ԵՐԵՎԱՆԻ ՊԵՏԱԿԱՆ ՀԱՄԱԼՍԱՐԱՆ

ՀԱՅԱՍՏԱՆԻ ՀԱՆՐԱՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ
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ՏԱՍՆԱՄԵԿԵՐՈՐԴ ՄԻՋԱԶԳԱՅԻՆ ԳԻՏԱԺՈՂՈՎԻ ՆՅՈՒԹԵՐ
ԵՐԵՎԱՆ, 23-25 ՀՈՒՆԻՍ

SEMICONDUCTOR MICRO- AND NANOELECTRONICS

PROCEEDINGS OF THE ELEVENTH INTERNATIONAL CONFERENCE
YEREVAN, ARMENIA, JUNE 23-25

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ICSMN ORGANIZING COMMITTEE

Տպագրվում է Երևանի պետական համալսարանի ռադիոֆիզիկայի ֆակուլտետի գիտական խորհրդի որոշմամբ:

Կ 510 **ԿԻՍԱՀԱՂՈՐԴՉԱՅԻՆ ՄԻԿՐՈ- ԵՎ ՆԱՆՈԷԼԵԿՏՐՈՆԻԿԱ ՏԱՍՆՄԵԿԵՐՈՐԴ ՄԻՋԱԶԳԱՅԻՆ ԳԻՏԱԺՈՂՈՎԻ ՆՅՈՒԹԵՐ ԵՐԵՎԱՆ, 23-25 ՀՈՒՆԻՍԻ**. – Եր.: ԵՊՀ հրատ., 2017. - 207 էջ:

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1. Ֆիզիկական երևույթները միկրո- և նանոկառուցվածքներում,
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Ժողովածուն տպագրության է պատրաստվել փորձագիտական և խմբագրական հանձնախմբի կողմից:

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After independence, since 1991 Armenian scientists carry out intensive investigations in the field of physics and technology of semiconductors, semiconductor micro- and nanosize devices and nanotechnologies. Since 1997, we have been constantly holding conferences devoted to the problems of semiconductor micro- and nanoelectronics. Over the past 20 years, our conference has acquired international significance. Over the years new important and interesting results in the field of micro- and nano-electronics are obtained. Many investigations of Armenian scientists made in co-authorship with colleagues from various countries. Important results were obtained in the last few years in Armenia when studying phenomena in physical and chemical sensors for various purposes, IR and UV photodetectors and solar cells, transistor-like nanostructures, large ICs, in the field of low-dimensional effects, low-frequency noises, noise spectroscopy, etc. The geography of our Conference is expanding. We hope that the conference will take place in a favorable and scientific atmosphere, where new scientific ideas and results will be presented and discussed, which can form the basis for new joint projects.

The Organizing Committee wishes the conference participants useful work, fruitful discussions, interesting polemics, the genesis of new ideas and concepts!

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ON THE THEORY OF INTRAVALLEY RAMAN SCATTERING IN INTRINSIC GRAPHENE

S.V. Melkonyan

Yerevan State University, Yerevan, Armenia, E-mail: smelkonyan@ysu.am

Introduction

Raman spectroscopy is one of the effective tools for accurate structural characterization of materials, for investigating phonon spectra, electron-phonon and phonon-phonon interactions in crystalline structures. Basic parameters of Raman spectrum are Raman line frequencies (Raman lines positions), Raman line widths and intensities of Raman peaks' (or bands). Graphite and graphene (single-layer, bilayer, few-layer and multilayer) Raman spectra are measured and widely discussed in mass of publications (see, e.g. [1 - 5]). The actual measurements are usually carried out by using a laser in the visible region with different excitation energies (wave numbers), for example, $E_l = 1.58$ eV ($q_l = 0.8\times10^5$ cm^{-1}), $E_l = 1.96$ eV ($q_l = 1\times10^5$ cm^{-1}), $E_l = 2.41$ eV ($q_l = 1.2\times10^5$ cm^{-1}) cm^{-1}, respectively. Main intensive Raman peaks of graphite and graphene are the so-called D (~ 1360 cm^{-1}), D' (~ 1620 cm^{-1}), G (~ 1560 ÷ 1580 cm^{-1}) and G' (or 2D) (~ 2690 ÷ 2700 cm^{-1}) bands. As it is well-known Raman spectrum is directly related to crystalline lattice vibrations. Graphite and graphene phonon spectra are practically similar for the major part of Brillouin zone (see, e.g. [4 - 6]). iLO and iTO phonon branches are degenerate at the Γ point (Brillouin zone centre): $\omega_\Gamma^{iLO} = \omega_\Gamma^{iTO} \approx 1583$ cm^{-1}, and at the K point: $\omega_K^{iTO} \approx 1232$ cm^{-1}, $\omega_K^{iLO} \approx 1300$ cm^{-1} (detailed, see [4, 5]). Literature data analysis shows that physical mechanisms of Raman bands origin [1 - 5] require more detailed qualitative and quantitative discussion.

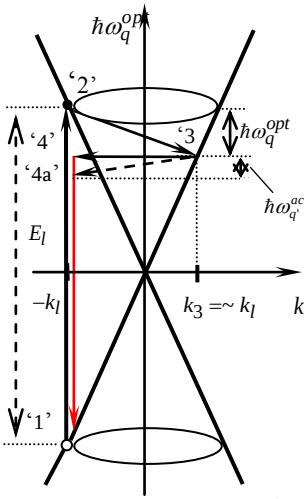

Fig.1. Graphical representation of double-resonant intravalley scattering scheme for the Raman D' peak for a single-layer graphene sample.

Theory

The task of the Raman peaks intensity is closely related to physical the mechanism of its origin. Here the Raman D' peak has been discussed mainly. D' peak is accepted to be interpreted via the mechanism of intravalley double-resonant Raman (DRR) scattering [1 - 4]. In the case of a single layer graphene with high concentration of lattice defects the process of DRR scattering is qualitatively shown in fig.1 in the form of '1'-'2'-'3'-'4'-'1' electron transitions. '1'-'2' and '2'-'3' are the resonant transitions (double resonant) and '3'-'4' transition is conditioned by electron-defect elastic scatterings.

It is of principal importance, to firstly analize the case of a defect-free single-layer graphene with intrinsic conductivity. For the high-quality (defect-free) graphene sample a physical model of intravalley DRR scattering is illustrated on the fig.1 as '1'-'2'-'3'-'4a'-'1' electron transitions. The microscopic interpretation of transitions is the following. The electron in the initial state '1' of valence π band is excited to the conduction π^* band state '2' by absorbing an incident photon with the energy $E_l = \hbar\omega_l$. After that, in the result of '2'-'3' intravalley scattering the electron

appears in the state ‘3’ emitting a photon with energy $\hbar\omega_{\mathbf{q}}$. The electron is then scattered back returning to the initial state ‘1’ through intermediate virtual state ‘4a’ (transition ‘3’-‘4a’-‘1’) by emitting a phonon with the enrgy $\hbar\omega_{q'}$ (transition ‘3’-‘4a’) and a photon with a much smaller energy $\hbar\omega_r = E_l - \hbar\omega_q - \hbar\omega_{q'}$ (transition ‘4a’-‘1’). The processes within a closed cycle where the electron performs the role of a mediator (catalyst), through which the photon-phonon interaction is realized.

DRR scattering involves two phonons at least one of which must be optical. The energy of the emitted (scattered) photon $\hbar\omega_r$ is determined by the sum $\hbar\omega_q^{opt} + \hbar\omega_{q'}^{ac}$ (or $\hbar\omega_q^{opt} + \hbar\omega_{q'}^{opt}$). Depending on the wave vector the phonon frequencies (energies) vary, for example, the frequencies of iLO optical and iLA acoustic modes in graphene first Brillouin zone varies within the ranges $\sim 1232 \div \sim 1583$ (cm^{-1}) and $0 \div \sim 1232$ (cm^{-1}), correspondingly [4, 5]. For the estimation of the possible numerical values of scattered photon energies $\hbar\omega_r$ it is necessary to base on the theory of intrinsic absorption of light by semiconductor taking into account the specificity of the two-phonon processes. According to intrinsic light absorption theory as a result of $\hbar\omega_l$ photon absorption an electron-hole quasi-particle pairs appear. However, for the real absorption of light it a disipative subsystem which will change the state of electron or hole is required, so that they will not be immediately annihilated (recombined) irradiating absorbed photons. In defect-free crystals such a disipative subsystem is the phonons of the lattice. But in the case of Raman scattering we deal with the opposite situation. Unlike real absorption of light, processes which bring to immediate annihilation of electron-hole pairs are responsible for Raman scattering.

According to quasi-particle method of probability calculation a two-phonon process of electron scattering is represented as two consecutive one-phonon transitions which can take place via real or virtual intermediate states. Probability of an electronic transition through a real intermediate state, as a rule, is much higher [8]. The only electron intravalley scattering is possible when the quasi-momentum transfer to the lattice is small. There are three types of two-phonon processes. If a pair of phonons, $\mathbf{q}$ and $\mathbf{q}'$ is emitted or absorbed, their wave vectors should be almost exactly opposite: $\mathbf{q} \approx -\mathbf{q}'$, if one phonon is absorbed and the other is emitted, their wave vectors should be almost equal: $\mathbf{q} \approx \mathbf{q}'$ [8]. Note, the phonons may belong to different regions of different branches.

These well-known features of the two-phonon processes allow assessing the $\hbar\omega_r$ energies of the scattered photon. So, near to the graphene allowed bands extremum (Dirac *K* points) the dispersion relation is linear,

$$E_k = \pm\hbar v_F |\mathbf{k}| = \pm\hbar v_F \sqrt{k_x^2 + k_y^2} \ ,$$

where v_F is the electron group (Fermi) velocity, $\mathbf{k}$ is the electron wave vector, (+) and (-) sings refer to conduction and valence bands, respectively. The magnitude of the wave vector $\mathbf{k}$ is measured from the Dirac *K* point. For ‘1’-‘2’ photo-transition owing to the energy and quasi-momentum conservation laws

$$v_F |\mathbf{k}'| = -v_F |\mathbf{k}| + c|\mathbf{q}_l| \ ,$$
$$\mathbf{k}' = \mathbf{k} + \mathbf{q}_l \ .$$

Here c is the light velocity, $\mathbf{q}_l$ is the light wave vector, $\mathbf{k}$, E_k and $\mathbf{k}'$, $E_{k'}$ is the electron wave vector and energy in the states '1' and '2', respectively.
Taking into account inequality $v_F << c$ from the conservation laws we obtain:

$$k = q_l c / 2v_F = E_l / 2\hbar v_F \equiv k_l .$$

Therefore, '1'-'2' photo-transition can be carried out by the electrons having quasi-momentun $\sim \hbar k_l$ (or energy $E_l / 2$). Note, the $\hbar k_l$ depends on the photon energy E_l via linear proportional law.

For '2'-'3' transition when an acoustic or optical phonon is emitted owing to conservation laws:

$$v_F|\mathbf{k}'| = v_F|\mathbf{k}| - \omega_q^{ac}, \qquad v_F|\mathbf{k}'| = v_F|\mathbf{k}| - \omega_q^{opt}, \tag{1.a-1.b}$$

$$\mathbf{k}' = \mathbf{k} - \mathbf{q}, \tag{2}$$

where $\mathbf{k}$ and $\mathbf{k}'$ are electron wave vectors in the states '2' and '3', respectively.

For the simplicity of calculations optical phonon dispersion can be ignored ($\omega_q^{opt} = \omega_0 = const$) and for acoustic phonons the linear dispersion law $\omega_q = v_{ac} q$ [4, 5, 7] is used, where v_{ac} is the velocity of longitudinal acoustic phonon. Taking into account inequality $v_{ac} / v_F << 1$ ($v_{ac}^{LA} \approx 2\times10^4$ m/s, $v_F \approx 10^6$ m/s [5, 7]), from equations (1.a) and (2) the well-known result is obtained: $0 \le q \le 2k$. Phonons with $q \approx 2k$ wave vectors provide effective change of electron quasi-momentum [8]. From equations (1.b) and (2) it follows that $k > k_0$, $\frac{k_0}{2} < k < k_0$ and $0 < k < k_0 / 2$ electrons interact with $k_0 < q < 2k - k_0$, $2k - k_0 < q < k_0$ and $k_0 - 2k < q < k_0$ optical phonons, respectively. Here $k_0 \equiv \omega_0 / v_F = 4.7 \cdot 10^5$ cm^{-1} is the electron characteristic wave number.

Taking into account inequality $k_0 / k_l = 2\hbar\omega_0 / E_l < 1$ it can be stated that DRR scattering involes acoustic and/or optical phonons whose wave numbers should be equal: $q \approx 2k_l$. Therefore, for the scattered photons one can have $\hbar\omega_r = \hbar\omega_{q=2k_l}^{ac} + \hbar\omega_{q=2k_l}^{opt}$ and $\hbar\omega_r = \hbar\omega_{q=2k_l}^{opt} + \hbar\omega_{q=2k_l}^{opt}$. From relation $q = 2k_l = E_l / \hbar v_F$ it follows that Raman peak position is determined by the phonon spectrum as well as by excitation laser energy $E_l = \hbar\omega_l$. Particularly, at excitation laser energy $E_l = 2.41$ eV one have $k_l = 2\times10^7$ cm^{-1}. As it follows from the experimental curves of phonon spectrum [4, 5], the phonon wave number $q = 2k_l = 4\times10^7$ cm^{-1} corresponds to $\omega_{q=2k_l}^{iLO} \approx 1620$ cm^{-1}, $\omega_{q=2k_l}^{iTO} \approx 1550$ cm^{-1}, $\omega_{q=2k_l}^{iLA} \approx 400$ cm^{-1} and $\omega_{q=2k_l}^{iTA} \approx 200$ cm^{-1} phonon frequencies. Phonons from the same as well as from different branches can participate in two-phonon processes. Therefore, according to DRR scattering mechanism in high-quality graphene sample, Raman peaks may be expected at following frequencies:

- related to optical and acoustic phonon branches:

$$\omega_{q=2k_l}^{iTO} + \omega_{q=2k_l}^{iTA} \ (1750 \text{ cm}^{-1}), \quad \omega_{q=2k_l}^{iLO} + \omega_{q=2k_l}^{iTA} \ (1820 \text{ cm}^{-1}),$$

$$\omega_{q=2k_l}^{iTO} + \omega_{q=2k_l}^{iLA} \ (1950 \text{ cm}^{-1}), \quad \omega_{q=2k_l}^{iLO} + \omega_{q=2k_l}^{iLA} \ (2020 \text{ cm}^{-1}), \tag{3a}$$

- related to the same optical branch:

$$2\omega^{iLO}_{q=2k_l} \text{ (3240 cm}^{-1}\text{) и } 2\omega^{iTO}_{q=2k_l} \text{ (3100cm}^{-1}\text{).} \quad (3b)$$

If an acoustic phonon is not emitted, but absorbed at electron transition, one may have

$$\omega^{iTO}_{q=2k_l} - \omega^{iTA}_{q=2k_l} \text{ (1350 cm}^{-1}\text{)}, \quad \omega^{iLO}_{q=2k_l} - \omega^{iTA}_{q=2k_l} \text{ (1420 cm}^{-1}\text{)},$$

$$\omega^{iTO}_{q=2k_l} - \omega^{iLA}_{q=2k_l} \text{ (1150 cm}^{-1}\text{)}, \quad \omega^{iLO}_{q=2k_l} - \omega^{iLA}_{q=2k_l} \text{ (1220 cm}^{-1}\text{)}, \quad (3c)$$

According to multiphonon scattering theory [8] transition probability per unit time of the '1' - '1' cycle process can be presented by the following form

$$W = \sum_{\mathbf{k}_l^{\pi^*}, \mathbf{k}_3^{\pi^*}} W_{\mathbf{k}_l^{\pi} \to \mathbf{k}_l^{\pi^*}} \tau_{\mathbf{k}_l^{\pi^*}} W_{\mathbf{k}_l^{\pi^*} \to \mathbf{k}_3^{\pi^*}} \tau_{k_3^{\pi^*}} W^{(2v)}_{\mathbf{k}_3^{\pi^*} \to \mathbf{k}_l^{\pi}}, \quad (4)$$

where $W_{k_l^{\pi} \to k_l^{\pi^*}}$ and $W_{k_l^{\pi^*} \to k_3^{\pi^*}}$ are probabilties of the transitions '1'-'2' and '2'-'3', respectively, $W^{(2v)}_{k_3^{\pi^*} \to k_l^{\pi}}$ is the probapility of the transition '3'-'1' through virtual intermediate electronic state '4a', $\tau_{k_l^{\pi^*}}$ and $\tau_{k_3^{\pi^*}}$ are electron lifetimes in the real states '2' and '3', respectively, which carachterize '2' and '3' energy level broadening, $\mathbf{k}_3^{\pi^*}$ is the electron wave vector in state '3'. Factor $\tau_{k_3^{\pi^*}} W^{(2v)}_{\mathbf{k}_3^{\pi^*} \to \mathbf{k}_l^{\pi}}$ is the conditional probability that the electron in state $\mathbf{k}_3^{\pi^*}$ will afterwards transfer specifically into $\mathbf{k}_l^{\pi^*}$ state. Here the particular case of emition of two phonons with $\mathbf{q} = \mathbf{q}' = 0$ wave verctors should be noted. For acoustic-optical phonon pair taking into account $\omega^{ac}_{q=0} = 0$ peculiarity, it can be stated that the two-phonon process is expanded to the one-phonon process. At transition is emitted one iLO (or iTO) optical phonon with $q = 0$ wave number. Then energy of the scattered phonon is determined as $\hbar\omega_r = \hbar\omega^{ac}_{q=0} + \hbar\omega^{opt}_{q=0} = \hbar\omega^{opt}_{q=0}$. It corresponds to the Raman band with frequency $\omega_r = \omega^{iLO}_{q=0} = \omega^{iTO}_{q=0} = 1583 \text{ cm}^{-1}$.

Conclusions

The task of intensity of Raman bands is closely related to Raman scattering mechanism. On the base of energy and quasi-momentum conservation laws the peculiarities of intravalley double-resonant Raman scattering processes are discussed above. In the high-quality intrinsic graphene set frequencies of Raman peaks is given by equations (3). Those frequencies depend on phonon spectrum as well as excitation laser energy E_l. However, the theoretical results practically do not coincide with the corresponding experimental data. So, the measurement results at $E_l = 2.41$ eV show [9] that in defect-free graphene G (~ 1580 cm^{-1}) and G' (or 2D) (~ 2700 cm^{-1}) relatively high intensity peaks and D (~ 1350 cm^{-1}) and 2D' (~ 2350 cm^{-1}) very weak intensity peaks have basically been observed; D' band is absent. Note D' band requires a defect and is observed only in non perfect samples with structural defects. The frequency $\omega_r = \omega^{iLO}_{q=0} = \omega^{iTO}_{q=0} = 1583 \text{ cm}^{-1}$ is in good agreement with measured Raman G band of graphene and graphite. That band, unlike the collection (3), is due to the single-phonon scattering of electron (single-resonant Raman scattering). On the other hand, it is currently assumed that the Raman G' band relates to the intervalley two-phonon scattering of an electron. Usually, as a rule, the probability of a single-phonon scatterings is higher and, therefore, is a more intensive process than a two-phonon one. Therefore, the intensity of the G band I_G must be much higher than the intensity of the G' band

$I_{G'}$. However according to the measurement data in defect-free grapene one comes accross the opposite situation, $I_G < I_{G'}$ (more than four time).

Thus, by comparing the results of the above presented theoretical analyses and experimental data the following can be concluded: the accepted double-resonant Raman scattering concept fails to give a successful and accurate explanation of the origin of Raman spectrum peaks and intensities of purely crystalline (without defects) intrinsic grapheme.

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