

CdTe Raman Line Shape in Resonance: a Space Correlation Zone Study

J.R. Molina-Contreras^{1,*}, C. Frausto-Reyes², C.I. Medel-Ruíz³, H. Pérez Ladrón de Guevara³

¹ *Instituto Tecnológico de Aguascalientes, Av. A. López Mateos 1801 Oriente, 20256 Aguascalientes, Ags., México*

² *Centro de Investigaciones en Óptica, Unidad Aguascalientes,*

Prolongación Constitución 607, Apartado postal 507, 20200 Aguascalientes, Ags., México

³ *Centro Universitario de los Lagos, Universidad de Guadalajara,*

Av. Enrique Díaz de León s/n, 47460 Lagos de Moreno, Jalisco, México

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We show that the line shape of resonant Raman spectra of CdTe can be reproduced using the spatial correlation model (SCM). Our results show that the resonant Raman spectrum for a surface with a RMS of 430 nm is characterized by the presence of two intense sharp peaks located at frequencies corresponding to LO and 2LO modes. The resonant Raman spectrum for a surface with a RMS of 6 nm on the other hand, can be reproduced using the contribution of high frequency phonons related with the acoustic transverse harmonics. These results suggest that under resonance conditions, such acoustic transverse modes define the line shape for a small size correlation region diameter. This study provides a new application of SCM to estimate the size grain of a surface where this information is not available.

Keywords: Roughness, Raman Spectroscopy, Acoustic Transverse Phonons, Size Grain.

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1. INTRODUCTION

From the perspective of applications, surface roughness is of much interest as it is directly related to optical scattering and resistivity due to grain boundary and thickness. Surface roughness and grain size characterization due to this, are important components to improve the electrical performance of materials, but the improvements to surface quality depend upon how well the surface is understood and how efficiently the characterization technique is developed. Raman scattering (RS) is a powerful probe to obtain information on the vibrational states of a solid and it is sensitively influenced by the surface. As a fast and non-destructive technique, RS of crystalline semiconductors has been successfully employed to determine sample qualities such as surface conditions, homogeneity and microcrystallinity [1]. Raman peaks broadness and shift, are effects that are not completely understood using excitation energy around the fundamental energy band gap E_0 of materials. In semiconductors materials several phenomena may appear. For example, acoustic phonon, cascade effect, hyper-Raman and folded-phonon doublets of acoustic modes [2,3]. The appearance of these effects is normally attributed to structures generated by superlattices, layer thickness fluctuations, limited phonon confinement zones, surface roughness and imperfect samples [1,2]. These effects are commonly attached to a partial breakdown of crystal-momentum conservation laws ($q \neq 0$) [4]. Knowing the phonon dispersion curves of the vibrating modes due the space correlation zone and the natural width of the peaks, the Space Correlation Model (SCM) [5-7] can be used to describe the Raman peak behaviours. The SCM assumes a Lorentzian peak line shape with a Gaussian attenuation factor that plays an important role as the crystal size or space correlation zone becomes smaller. The fittings achieved using the SCM in semiconductors materials are generally in good agree-

ment with the experimental measuring even when shifts and asymmetrical broadenings occur. This fact is due to the crystal size decrease, what suggests that a partial breakdown of the selection rules allows such behaviours. In a previous work it was shown that there is a direct correlation between the line shape of the Raman spectra and the surface roughness when it is used a laser with excitation energy around the fundamental energy band gap E_0 of the analysed sample [8]. In this work we report results of the application of the SCM to the Raman spectra obtained for CdTe with an excitation wavelength of 830 nm in order to explain the effect of the grain size in the Raman spectra under resonance conditions.

2. EXPERIMENTAL DETAILS

CdTe is an II-VI cubic semiconducting compound with zinc blende-type symmetry and an energy gap of 1.51 eV at room temperature. The bulk sample used in this experiment was a (001) oriented undoped commercial wafer, single side polish from Bertram Laboratories. The sample surfaces were cleaned before the experiment with methanol and the experiment was done at room temperature. The Raman spectra was measured using a micro-Raman (Ranishaw system 1000B) with a 600 lines/mm grating, a CCD camera (Rem Cam 1024×256 pixels), which focus its 830 nm wavelength laser beam in a back scattering geometry [9], with a spot-size of about 2 μm onto the sample, with a 50×objective of a Leica (DMLM) microscope. A Notch filter was allocated between the optical way of the laser and the microscope in order to suppress the Anti-Stokes contribution due the frequencies lower than 130 cm^{-1} . The calibration of the instrument was done using the 520 cm^{-1} Raman line of a silicon wafer and for the data acquisition it was used the Grams software. The experimental set up used to study the surface morphology and to obtain the mean roughness was an Atomic Force Microscope (Digital Instruments, Dimension 3100).

*jrmolinacon@gmail.com

3. RESULTS AND DISCUSSION

Figures 1(a) and 2(a) show that the Raman line shape of CdTe is sensitively influenced by the surface boundary conditions when it is measured under resonance conditions. As the experimental Raman line shape for a surface with a 6 nm RMS roughness exhibits a strong asymmetric behaviour characterized by a significant line width of around 200 cm⁻¹, the line shape for a surface with a 430 nm RMS roughness, is characterized by the sharp peaks of the first and second LO phonon modes of CdTe. These experimental results clearly show that the first-order Raman peaks are inverse size-dependent asymmetric broadening due to the roughness when the excitation energy is around the fundamental energy band gap E₀ of the material. That is, the greatest the roughness, the least the size-dependent asymmetric broadening.

Our results also show that as the size grain increases, the Raman spectra are sharper, contrary to the expected behaviour for a crystalline sample. To gain further insight into the inverse size-dependent asymmetric broadening due to the roughness; we carried out simulations of the Raman spectra using the SCM model. This model is based in the space confinement region of the phonon in the crystal, due to the decrease of volume, or the space correlation size. It can be considered that regarding the roughness, the phonon cannot penetrate beyond the rough surface surrounded by the bulk crystal, where phonon can be represented by a plane-wave-like function; having a spatial extension over the

whole crystal which can be considered infinite. This way, the confinement of the phonon, within the volume of the roughness, results in the relaxation of the conservation of crystal momentum. In the process of creation and decay of phonons, the relaxation of the q = 0 selection rule results in the appearance of additional contributions of phonons with q ≠ 0, which in turn, leads to asymmetric broadening. See the CdTe AFM images in Figure 3.

The solid line in Figure 1(a) shows the result of the simulation of the Raman spectrum for the 6 nm RMS roughness. For the simulation, we considered that the propagation of a confined phonon, due to the roughness, has a Gaussian weighting function as:

$$\exp(-q^2L^2/4) \tag{1}$$

And that the total Raman intensity at a frequency ω is given by [7]:

$$I(\omega) \sim \int_0^1 \exp(-q^2L^2/4) \frac{d^3q}{[\omega - \omega(q)]^2 + (0.5\Gamma_0)} \tag{2}$$

where L is the correlation region diameter (crystal size in Å), q is the wave vector expressed in 2πa units, a is the lattice constant (Å), Γ₀ is the full-width at half-maxima (FWHM) (cm⁻¹) of the unperturbed Raman peak and ω(q) is the phonon dispersion curve for CdTe.

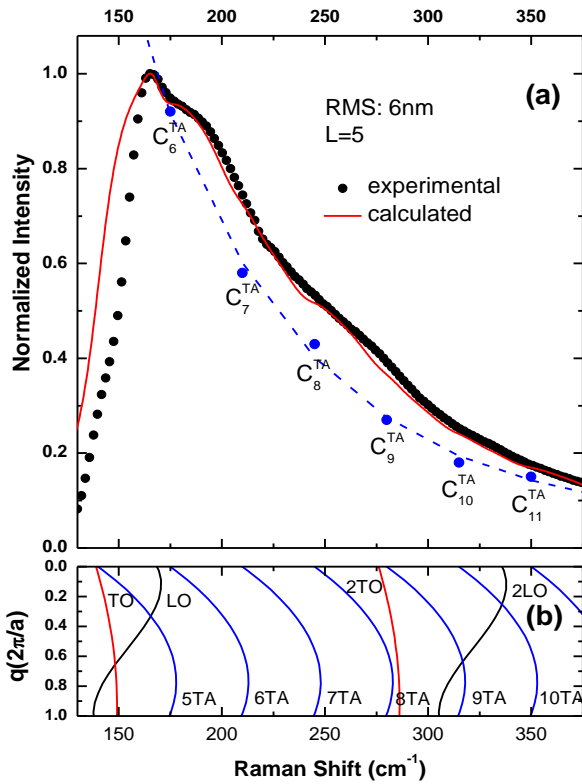


Fig. 1 – (a) Experimental Resonant Raman spectra of 6 nm RMS roughness CdTe surface (dots) and best fit calculated using SCM extended (continuous line). (b) Phonon dispersion curves used in the simulation of the experimental resonant Raman spectra.

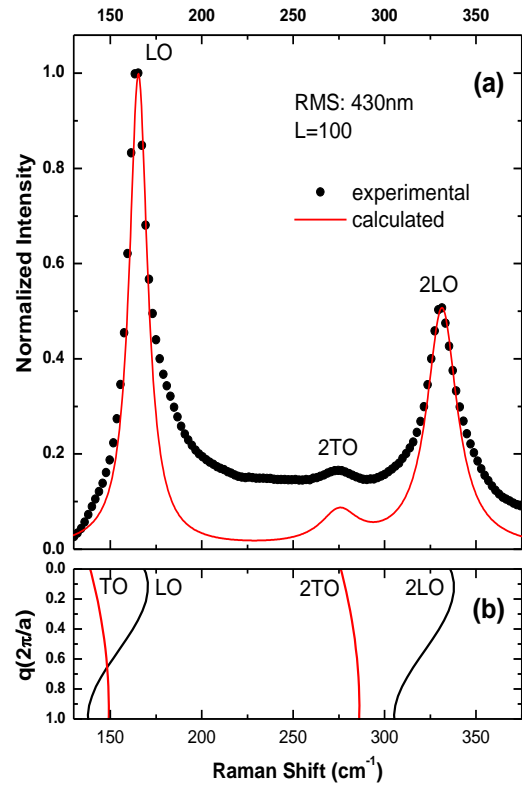


Fig. 2 – (a) Experimental Resonant Raman spectra of 430 nm RMS roughness CdTe surface (dots) and best fit calculated using SCM (continuous line). (b) LO and TO phonon dispersion curves used in the simulation of the experimental resonant Raman spectra.

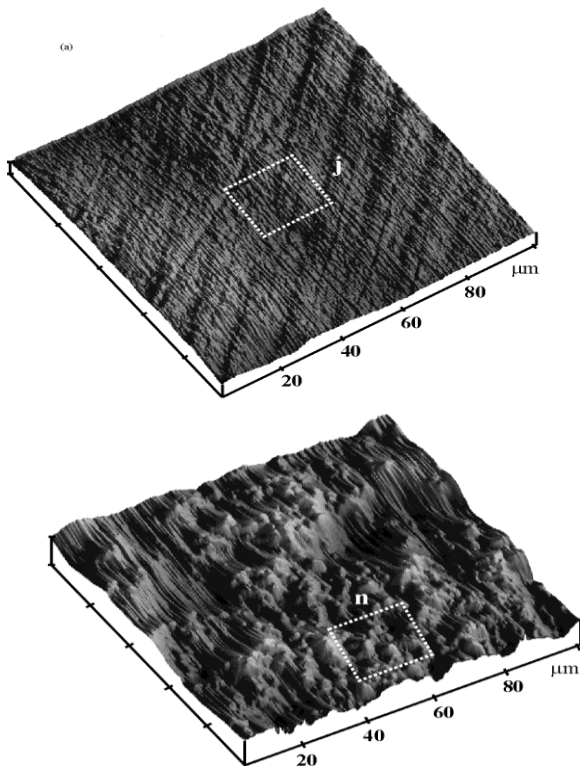


Fig. 3 – (j) CdTe AFM image 6nm mean roughness (n) CdTe AFM image 430nm mean roughness (back of the sample).

The asymmetrical broadening and the Raman shifts allowed by the phonon dispersion curves, even for the small space correlation size, do not contribute to the whole Raman spectra in the overlap wing zone. So, the whole spectrum is reproduced using the transversal acoustic (TA) mode and its harmonic mode contribution. These harmonics were included into the sum of the integrals. The phonon dispersion curves used were of the form:

$$35n + 98.38q - 63.81q^2 \quad (3)$$

Where n is the harmonic of the TA mode. This consideration was done because it is possible to observe the acoustic modes in the Raman spectra using an excitation wavelength around the energy gap of the sample. The solid curve shown in Figure 1(a) is the fitted line

shape for $L = 5$ (finite crystal) obtained by applying Eq. (2) and the phonon dispersion curves shown in Figure 1(b). In Figure 1(a), it is evident that the inclusion of higher harmonic modes, improves the total fitting quality. The weight factor constants C_i^{TA} (for $i = 5 - 11$) associated to the intensities of each harmonic mode, obeys an exponential decreasing line shape as it is shown in Fig. 1(a) (dashed line). This is in accordance with the reported in [10].

The solid line in Figure 2(a) shows the result of the simulation of the Raman spectrum for a 430 nm RMS roughness. The continuous curve shown in Figure 2(a) is the best fitted line shape for $L=100$ (infinite crystal) obtained by applying Eq. (2) and using the phonon dispersion curves: $\omega(q) = 154.5 + 14.5\cos(\pi q)$ and $\omega(q) = 144 + 4\cos(\pi q)$ for the LO and TO in the $\Gamma \rightarrow X$ transition branches respectively. For the second harmonic peaks of the LO and TO in the $\Gamma \rightarrow X$ transitions branches, the phonon dispersion curves used for CdTe were $\omega(q) = 320 + 15.5\cos(\pi q)$ and $\omega(q) = 280 + 4\cos(\pi q)$ respectively. Figure 2(b) shows the shape of the dispersion curves used for the simulation. This simulation indicates a very good agreement but a very clear difference for the one obtained for a 6 nm RMS roughness. The modes which contribute in each case are clearly different.

4. CONCLUSIONS

The simulations of the Raman spectrum for a 6 nm RMS roughness; indicate that the TA harmonic modes strongly contribute to the Raman line shape. This is not the case for a surface with a RMS of 430 nm, which can be characterized just by the two intense sharp LO and 2LO peaks of CdTe. In principle, this effect can be used to know the surface morphological state of a material.

Besides to suggest that the Raman line shape is directly determined by the size of the grain on the surface of the material, our results indicate that the Space Correlation Model has to include the TA harmonic modes.

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