Strain-fluctuation effect on Raman spectra

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We show that the interaction of phonons with static strain fluctuations induces an inhomogeneous shift and a broadening of Raman spectra. The Raman scattering cross section is calculated in terms of the averaged strain, which relaxes smoothly in real space, and of the strain correlation function. Two regimes of short- and long-range disorder with different line shapes are found. The agreement with experiment data collected on the 3*C*-SiC/Si interface is satisfactory. [S0163-1829(97)51922-9]

The Raman spectra present a very complex picture and attention to their subtle aspects was paid only recently. In particular, it was lately discovered that the interaction of the phonon resonances with the electron-hole continuum leads to characteristic changes in the resonance line shape (the Fano resonance).[1–3] The metal-insulator transition also results in the change of Raman line shape through the electron-phonon interaction (e.g., see the experimental results on fullerides[4]). Another aspect of this problem can be found in the interaction of vibration modes with crystal imperfections (see Ref. 5 and references therein).

In this work we consider the influence of stress inhomogeneity on the Raman mode. From the experimental point of view, Raman scattering is a very useful tool to investigate the microstrain in bulk materials and multilayered semiconductor structures. However, up to now, only the line shift resulting from a constant strain has been studied both experimentally and theoretically.[6,7] However, in many cases the strain changes in samples. For instance, the strain induced by the differences of lattice constants and thermal coefficients between adjacent heteroepitaxial layers relaxes when moving from the interface to the free surface. This is illustrated in Fig. 1, where a Si (substrate)/SiC (epilayer) interface is drawn.

Because the strain may change its value on the large range, one can observe the smooth strain variation in heteroepitaxial layers by displacing a laser spot on the lateral surface and measuring the phonon line shift $\Delta\omega^{(un)}$.[8] We call this effect *the uniform shift*. Since there are layers in the laser spot with different strains, the uniform strain relaxation results in a Raman linewidth $\Gamma^{(un)}=d\,\partial(\Delta\omega^{(un)})/\partial z$, where d is the laser spot diameter. A typical example is shown for the LO phonon modes of SiC in Fig. 2 (left panel). From bottom to top, the three different spectra correspond with different spot positions: at the interface, 1.5 μm away from the interface, and 3 μm from the interface. The spectra show clearly that the strain relaxes over distances ~ 5 μm and induces a line shift $\Delta\omega^{(un)}\sim 2$ cm^{-1}. In our experiment $d\simeq 1$ μm, and then the broadening $\Gamma^{(un)}$ is negligible in comparison with the observed linewidth (several cm^{-1}). We see that the very small shift cannot explain the observed large width as well as the asymmetry of the line shape.

In this theoretical and experimental study, we show that the strain consists of a spatial fluctuating component besides the term which reduces smoothly. The strain fluctuations over distances of the order of the optical wavelength originate from dislocations, block structures and other structural defects. In the back-scattering Raman geometry, an optical phonon excited by light has the double light wave momentum and ''sees'' smooth strain effects averaged over the range of the light wavelength. The fluctuating strain induces *an inhomogeneous broadening* $\Gamma^{(inh)}$ and *a shift* $\Delta\omega^{(inh)}$ of the Raman lines. To our knowledge, the influence of such a disorder on the Raman phonons has never been considered.

We propose a model of phonon interaction with strain fluctuations, which brings us to the asymmetric line form. From the theoretical point of view, our problem has several peculiar features. First, because of the small uniform splitting of the degenerate phonons, both interband and intraband transitions of phonons are possible in the scattering process by the static strain fluctuations. Second, the momentum transfer from light to phonons is relatively small. We calculate the phonon shift and width near the top of the optical phonon branches, where the momentum transfer from the strain fluctuations is comparable to the phonon width. Third, since the phonon Raman scattering is determined by the pho-

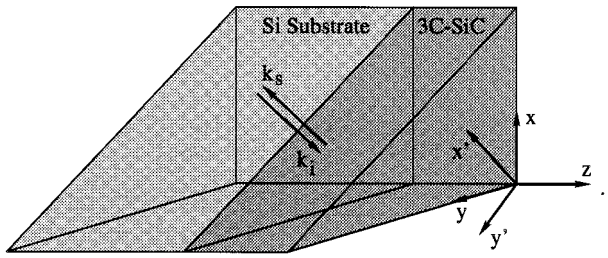

FIG. 1. Raman back-scattering geometry used to investigate the strain relaxation at a 3*C*-SiC/Si interface. The incident and scattered light propagate parallel to the $\langle 110\rangle$ direction (x' axis); x,y,z are cubic axes.

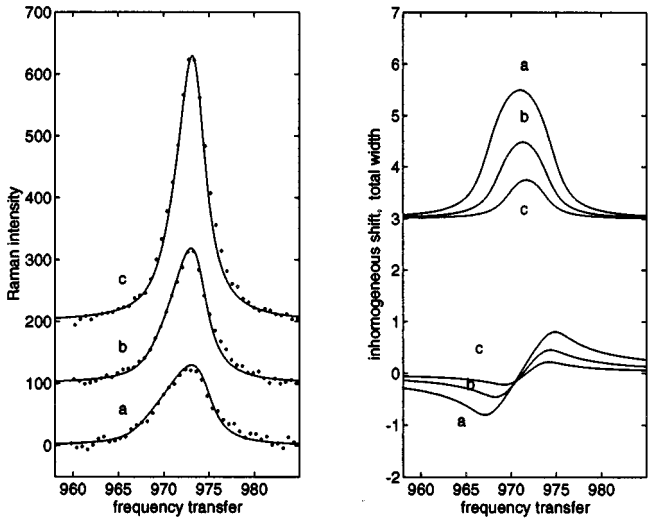

FIG. 2. Raman spectra of the LO phonon of a 3 μm thick commercial sample (Ref. 11) for various laser spot positions (left panel). Starting from interface (a), at 1.5 μm (b), and at 3 μm from the interface (c), the Raman line becomes more narrow but stays asymmetric. This is clear evidence of inhomogeneous short-range disorder. The total width including the inhomogeneous broadening (cm^{-1}, top) and shift (bottom) as a function of the frequency transfer (cm^{-1}) are shown in the right panel. Theoretical model assumes anisotropic strain fluctuations with small correlation radius $r_o/a=6$. The fits for line position, intrinsic and total width (at the center of lines) give, respectively, (a) 972.7, 3.0, 5.2, (b) 972.9, 3.0, 4.3, (c) 973.1, 3.0, 3.6 cm^{-1}.

non Green's function averaged over the strain fluctuations, we solve the appropriate Dyson's equation for the Green's function considering the interaction of phonons with the static strain fluctuations. We emphasize that the integral equations for the width and shift, which are functions of the frequency transfer, are solved self-consistently. We have found the inhomogeneous broadening and shift in terms of the strain correlation function. Using the obtained width and shift, we calculate the Raman line shape. Our method can be applied also to the scattering of optical phonons by imperfections and other problems where the momentum transfer is comparable to the collision rate.

We have compared the theory with Raman spectra collected on two different 3*C*-SiC/Si samples. More experimental results, as well as the details of calculations will be presented in a later work.

The interaction of optical phonons displacements $u_i(r,\omega)$ with strain $\varepsilon_{lm}(\mathbf{r})$ in the form $V_{ij}(\mathbf{r})=\lambda_{ijlm}\varepsilon_{lm}(\mathbf{r})$ was proposed previously for the constant strain case.[6] In cubic crystals there are three optical phonons in the Γ point with a triple degenerate frequency ($i=1,2,3$). The long-range Coulomb forces split this degeneracy in such a way that the LO phonon has a higher frequency than the two-times degenerate TO modes.

The averaged phonon Green's function depends on the coordinates difference $\mathbf{r}-\mathbf{r}'$. For its Fourier transform, collecting the important diagrams, we obtain the Dyson's equation

$$D_{ij}^{-1}(\mathbf{k},\omega)=D_{ij}^{(o)-1}(\mathbf{k},\omega)-\int\frac{d^3k'}{(2\pi)^3}\times W_{imlj}(\mathbf{k}'-\mathbf{k})D_{ml}(\mathbf{k}',\omega), \quad (1)$$

where the matrix

$$D^{(o)-1}(\mathbf{k},\omega)=H(\mathbf{k})-i\omega\Gamma^{(int)}+\langle V(\mathbf{r})\rangle-\omega^2 \quad (2)$$

includes the long-wave expansion of the dynamic matrix $H_{ij}=\chi_{ij}-\mu_{ijlm}k_lk_m$, the intrinsic phonon damping $\Gamma^{(int)}$ (Ref. 9) and the averaged strain effect $\langle V_{ij}(\mathbf{r})\rangle=\lambda_{ijlm}\langle\varepsilon_{lm}(\mathbf{r})\rangle$. For cubic crystals, the tensor $\chi_{ij}=\omega_o^2\delta_{ij}$, both λ_{ijlm} and μ_{ijlm} have three independent components. The symmetry of the averaged $\langle\varepsilon_{ij}\rangle$ is determined by the experimental conditions.

The transition probability $W_{imlj}(\mathbf{k}'-\mathbf{k})$ is the Fourier transform of the correlation function $W_{imlj}(\mathbf{r}-\mathbf{r}')=\langle\delta V_{im}(\mathbf{r})\delta V_{lj}(\mathbf{r}')\rangle$. The poles of $D^{(o)-1}(\mathbf{k},\omega)$ give the phonons dispersion law in the absence of disorder $\omega_j^2(k)=\omega_j^2(k=0)-s_j^2k^2-i\omega\Gamma_j^{(int)}$. The parameters s_j have the order of sound velocity and depend on the $\mathbf{k}$ direction (we will neglect this dependence). The uniform shift is included in $\omega_j^2(k=0)$.

Being transformed to the diagonal form, Eq. (1) gives the inhomogeneous broadening and shift. Its solution can be found in the form

$$D_{jj}^{-1}(\mathbf{k},\omega)=\omega_j^2-s_j^2k^2-i\omega\Gamma_j-\omega^2, \quad (3)$$

where $\omega_j=\omega_j(k=0)+\Delta\omega_j^{(inh)}(\mathbf{k},\omega)$ and $\Gamma_j=\Gamma_j^{(int)}+\Gamma_j^{(inh)}(\mathbf{k},\omega)$. Substituting Eq. (3) in Eq. (1) and taking the imaginary and real parts, we arrive at a system of coupled integral equations for $\Gamma_j^{(inh)}(\mathbf{k},\omega)$ and $\Delta\omega_j^{(inh)}(\mathbf{k},\omega)$.

To make estimates, we approximate the strain correlator by a Gaussian function with the Fourier transform

$$W_{imlj}(\mathbf{k})=(2\pi)^{3/2}\varepsilon^2\omega_o^4r_o^3w_{imlj}e^{-k^2r_o^2/2}, \quad (4)$$

where parameter w_{imlj} is the mean-squared fluctuation at point $\mathbf{r}$, divided by the squared mean strain and the frequency parameter ω_o to the fourth power. The correlation radius r_o defines the average domain size with a more or less constant strain value.

The Raman cross section is proportional to $\mathrm{Im}D(\mathbf{k},\omega)$, where the momentum $\mathbf{k}$ and frequency ω have the sense of a momentum and frequency transfer from the light. In the optical range $k\sim10^5$ cm^{-1}, the frequencies and damping of optical phonons $\omega_o\simeq10^3$ cm^{-1}, $\Gamma\simeq1-3$ cm^{-1}, the dispersion parameter $s\simeq5.10^5$ cm/s. Therefore, the condition $sk\ll\sqrt{\omega_o\Gamma}$ is valid in all experiments discussed below. Then $\Gamma_j^{(inh)}(\mathbf{k},\omega)$ and $\Delta\omega_j^{(inh)}(\mathbf{k},\omega)$, given by the integral (1), can be regarded as $\mathbf{k}$ independent. Concerning $\mathbf{q}=\mathbf{k}'-\mathbf{k}$, the values $q^2\leqslant2/r_o^2$ determine the final states for phonons scattered by the strain fluctuations. The domain $q^2\leqslant2\omega_o\Gamma/s^2$ is essential in the integrand Green's function D, given in Eq. (3). This is because we are interested in $|\omega_j-\omega|\simeq\Gamma$. We see that two limiting cases are possible, depending on whether the parameter $\sqrt{\Gamma/\omega_o}\pi r_o/a$ is small or large ($a\simeq\pi s/\omega_o$ being of the order of the lattice parameter). In both cases, all integrals can be done analytically, and we obtain the system of coupled algebraic equations for $\Gamma_j^{(inh)}(\omega)$ and $\Delta\omega_j^{(inh)}(\omega)$.

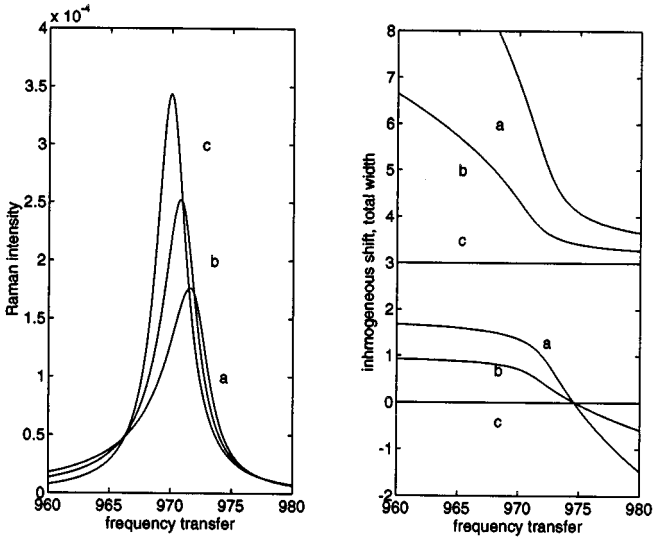

FIG. 3. Theoretical Raman intensity (left panel), phonon width (top of the right panel) and shift (inhomogeneous component only, bottom) plotted as a function of the frequency transfer in the case of small correlation radius $r_o/a=3$ for three values of the interaction constant A, cm^{-1}: (a) $A=1.5$, (b) $A=.3$, (c) $A=0$, no strain fluctuation.

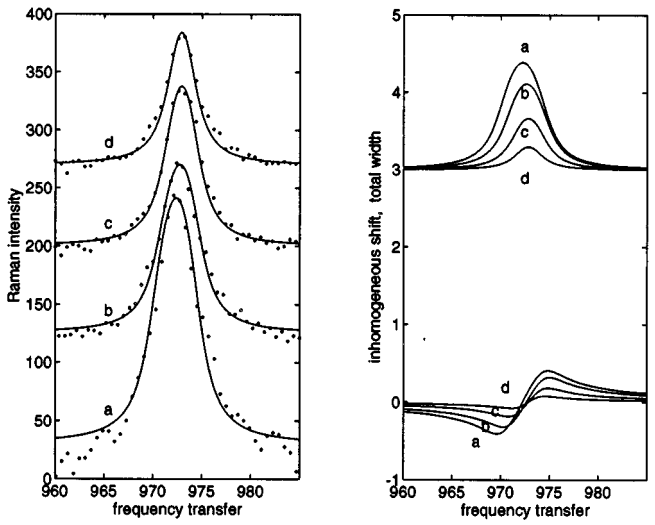

FIG. 4. Same as Fig. 2 for a 6 μm thick noncommercial sample (Ref. 12). Spectra correspond with the four spot positions: at interface (a), at distances 2 μm (b), 3 μm (c), and 6 μm (d) away from interface. This is an example of long-range disorder with correlation radius $r_o/a\simeq 25$ (parameter $r_o\omega_o/s=80$). The fit gives for the line position, intrinsic and total width (at center of line) and the interaction constant B, respectively, (a) 972.4, 3.0, 4.38, 20, (b) 972.8, 3.0, 4.11, 15, (c) 973.0, 3.0, 3.66, 8, (d) 973.0, 3.0, 3.29, 3.2 cm^{-1}.

(i) *The correlation radius is small:* $\sqrt{\Gamma/\omega_o}\pi r_o/a\ll 1$. In this case $r_o/a<10$ for the above-listed set of parameters and a phonon can considerably change its momentum when scattered by the strain fluctuations. In the integral for the width [imaginary part of Eq. (1)] we can take the correlator at $q=0$ and integrate over $\mathbf{k}'$. The leading contribution in the integral for the shift [real part of Eq. (1)] comes from the large q values, where the exponent factor is only essential. The next term should also be held, since it depends on ω. For the nondegenerate case (e.g., the LO phonon in SiC), subscripts in s_j, Γ_j, and w_{imlj} take one value and will be omitted. Then only one intraband constant w describes the inhomogeneous width. Typical computer solutions of the coupled system together with the Raman cross section which is proportional to $\mathrm{Im}D(\mathbf{k},\omega)$ are shown in Fig. 3. The Raman line is asymmetric and, for large scattering, resembles the Fano resonance. One can see that the inhomogeneous width essentially increases below the branch maximum. The explanation of this behavior is to be found in the LO-phonon density of state, which is equal to zero for $\omega^2>\omega_{LO}^2$ (if $\Gamma^{(int)}\to 0$) and proportional to $\sqrt{\omega_{LO}^2-\omega^2}$ below the top of branch. The square-root singularity exists also in the frequency dependence of the shift.

At the center of the line, i.e., at $\omega=\omega_{LO}$, the width and shift can be found analytically. We obtain the total width

$$\Gamma=\Gamma^{(int)}+A/2+[(A/2)^2+\Gamma^{(int)}A]^{1/2}, \tag{5}$$

where A is associated with the phonon scattering by strain fluctuations:

$$A=\frac{\pi}{4}\omega_o\varepsilon^4\left(\frac{\omega_o r_o}{s}\right)^6 w^2\simeq\frac{\pi}{4}\omega_o\varepsilon^4\left(\frac{\pi r_o}{a}\right)^6 w^2.$$

If the intrinsic width $\Gamma^{(int)}\ll A/4$, the total width $\Gamma=A+2\Gamma^{(int)}$. In the opposite case, $\Gamma=\sqrt{\Gamma^{(int)}A}+\Gamma^{(int)}$.

We see that the disorder width and the intrinsic damping *are not additive*. The inhomogeneous shift of the LO phonon in the leading approximation is

$$\Delta\omega^{(inh)}=(A/\pi\omega_o)^{1/2}s/r_o.$$

The extension of the theory to the degenerate case (which corresponds with the TO phonons in SiC) gives a more complicated picture. There are two intraband and one interband constants w, which describe the phonon interaction with the strain fluctuations. We shall not discuss this case any longer.

(ii) *The correlation radius is large:* $\sqrt{\Gamma/\omega_o}\pi r_o/a\gg 1$. Now we consider the long-scale disorder and, consequently, the small-angle scattering of phonons by the strain fluctuations. Then the correlator is a sharp function, and the phonon Green's function in the integrand should be expanded in powers of $\mathbf{q}$. The zeroth-order term gives the final result for the width but terms up to the second order are needed for the shift (the zero-order term vanishes at the top of branch and the first-order term vanishes since the correlator is an even function). We obtain again the system of two coupled algebraic equations. Computer solutions of the system (the total width and the inhomogeneous shift as a function of frequency transfer) together with $\mathrm{Im}D(\omega)$ are shown in Fig. 4. Raman spectra collected on a second SiC sample are shown for comparison. The line shape is non-lorentzian, but appears more symmetric than in the previous case of short-range disorder. At the center of line ($\omega=\omega_{LO}$):

$$\Gamma=\Gamma^{(int)}/2+[(\Gamma^{(int)}/2)^2+B^2]^{1/2},$$

$$\Delta\omega^{(inh)}=1.5(sB/r_o\Gamma)^2/\omega_o\simeq 1.5\omega_o(aB/\pi r_o\Gamma)^2,$$

where $B^2=\varepsilon^2\omega_o^2 w$.

We wish to emphasize that all foregoing formulas give observed values of width and shift, when using the above-listed set of phonon parameters, the value $\varepsilon \simeq 10^{-3}$ known from various experiments[10] and $w_{imlj} \simeq 1$.

So far it was assumed that the disorder is isotropic. However, in the presence of a heterointerface, the strain correlation function may have an anisotropic behavior. The lattice mismatch at the interface creates dislocations which appear as line imperfections. This disorder can be described using a two-dimensional correlation function. If it has the short-range behavior, we obtain the asymmetric Raman line shape with a smoother high frequency side in comparison with the three-dimensional short-range disorder. Such an effect was indeed observed on the first sample and corresponds with the series of theoretical lines displayed in Fig. 2.

In closing, the conditions of validity for the basic Eq. (1) should be outlined. The line shape on wings can be obtained using the perturbation theory (the Born approximation). At the center of the lines, the diagrams with intersections of the correlator lines make the contribution of order of the leading diagram (1) and a more sophisticated theory is needed. Then one can consider Eq. (1) as a sensible interpolation between the extreme limits. Finally, we should compare the effect of strain inhomogeneity with the Fano resonance effect. The Fano resonance in conducting systems is due to the phonon-electron interactions or, in another way, arises from an appearance of the imaginary part in the electron loop, which does not depend on the phonon density of states. The results of our paper show that a similar asymmetric line shape originates from the phonon density of final states, when we consider the phonon scattering by imperfections.

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[1] B. Friedl, C. Thomsen, and M. Cardona, Phys. Rev. Lett. **65**, 915 (1990).

[2] T.P. Devereaux, A. Virosztek, and A. Zawadowski, Phys. Rev. B **51**, 505 (1995).

[3] L.A. Falkovsky and S. Klama, Physica C **264**, 1 (1996).

[4] S.J. Duclos *et al.* Science **254**, 1625 (1991).

[5] M.V. Klein, in *Dynamical Properties of Solids*, edited by G.K. Horton and A.A. Maradudin (North-Holland, Amsterdam, 1990), Vol. 6, pp. 65–127.

[6] F. Cerdeira, C.J. Buchenauer, F.H. Pollak, and M. Cardona, Phys. Rev. B **5**, 580 (1971).

[7] P. Merle, J. Pascual, J. Camassel, and H. Mathieu, Phys. Rev. B **21**, 1617 (1980).

[8] J.M. Bluet, J. Camassel, L.A. Falkovsky, and A. Leycuras, Proceedings of the First European Conference on SiC and Related Materials, Crete, 1995 [Diam. Relat. Mater. (to be published)].

[9] L.A. Falkovsky and E.G. Mishchenko, Phys. Rev. B **51**, 7239 (1995).

[10] Z.C. Feng, W.J. Choyke, and J.A. Powell, J. Appl. Phys. **64**, 6827 (1988).

[11] Cree Research Inc., 2810 Meridian Parkway, Durham, NC 27713.

[12] N. Becourt *et al.*, Physica B **185**, 79 (1993); N. Becourt *et al.*, Appl. Surf. Sci. **68**, 461 (1993).