

Communication

Fano effect in resonant Raman spectrum of CdTe

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ABSTRACT

In this work, we show a line-shape analysis of the resonant Raman scattering spectrum of un-doped CdTe single crystal. We found that the main peak correspondent to the longitudinal-optic (LO) phonon mode is asymmetrically broadened toward the high-frequency side. We attributed this asymmetry to an electron-phonon coupling effect, which was demonstrated using a Fano-type function to describe the spectrum line-shape. In our fitting we have additionally considered the weak contribution (in the low-frequency region) of two added phonons, whose presence is attributed to the rupture of the symmetry due to the surface. Results show an excellent agreement between the experimental data and the fitting model, where Fano asymmetry parameter was found to be $q = 4.5$. The results obtained, are a tool that contributes to the understanding of the origin of LO phonon line-shape asymmetry of the Raman spectrum; and its use will be helpful to investigate the strength of electron-phonon coupling in semiconductors.

1. Introduction

Raman spectroscopy is a versatile and fast non-contact characterization technique often used to investigate the vibrational and electronic properties of materials like bulk semiconductor crystals, thin films, superlattices and low-dimensional systems [1]. The resonant Raman scattering (RRS) technique is more selective compared to non-resonance Raman spectroscopy, it works by exciting the sample with incident radiation corresponding to the near the energy band gap. This causes an augmentation of the emission up to a factor of 10^6 in comparison to non-resonance Raman [2]. Raman scattering in semiconductors is caused by the inelastic interaction of the incidence photons with lattice vibrations or phonons. In crystalline bulk materials, the Raman scattering is limited to the near zone centered phonons, due to the selection rule of momentum conservation law. As a result, sharp symmetric line-shapes of Raman spectra (Lorentzian peak) are observed, due to the zone-centered phonons. In the case of nanostructures, the selection rule regarding the quantum confined effect originating due to the low dimensionality of the crystal (sizes comparable to the Bohr exciton radius), is relaxed and other phonons than those of the zone centered, also contribute due to confinement of the phonons in a crystallite of finite dimension [3]. This results in a change in the line-shape of the first

order Raman spectrum, which shows a red-shift in the Raman peak position along with an asymmetric line-shape broadening, compared to the typical spectra of a bulk crystalline crystal [4]. In addition to quantum confinement effect, an electron-phonon interaction (or Fano interaction) also results in an asymmetric broadening of the Raman line-shape. Literature reports for example, an asymmetric longitudinal-optic (LO) phonon mode in bulk silicon under both *n*- and *p*-doping condition. In this case the asymmetry was interpreted as arising due to the Fano interaction of the discrete LO phonon mode with a continuum of either electron (*n*-type) or hole (*p*-type) excitations [5]. This leads us to consider that in a semiconductor, the Fano interaction takes place where a discrete phonon state and a continuum of electronic states exist; and that manifests as an asymmetric Raman line-shape [6]. The origin then of the Fano resonance in a semiconductor, could be due to the phonon interference with the continuum of electronic states created by a heavy doping or due to the photoexcitation as suggested in Ref. [7]. Fano line-shape has been seen in many systems like silicon [5], graphene [8], diamond [9], SrTiO₃ and Ca_xSr_{1-x}TiO₃ [10]. In this paper as we know, it is reported an intrinsic Fano-type line-shape in resonant Raman scattering for the first time. It means, for an un-doped Cadmium Telluride (CdTe) substrate. CdTe is an important II-VI direct band gap (1.45 eV) [11] semiconductor compound due to its increasing

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applications in various electronic devices, such as radiation detectors, photovoltaic devices, light transmitter diodes and luminescent probes [12] among others. CdTe is a p-type polar compound and crystallizes in the cubic zinc blende structure as its stable form. The aim of this work was to contribute to the understanding of the origin of the LO phonon mode asymmetry line-shape in CdTe, so that it can be used in the study of the electron-phonon coupling interaction in semiconductors.

2. Material and methods

The sample used in our experiment was a (001) oriented un-doped CdTe commercial wafer from Bertram Laboratories. This means that its orientation is perfectly specified, and that the only carriers that could manifest in the sample in the case of breaking the covalent bond, would be the *intrinsic* carriers. Literature report that the *intrinsic* carriers per unit volume for the CdTe, is around 6.9×10^5 [13] or 10^6 [14], amount that is very far from the 10^{18} , typical of doped samples. In order to rule out any quantum confinement effect, the substrate, with a polished surface with a mean surface roughness (MSR) of 6 nm, was gently polishing with diamond paste to get the value of 279 nm MSR mentioned below.

The Raman spectra were measured, in a back-scattering geometry [15], at room temperature, in the range of 120 – 220 cm^{-1} , using a NIR micro-Raman system (Renishaw 1000B). The excitation source of the system is a laser diode that emits a wavelength of 830 nm (1.49 eV). The laser beam was focus onto the sample with a $50 \times$ objective (Leica DMLM microscope, spot-size of about $2 \mu\text{m}$). The calibration of the instrument was done using the 520 cm^{-1} Raman line of a silicon wafer.

The MSR of 279 nm was measured using an atomic force microscope (AFM-Digital Instruments, model Dimension 3100). Reference [16] shows AFM images in more detail.

3. Results

Fig. 1 shows the PL spectrum obtained for the CdTe sample with a 532 nm laser. The sharp peak is centered around the resonance and has a full width half maximum (FWHM) of 40 milli electron volt (meV) and a continuum of electronic transitions width of 160 meV, measured at the points indicated by the arrowheads that unites the start of the function's tails. Fig. 2 shows with open circles, the normalized resonant Raman spectrum of the main active LO phonon mode of CdTe. The line-shape as can be seen, is characterized by a sharp peak with maximum intensity around 165 cm^{-1} . This is indicated with a vertical discontinuous line.

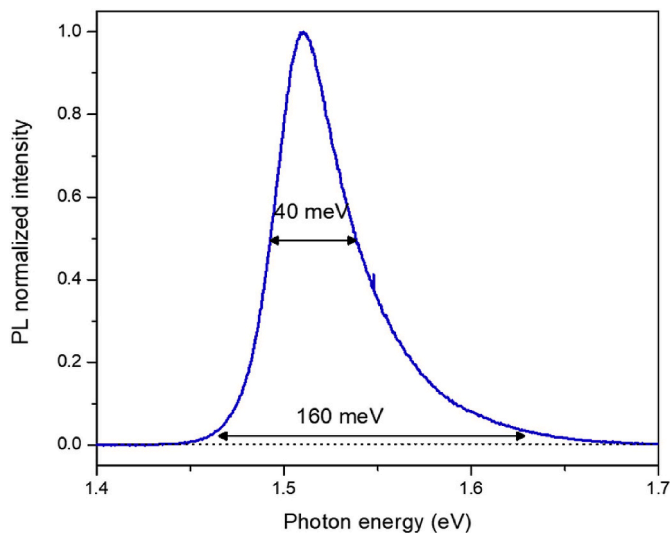


Fig. 1. PL spectrum obtained for the CdTe sample with a 532 nm laser which shows a continuum of electronic transitions width of 160 meV.

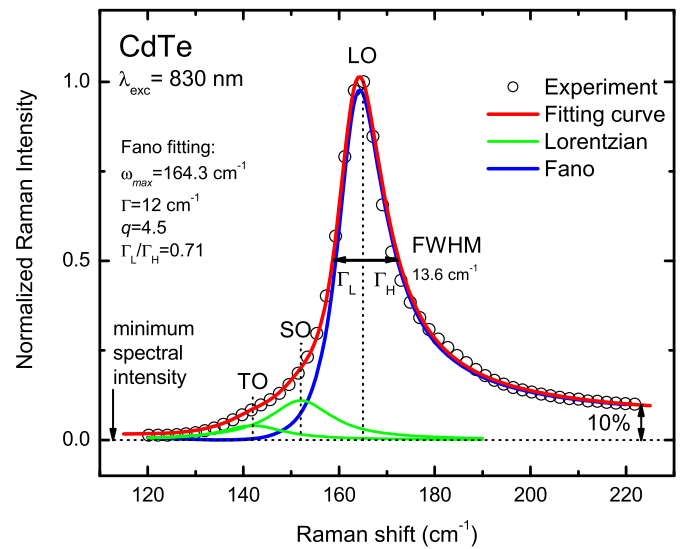


Fig. 2. Raman room-temperature spectrum of the LO phonon mode (open circles) with corresponding Fano line-shape (blue solid line) and Lorentzian (green solid line) fits. The resultant Raman signal line-shape fit is shown as a bold red line. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The figure also shows a broader half-width (Γ_H) on the higher-frequency side of the peak position. In addition to this, the left and right ends of the peak, do not have the same intensity. While on the left side the intensity practically follows a line that ends at a minimum spectral intensity near zero, on the right side, for higher frequencies, as can be seen, the intensity has an increase of the order of 10%, shown by the line's tail; referred to what is observed on the left side. That is, the intensity distribution of the LO mode of the CdTe phonon is an unbalanced function. The FWHM measured on the Raman spectrum is ~ 13.6 cm^{-1} . The Fano effect is characterized by a drop-in intensity and the average widening of the peak. We presume, that the Fano effect reported in this work is due to the interaction of the typical discrete polarization wave $P = P_0 e^{-ikr}$ of the characteristic LO phonon with an energy of 20.6 meV [17], associated to the CdTe, polar semiconductor II-VI, with the continuum of the electronic transitions shown in Fig. 1, which has a width of 160 meV of energy. That is, we consider that what we are seeing is an electron-phonon interaction. In the case under discussion, it will be proven that the observed behavior in the opposite tails of the Raman LO mode peak of the CdTe, can be explained in terms of the Fano effect.

4. Discussion

The Raman line-shape asymmetric broadening is often characterized by the asymmetric ratio defined as $AR = \Gamma_L/\Gamma_H$ where Γ_L and Γ_H are the half widths on the left and right side respectively, taking as reference the center line of the peak [5,6], just as indicated in Fig. 2. As seen in Fig. 2, our measured Raman line-shape is asymmetric with an $AR \sim 0.71$. Based on the selection rule for the (001) surface of CdTe, which says that the scattering of the LO phonon modes are allowed, but the transverse-optic (TO) phonon modes are forbidden [18]; and taking into account that the polarization wave of the LO phonon has associated a positive charge $\rho = \nabla \cdot P$, the initial hypothesis in this work was to assume that the asymmetry observed in the LO mode of the Raman peak was due to an electron-phonon coupling. This was done after ruling out that the quantum confinement effect could not occur with an MSR of 279 nm. The quantum confinement in semiconductors as is well known, can be observed just when they have sizes comparable to the Bohr exciton radius, which in the case of CdTe is 1.05 nm [19].

Coupling between an electron and a phonon is an important issue in

semiconductor materials because it has significant influence on the optical and electrical properties of semiconductors [20]. Electron-phonon interaction, also called Fano interaction, as have been say before, occur due to the interference between the electronic continuum of states and the discrete phonon. In this work we made a theoretical fitting of the Raman scattering data in Fig. 2 to confirm our initial hypothesis that the Fano effect was due to an electron-phonon coupling. The Raman line-shape originating due to the Fano interaction is given by equation (1) [21].

$$I(\omega) = I_0 \frac{[q + 2(\omega - \omega_0)/\Gamma]^2}{1 + [2(\omega - \omega_0)/\Gamma]^2} \quad (1)$$

where $I(\omega)$ is the Raman intensity as a function of frequency (ω), I_0 is the peak intensity, ω_0 is the uncoupled phonon frequency, q is the asymmetry parameter, and Γ is the FWHM of the uncoupled phonon mode. The interaction strength between the LO phonon mode and the electronic continuum on the other hand, is quantified by the relationship $|1/q|$, which is known as the coupling strength. In the limit, when $|1/q| \rightarrow 0$, the Fano resonance line-shape, can be expressed as a Lorentzian line-shape like the one given by equation (2) [22]:

$$I(\omega) = \frac{I_0}{1 + \frac{4(\omega - \omega_0)^2}{\Gamma^2}} \quad (2)$$

As far as we know, the fitting of the Fano-type line-shape for optical phonon has not been reported previously for CdTe. In Fig. 2, represented as the blue solid line, we display the best fit obtained for the LO phonon mode using equation (1), for: $I_0 = 0.046$, $\omega_0 = 163 \text{ cm}^{-1}$, $q = 4.5$ and $\Gamma = 12 \text{ cm}^{-1}$. The positive q value is consistent with an asymmetry caused by the Fano effect [5]. This means, that the Fano interaction is causing the asymmetry seen in the higher frequency side of the LO line shape of our substrate of CdTe. In Fig. 2 we can appreciate good agreement of the blue line-shape and the observed peak except for a pronounced drop on the low-frequency side that does not correspond to the experimental data. As a characteristic of the Fano effect, the minimum spectral intensity (or destructive interference) and the wider half width are observed on the opposite sides of the Raman peak position. In Fig. 2 at 120 cm^{-1} is the minimum spectral intensity and at 220 cm^{-1} the Raman intensity is 10% greater. In our attempt to explain this behavior, we considered that in the region of the Raman spectrum (130 cm^{-1} to 160 cm^{-1}) there is the contribution of additional phonons. The graph as you can see, in addition to the LO mode, shows an extra band that develops as a shoulder in the low-frequency side of the LO mode. This shoulder was deconvoluted by multi-Lorentzian fitting, and the Raman line shape was fit using equation (2). The green lines in Fig. 2 show the fitting. These phonon modes have vibration frequencies corresponding to the transverse-optic phonon (TO) mode at 142 cm^{-1} and to the surface optical (SO) phonon mode at 152 cm^{-1} .

In any case, the Fano asymmetry parameter $q = 4.5$ calculated by our fitting in order to know, if the asymmetry observed in the LO mode of the Raman peak of our sample, was due to an electron-phonon coupling shows that it is very close to the value of $q = 4$ obtained for p -type silicon nanowires [5] and that it is near to the $q = 5.07$ of SrTiO_3 of nanocubes [10]; what reinforces our prediction.

The dimensionless parameter $1/q$ characterizes the electron-phonon coupling strength as has been said. A stronger coupling ($q \rightarrow 0$) causes the peak to be more asymmetric. In the limit of the weak electron-phonon interaction ($q \rightarrow \infty$), which means, as have been said previously, that the Fano line-shape can be reduced to a Lorentzian line-shape.

For our un-doped CdTe sample the coupling strength gave a $1/q = 0.23$, which means that the electron-phonon coupling it is not so intense, but it is comparable to that of the doped silicon. When the coupling between the discrete mode (phonon) and the continuum (electron/holes) is significant, the Fano resonance peak position may blue shift or red shift significantly due to the frequency renormalization.

In coupled resonance, the peak frequency of Fano line-shape becomes $\omega_{\text{max}} = \omega_0 + \Gamma/2q$ and its Fano FWHM is $\Gamma(q^2 + 1)/|q^2 - 1|$ [23]. From our fitting parameters, we found that $\omega_{\text{max}} = 164.33 \text{ cm}^{-1}$ and FWHM = 13.24 cm^{-1} which is in accordance with the experimental data.

According with the theory, the TO phonon mode is not allowed by symmetry conditions [18], but become Raman active due to the breaking of the translational crystal symmetry (breaking of crystal symmetry induced by the surface). The frequency mode located between the TO and the LO modes is commonly related with the SO mode of the CdTe [24,25]. This mode is not Raman active; but it can be activated due to the electron-phonon interaction as a result of the relaxation of the selection rules. In order to complete our analysis, we used the analytical expression that results for the Raman intensity including all three modes

$$I(\omega) = \frac{0.04}{1 + \frac{4(\omega - 142)^2}{16^2}} + \frac{0.1}{1 + \frac{4(\omega - 152)^2}{16^2}} + 0.046 \frac{[4.5 + 2(\omega - 163)/12]^2}{1 + [2(\omega - 163)/12]^2} \quad (3)$$

The line-shape fitting of the Raman signal using the whole model is shown in Fig. 2 with the red line, such line, as can be seen, is in an excellent agreement with the experimental data. This also suggests that not only the asymmetry observed in the LO mode of the Raman peak of our sample, is due to the electron-phonon coupling, but that the TO and even the SO modes of our substrate can be activated due to the electron-phonon interaction.

5. Conclusion

In summary, we report the resonant Raman spectrum measured for un-doped single crystal of CdTe. As far as we know, this is the first time that the asymmetric broadening of the LO phonon line width of CdTe is fitting using a Fano line-shape. Our results show that Fano effect in resonant Raman scattering can be caused by the coupling of the LO Raman phonons with the photoexcitation electron in the resonant condition. Asymmetric Fano profiles in the resonant Raman spectra are especially helpful for analyzing the Raman-active (bulk-like and surface) phonon modes, electron-optical-phonon interactions, and carrier relaxation mechanisms in semiconductors [26]. These results advance the understanding of the electron-phonon coupling; since for the first time, the magnitude of the coupling strength has been obtained for un-doped CdTe.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

C.I. Medel-Ruiz: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft. **H.Pérez Ladrón de Guevara:** Resources, Writing - review & editing. **J.R. Molina-Contreras:** Conceptualization, Writing - review & editing, Resources. **C. Frausto-Reyes:** Conceptualization, Writing - review & editing, Resources.

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