter equation even more complicated in that one performs integration within another numerical integration with the second integration being complex in nature. A simpler approach to modifying the Richter equation to include other novel nano-crystal shapes has been considered. Following this argument, the Richter equation has been modified to account for the geometry of nano-wires by Piscanec et al. [22] and by Adu et al. [23,24] by changing the $d^3\mathbf{q}$ term for a sphere to $2\pi\mathbf{q}_\perp d\mathbf{q}_\perp$ for rods such that the Fourier coefficient is given by $2\pi\mathbf{q}_\perp \exp(-\mathbf{q}_\perp^2 d^2/16\pi^2) d\mathbf{q}_\perp$. Note that the constant $16\pi^2$ has been replaced with a scaling parameter α_{wire} that can be evaluated during the data fitting, as was performed by Mwakikunga et al. on WO_3 nanowires [25]. As for quantum dots, it is assumed that these structures are quasi-zero dimensional and hence all the atoms are surface atoms. Therefore, the d^3q term in Richter equation has been approximated to $d^3q \propto \mathbf{q}^2 d\mathbf{q}$ [22]. Appropriately, this is equivalent to replacing $d^3\mathbf{q}$ by the momentum volume of $4\pi\mathbf{q}^2 d\mathbf{q}$ to give $|C(0, \mathbf{q})|^2 = 4\pi\mathbf{q}^2 \exp(-\mathbf{q}^2 d^2/a_{\mathrm{QD}}^2) d\mathbf{q}$ for quantum dots.

Slab-like nano-structures such as nano-belts, nano-platelets and nano-ribbons have phonon confinement only in one dimension. Dielectric continuum models developed as early as 1965 [26] and given in a review by Ruppin and Englman [27] have been extensively used to explain surface optical (SO) phonons as a function of dielectric constants of the material and the surrounding media. The SO phonon frequencies in this case are between transverse optical (TO) and longitudinal optical (LO) phonon frequencies given as [28]: $\omega_{\mathrm{SO}} = \sqrt{[(\{(m+1)/m\}\omega_{\mathrm{TO}}^2 + (\varepsilon_\infty/\varepsilon)\omega_{\mathrm{LO}}^2)/(\{(m+1)/m\} + \varepsilon^{-1}\varepsilon_\infty)]}$. Such phonons have been reported to bear phonon dispersion relations given for symmetric (S) and anti-symmetric (AS) modes respectively as: $\omega_{\mathrm{SO}}^2(q)_{\mathrm{S}} = \omega_{\mathrm{TO}}^2[(\varepsilon_0 \tanh(q_i L_i/2) + \varepsilon_{\mathrm{m}})/(\varepsilon_\infty \tanh(q_i L_i/2) + \varepsilon_{\mathrm{m}})]$ and $\omega_{\mathrm{SO}}^2(q)_{\mathrm{AS}} = \omega_{\mathrm{TO}}^2[(\varepsilon_0 \coth(q_i L_i/2) + \varepsilon_{\mathrm{m}})/(\varepsilon_\infty \coth(q_i L_i/2) + \varepsilon_{\mathrm{m}})]$.

SO phonons in cylindrical nanowires were noticed in core–shell GaP@GaN nanowires [29] and explained by Gupta et al. [30] and by Xiong et al. [31,32] in rectangular cross-section nanowires of ZnS. Recently, SO phonons from 50-nm thick GaN nano-ribbons were reported [33]. Although, Xiong et al. [34] has reviewed SO phonon frequency to relate SO phonons to the particle size and shape, this has been done on ribbons no thinner than 20 nm and the theory employed has been up to the traditional dielectric continuum
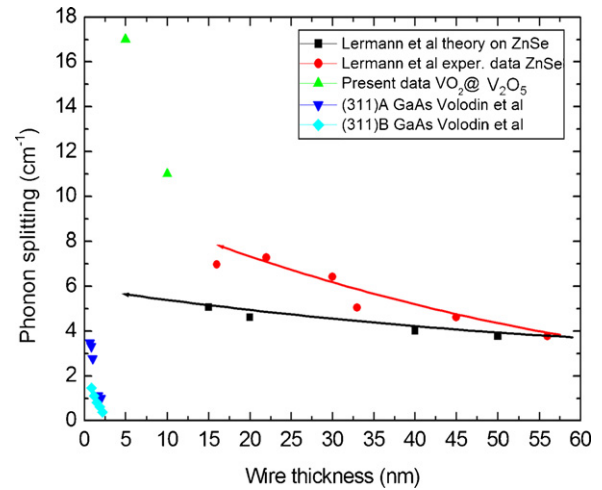

Fig. 1. Lermann's theory of phonon splitting based on stress studies could fit experimental data only if the wire width was not less than about 70 nm.
Adapted from Ref. [37]

models already mentioned. Around this thickness, the Richter phonon confinement model is pushed to its limits and therefore such ribbons can be regarded as bulk [35,36]. Also, SO frequencies falling between TO and LO cannot explain new phonons having frequencies outside this range, but have often been explained by TO-splitting and LO-splitting. This is now a new phenomenon.

Lermann et al. [37] have previously derived a theory based on stress in multilayered ZnSe quantum wires to relate the LO-splitting range to the wire width, but their calculated splitting matched experimental data only down to about 70 nm of wire width. The theory failed to fit experimental data below 50 nm as re-produced in Fig. 1. Kim and Jang [38] however were some of the earliest in employing a quantum-mechanics-based Richter equation to explain confinement in isolated slabs but not TO-splitting or LO-splitting. Since they did not notice LO- and/or TO-splitting due to SO phonons in their Raman spectra, they supposed that the Fourier coefficient must generally be given by $f(\mathbf{q}) \exp(-\mathbf{q}^2 d^2/\alpha_{\mathrm{slab}}) d\mathbf{q}$ where $f(\mathbf{q}) = 1$ for slabs. However, changing only the weighting function without changing the phonon dispersion relations can only help adjust the amplitude of the confined phonons with the aid of α_{slab} but without the explanation of the phonon splitting.

In this paper, we suggest re-starting from Richter et al. optical confinement model and following the simpler approach of simply changing not only the dimensionality of the $d^3\mathbf{q}$ momentum volume in the exponential function but also manipulating the dimensionality of the phonon dispersion relations to suit the nano-ribbon geometry in the present case.

This way, we have a new proposed model that would easily explain the phonon splitting in nano-ribbon and other flat structures.

3. New dimensionality in OPC that suits the ribbon geometry

Let us consider the following schematics of Fig. 1(a) and (b) of a ribbon interacting with a laser beam in a typical Raman spectroscopy set-up. In performing Raman spectroscopy on ribbons whose typical length (L_x), width (L_y) and thickness (L_z) are about 1 μm × 400 nm × 10 nm as shown by our AFM results presented in the forthcoming sections, one expects that confinement of optical phonons ought to be only in one dimension, that is, the z direction which denotes the thickness of the ribbon as illustrated in the inset of Fig. 1(a). We start from the Fourier coefficients and dispersion