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2007 J. Phys.: Conf. Ser. 92 012165

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Surface optical phonons in cylindrical ZnO nanoparticles : dielectric effect of outer medium

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Abstract. Surface optical phonons in freestanding cylindrical ZnO nanoparticles surrounded by organic molecules have been theoretically investigated using a dielectric continuum model and experimentally with Raman spectrometry. From a theoretical point of view, we calculate surface optical phonons in the cases of cylindrical and planar surfaces of nanoparticles. We also investigate the dispersion of these modes regarding the dielectric constant of the outer medium. By modelling the organic shell of nanoparticles with a dielectric constant and based on experimental results of Raman spectrometry, we show that we observed a top surface mode of nanoparticles.

1. Introduction

Zinc Oxide (ZnO) is a wide band gap semiconductor (3.37 eV) which has become in recent years a hot topic, because of its potential applications in ultraviolet light emission devices, chemical or biological sensors and piezoelectric devices [1]. Following this trend, ZnO nanostructures also aroused great interest, since the mechanical, optical and vibrational properties can be modified by size reduction, shape modification and surface properties. Nanostructures can be synthesized *via* different methods, for instance solid-vapor process [2] or wet chemistry method [3].

2. Sample preparation

The objects studied here are freestanding nanoparticles (NP) synthesized by a room temperature organometallic method [4]. They are shaped as straight prisms with hexagonal basis, the *c* axis of the würtzite structure being perpendicular to the basis. The NPs aspect ratio (height of NP divided by its diameter) depends on the experimental conditions, which can be accurately tuned to get either nanoparticles or nanorods. More details about synthesis are available in [4].

Previous nuclear magnetic resonance [4] and luminescence [5] studies deal with the coordination of ligands from the synthesis of NPs. The control of shape and size of NPs, as well as low size

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dispersion, allows to investigate how the presence of ligands around the NPs modify their vibrational properties. This point is investigated theoretically using a dielectric continuum model in the approximation of a cylinder and experimentally with Raman spectrometry.

First, within the framework of the dielectric continuum model, we calculate the dispersion of surface optical modes in a würtzite ZnO nanocrystal of cylindrical shape. Surface optical modes in such a geometry are of two kinds : side surface mode and top surface mode, whether vibrating atoms are respectively located at the lateral or the flat basis of the NP. Then, we discuss the experimental results we obtained by Raman spectrometry. We show that by modeling the surrounding organic media with a dielectric constant, it is possible to conclude that we observed a top surface mode of NPs.

3. Surface optical phonons in ZnO nanoparticles

3.1. Model

We consider an interface between würtzite ZnO and an outer medium of dielectric constant $\varepsilon^{(ext)} = \varepsilon_D$. Let us remind the geometry of our systems has an axis of revolution noted Oz in cylindrical coordinates (r, θ, z) , and parallel to c axis of würtzite structure. Thus, the permittivity

tensor of ZnO is given by : $\varepsilon^{(NP)} = \varepsilon_{\perp}(\omega) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & g(\omega) \end{pmatrix}$, where $g(\omega) = \frac{\varepsilon_{\parallel}(\omega)}{\varepsilon_{\perp}(\omega)}$. Components of $\varepsilon^{(NP)}$

are given by Loudon's uniaxial crystal model [7] : $\varepsilon_{\perp}(\omega) = \varepsilon_{\perp}^{\infty} \frac{\omega^2 - \omega_{\perp LO}^2}{\omega^2 - \omega_{\perp TO}^2}$ and

$\varepsilon_{\parallel}(\omega) = \varepsilon_{\parallel}^{\infty} \frac{\omega^2 - \omega_{\parallel LO}^2}{\omega^2 - \omega_{\parallel TO}^2}$, where $\varepsilon_{\perp}^{\infty}, \varepsilon_{\parallel}^{\infty}$ are respectively the perpendicular and parallel to c axis high

frequency dielectric constants, and $\omega_{\perp LO}, \omega_{\perp TO}, \omega_{\parallel LO}, \omega_{\parallel TO}$ are the zone center frequencies of $E_1(LO)$, $E_1(TO)$, $A_1(LO)$ and $A_1(TO)$ symmetry modes respectively. Numerical values of these parameters were taken from [1, 8]. The dielectric continuum model is based on Maxwell's equations and the continuity of the displacement vector at the surface separation between NP and the outer medium as a boundary condition. We consider Maxwell Gauss equation of the electrostatic potential $V^{(i)}$: $\nabla[-\varepsilon^{(i)}\nabla V^{(i)}] = 0$ where $i = NP$ or ext respectively stands for the NP and the outer medium. The resolution of this equation uses the variable separation method: $V^{(i)}(r, \theta, z) = f^{(i)}(r)g^{(i)}(\theta)h^{(i)}(z)$, where f, g and h are three independent functions. In the following of this section, we solve in cases of cylindrical and planar interfaces the equations described above.

3.1.1. Cylindrical interface of radius a : Side Surface Optical (SSO) modes. Considering a cylindrical interface of radius a , the electrostatic potential reads :

$$V^{(NP)}(r, \theta, z) = \frac{I_m(\sqrt{g(\omega)}rq_z)}{I_m(\sqrt{g(\omega)}aq_z)} \cos(m\theta) \exp(iq_z z) \quad \text{for } r \leq a$$

$$V^{(ext)}(r, \theta, z) = \frac{K_m(rq_z)}{K_m(aq_z)} \cos(m\theta) \exp(iq_z z) \quad \text{for } r \geq a$$

where m is an integer, q_z is the real wave vector of a plane wave propagating along Oz direction and I_m (resp. K_m) is the modified Bessel function of the first (resp. second) kind. In the following, we focus on polar optical mode without angular dependency ($m = 0$), which are likely observable in

Raman spectra because of their high symmetry. Writing the continuity of the normal component of the displacement vector at $r = a$, frequencies of polar optical modes are solutions of :

$$\varepsilon_{\perp}(\omega)\sqrt{g(\omega)}I_1(\sqrt{g(\omega)}aq_z)K_0(aq_z) + \varepsilon_D I_0(\sqrt{g(\omega)}aq_z)K_1(aq_z) = 0 \quad (1)$$

By formally neglecting the anisotropy of ZnO, *i. e.* if $g(\omega) = 1$, equation (1) reduces to equation (9) of [9]. Solutions of equation (1), named SSO modes with frequency noted ω_{SSO} , are plotted with respect to ε_D in figure 1a for $q_z = 1/a$ which is in order of magnitude the first non zero wave vector activated due to axial confinement of NPs. Figure 1a shows SSO modes are strongly dispersive regarding the dielectric constant of the outer medium.

3.1.2. Planar interface of thickness l : Top Surface Modes (TSO). We now consider a disk of thickness l , the origin of z axis is taken in the middle of the disk, so that the interfaces between ZnO and the outer medium are located at $z = \pm l/2$. In this case, two independent solutions of Maxwell Gauss equation have to be considered whether the electrostatic potential is even or odd (respectively symmetric or antisymmetric with respect to the plane $z = 0$). Noting q_r the wave vector now along the radial direction, the equations that define symmetric and antisymmetric TSO modes are respectively :

$$\tanh\left(\frac{q_r l}{2\sqrt{g(\omega)}}\right) + \varepsilon_D \frac{\sqrt{g(\omega)}}{\varepsilon_{\parallel}(\omega)} = 0 \quad \text{and} \quad \coth\left(\frac{q_r l}{2\sqrt{g(\omega)}}\right) + \varepsilon_D \frac{\sqrt{g(\omega)}}{\varepsilon_{\parallel}(\omega)} = 0 \quad (2)$$

Considering isotropic ZnO, equation (2) becomes equations (1a) and (1b) of [10]. Figure 1b shows the dispersion of TSO modes (frequency ω_{TSO}) with respect to the dielectric constant of the outer medium, in the case of $q_r = 0.4/l$, which is the value deduced from our experiments as described in section 3.2.

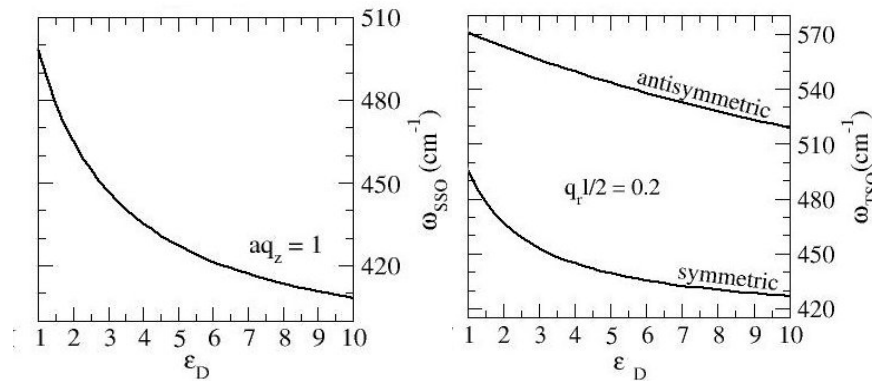


Figure 1. *Left* : Dispersion of SSO mode with respect to ε_D (figure 1a). The curve was plotted with $aq_z = 1$. *Right* : Dispersion of TSO modes with respect to the same quantity (figure 1b). The value of q_r was taken equal to $q_r = 0.4/l$.

As in the case of SSO modes, both symmetric and antisymmetric TSO modes exhibits a strong dependency regarding the dielectric constant of the outer medium.

3.2. Experimental results and discussion

It is important to note that considering without differentiation SSO or symmetric TSO (likely observable in Raman spectra) modes, surface mode of a nano cylinder occur in a different range of frequencies than surface mode of a nano sphere. Indeed, these last are predicted [11] and observed [12] around 550 cm^{-1} . This shows the importance of the shape and surface continuity of NP.

Moreover, the above calculations have experimental confirmations. We recently report [13] an observation of a strong intense peak located at 490 cm^{-1} on Raman spectra of ZnO NPs of sizes in the

range of 2.1-6.8 nm. Based on available calculations [11], we assign the peak to a surface mode, although we were unable to explain some discrepancies pointed out [13]. According to the calculations we present here, and given ligands are located on the NP lateral basis [5] (so that top basis of NP are in contact with the air, $\varepsilon_D = 1$) we conclude from the independency of the 490 cm^{-1} mode frequency regarding the variety of dielectric constants of ligands (see table I and figure 1 of [13] for details) that we observed a symmetric TSO mode. The phonon wave vector is equal to $q_r = 0.4/l$. Typically, $l = 4$ nm for our NPs, thus $q_r = 0.1\text{ nm}^{-1}$ which is in good agreement with values already reported [10]. In addition, our assignment is reinforced by several experimental observations of surface mode in ZnO nanostructures : surface mode related to planar interface has been observed at 486 cm^{-1} in opal structures [14], 498 cm^{-1} in one dimensional structures [15] and 475 cm^{-1} in nanorods [16]. These frequencies are all close to the frequency we report. The reasonable discrepancy is mainly attributed to the unawareness of the phonon wave vector.

4. Conclusion

Using dielectric continuum model, we derive equations defining spectrum of surfaces modes in a single freestanding würtzite ZnO nanoparticle of a cylindrical shape. The role of the outer medium, in terms of dielectric properties, is also discussed. These calculations are useful to assign a peak located at 490 cm^{-1} on Raman spectra of ZnO NPs to a top surface mode, related to the flat surfaces of NPs.

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