Raman Scattering by Surface Polaritons

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A theoretical analysis of Raman scattering at a slab (two-interface) configuration shows that the forward-scattering efficiency of the surface polariton can be comparable to that of the volume modes, in agreement with experiments. On the other hand, the backward-scattering efficiency of the surface polaritons at single-interface and two-interface configurations is relatively very small, which accounts for the inability to observe Raman scattering by surface polaritons at single interfaces.

Although there have been extensive efforts by various groups, including our own, to observe Raman scattering by optical-phonon–type surface polaritons at a semiconductor-air interface, these efforts have thus far been unsuccessful. Recently, Evans, Ushioda, and McMullen[1] have reported the observations of Raman scattering of 4880-Å radiation by the surface polaritons of a thin (111) "slab" (~2500 Å) of GaAs on a (0001)-surface sapphire (Al_2O_3) substrate using a forward-scattering configuration. From their data on the variation of the frequency of the observed peaks with scattering angles they established that the peaks correspond to modes of the lower branch of the dispersion curve of the asymmetric-slab surface polaritons.[2] They attributed their ability to observe Raman scattering by these modes solely to the fact that the frequencies of the surface polaritons were sufficiently displaced from the frequency of the $q \approx 0$ volume LO phonons in GaAs to allow separate peaks for the surface modes to be observed.

We present here the results of a theoretical analysis of the relative scattering efficiencies of optical phonons and optical-phonon–type surface polaritons which accounts for the lack of success in observing scattering by surface modes at single-interface configurations. Our analysis shows, moreover, that the reason Evans, Ushioda, and McMullen were able to observe Raman scattering by surface polaritons in their experiments is that they used a thin-slab (two-interface) configuration which allowed them to carry out *forward-scattering* measurements.

Theoretical discussions of the scattering of light by surface polaritons at single interfaces have previously been given by Ruppin and Englman[3] and more recently by Agranovich and Ginzburg.[4] However, these discussions do not shed any light on the factors which determine the observability of Raman scattering by surface polaritons.

Surface polaritons are interface electromagnetic (EM) modes whose amplitudes decay exponentially with distance from the interface. Raman scattering by surface polaritons is therefore confined to the penetration depth of the surface polaritons in the scattering medium. Since the penetration depth of the optical-phonon-type surface polaritons is typically 5 μm or less, Raman scattering by the surface polaritons can only be observed under strong resonance-enhanced conditions. In the case of single-interface configuration one is, therefore, limited to *backward-scattering* configuration.

We consider first the case of Raman scattering by surface polaritons at a semiconductor-air interface. The Raman-scattering efficiencies of the volume and the surface modes are calculated using the formalism of Mills, Maradudin, and Burstein.[5] In calculating the scattering efficiency of surface polaritons, one simply takes into account the fact that the surface modes have wave vectors whose components normal to the interface are imaginary.

As already shown by Mills, Maradudin, and Burstein the expression for the backward, $z(\zeta\beta)\bar{z}$ scattering efficiency of the volume modes at a semiconductor-air (designated as 1-2) interface lying in the xy plane, for the case of a cubic semiconductor which has only one type of optical phonon, has the form

$$S_{\zeta\beta}(\omega_j) \propto \left|\sum_{\gamma\sigma\rho} g_{\beta\gamma}\Gamma_{\sigma\zeta}\left[a_{\gamma\sigma\rho}+b_{\gamma\sigma\rho}\frac{(\omega_T^2-\omega_j^2)\overline{m}}{e_T^*}\right]\hat{d}_{j\rho}\right|^2\frac{\omega_j(\overline{n}+1)}{k_{iz}''+k_{sz}''}, \tag{1}$$

where $\beta,\gamma,\sigma,\rho,\zeta$ represent x,y,z; $\underline{\Gamma}$ and $\underline{g}$ are the transfer functions across the interface of the incident and scattered radiation into and back out of the scattering medium, respectively: $\underline{a}$ and $\underline{b}$ are the atomic displacement and electro-optical Raman tensors of the semiconductor; ω_T, $\overline{m}$, and e_T^* are the frequency, reduced mass, and effective charge of the TO phonons, ω_j is the frequency of the volume mode j involved in the scattering; $\hat{d}$ is the polarization vector of the volume mode; k_{zi}'' and k_{zs}'' are the imaginary parts of the normal components of the wave vectors of the incident and scattered radiation, respectively, in the semiconductor; and we have neglected the damping of the phonon modes.

The corresponding expression for the scattering efficiency of surface modes is readily shown to have the form[6]

$$S_{\zeta\beta}(\Omega) \propto \left|\sum_{\gamma\sigma\rho} g_{\beta\gamma}\Gamma_{\sigma\zeta}\left[a_{\gamma\sigma\rho}+b_{\gamma\sigma\rho}\frac{(\omega_T^2-\Omega^2)\overline{m}}{e_T^*}\right]\left(d_\parallel+\frac{ik_\parallel}{\alpha_1}d_\perp\right)\right|^2\left\{\frac{\alpha^*\Omega(\overline{n}+1)}{(\Delta k_z')^2+(\Delta k_z''+\alpha_1)^2}\right\}, \tag{2}$$

where Ω and $k_\parallel$ are the frequency and wave vector of the surface mode; $\Delta k_z'^B = k_{iz}'+k_{sz}'$ and $\Delta k_z''^B = k_{iz}''+k_{sz}''$; $d_\parallel$ and $d_\perp$ are the parallel and perpendicular components of the polarization vector of the atomic displacement coordinate $\vec{u}_j$ of the surface mode; α_1 is the attenuation constant of the surface mode in the semiconductor; and α^* is a composite attenuation constant of the surface mode. When the energy of the surface modes is predominantly within the semiconductor, which is true for the surface modes whose frequencies are not close to ω_T, α^* is effectively equal to α_1.

The relative scattering efficiency $S(\Omega)/S(\omega_j)$ of the surface and volume modes is, apart from frequency, orientation, and polarization factors, equal to the ratio of the "effective" scattering lengths of the surface and volume modes,

$$\frac{l_s}{l_v}=\frac{\alpha_1}{(\Delta k_z')^2+(\Delta k_z''+\alpha_1)^2}\left(\frac{1}{\Delta k_z''}\right)^{-1}. \tag{3}$$

In the case of scattering at 4880 Å by the surface and volume modes of a GaAs-air–interface configuration, $\Delta k_z'^B \approx 1.2\times10^6$ cm^{-1}, $\Delta k_z''^B\approx 1.1\times10^5$ cm^{-1}, and α_1 ranges from a minimum value of 3.6×10^3 cm^{-1} at $\Theta_1=\Theta_1(\vec{k}_i,\vec{k}_s)=0.27°$ to 1.3×10^5 cm$^{-1}\approx k_\parallel$ at $\Theta_1=13.9°$, the critical angle. The values of l_s/l_v range from $\sim 2.3\times10^{-4}$ at $\Theta_1=0.27°$ to $\sim 1.09\times10^{-2}$ at $\Theta_1=13.9°$. The numbers do not change appreciably when Al_2O_3, rather than air, is used as the surface-inactive medium. They are somewhat higher for InAs-air interfaces.

We note that it is the presence of the term $(\Delta k_z')^2$ in the denominator of $S(\Omega)$ and its large magnitude in backward scattering that is responsible for the very small relative scattering efficiency of the surface modes in the single-interface configuration, even under resonance-enhanced conditions.

We consider next the backward- and forward-scattering efficiencies of the surface and volume modes in an air-semiconductor-dielectric (2-1-3) two-interface configuration. The surface modes of the slab correspond to coupled air-semiconductor (2-1) and semiconductor-dielectric (1-3) single-interface modes and there are two branches, designated Ω_- and Ω_+, to the dispersion curve.

The volume modes of the semiconductors are also modified in the slab configuration.[7] The LO-phonon modes of the slab are wave-guide modes whose frequencies are the same as those of the bulk $q\approx 0$ LO phonons. The TO-phonon modes are also largely confined within the slab, since $d\omega_T/c \ll 1$, and have frequencies which are close to those of bulk TO phonons. We note further that the volume modes involve a superposition of $\exp(iq'z)$ and $\exp(-iq'z)$ plane waves, both of which participate in forward scattering.

The expressions for the scattering efficiencies of the surface modes of the slab configuration are somewhat more complicated because of internal reflections of the EM radiation at the interfaces and because of the coupled-mode character of the modes. We will discuss in detail only the case which corresponds to the experiments of Evans, Ushioda, and McMullen[1] on the Al_2O_3-GaAs-air configuration ($d=2500$ Å and $d/\delta_{EM}\approx 2.8$ at 4880 Å) and for which the intensity of the EM radiation reflected at the second interface can therefore be neglected. For this case the scattering efficiency of the surface modes depends on the direction of propagation of the incident EM radiation across the interfaces, particularly in the case of backward scattering, as well as on the relative amplitudes of the 2-1 and 1-3 single-interface-mode parts of the surface modes.

For $d/\delta_{\rm EM} > 1$, the expression for the scattering efficiency of the surface modes when the EM radiation is incident at the 3-1 (dielectric-semiconductor) interface has the form

$$S_{312}^{(F,B)}(\Omega_\pm) \propto \Bigg| \sum_{\gamma\sigma\rho} g_{\beta\gamma}^{(F,B)} \Gamma_{\sigma\zeta}\left[a_{\gamma\sigma\rho} + b_{\gamma\sigma\rho}\frac{(\omega_T^2-\Omega^2)\bar{m}}{e^*}\right] \times \Bigg\{ [1-\exp(i\Delta k_z' - \Delta k_z'' - \alpha_1)d]\frac{[(ik_\parallel/\alpha_1)\hat{d}_{3-1\perp} + \hat{d}_{3-1\parallel}]R_{3-1}(\Omega_\pm)}{-i\Delta k_z' + \Delta k_z'' + \alpha_1} \pm \exp(-\alpha_1 d)[1-\exp(i\Delta k_z' - \Delta k_z'' + \alpha_1)d]\frac{[(ik_\parallel/\alpha_1)\hat{d}_{2-1\perp} - \hat{d}_{2-1\parallel}]R_{2-1}(\Omega_\pm)}{-i\Delta k_z' + \Delta k_z'' - \alpha_1}\Bigg\}\Bigg|^2 \alpha^*\Omega_\pm(\bar{n}+1), \quad (4)$$

where $\underline{\Gamma}(d) \approx \underline{\Gamma}_{3-1}$; $\underline{g}^F(d) \approx \underline{g}_{1-2}\exp(-k_{sz}''d)$, and $\underline{g}^B(d) \approx \underline{g}_{1-3}$ are the forward- and backward-scattered radiation transfer functions across the 1-2 and the 1-3 interfaces, respectively; $\hat{d}_{3-1}$ and $\hat{d}_{2-1}$ are the unit polarization vectors of the 3-1 and 2-1 single-interface-mode parts of the surface modes; $R_{2-1}(\Omega_+) = u_{2-1}^0/u_{2-1}^0 = 1$, $R_{3-1}(\Omega_-) = u_{3-1}^0/u_{3-1}^0 = 1$, $R_{3-1}(\Omega_+) = u_{3-1}^0(\Omega_+)/u_{2-1}^0(\Omega_+)$, $R_{2-1}(\Omega_-) = u_{2-1}^0(\Omega_-)/u_{3-1}^0(\Omega_-)$ are the relative amplitudes of the 3-1 and 2-1 single-interface-mode parts; α^* is a composite attenuation constant; $\Delta k_z'^F = k_{iz}' - k_{sz}'$ and $\Delta k_z''^F = k_{iz}'' - k_{sz}''$. (We are grateful to J.-Y. Prieur for pointing out that $\Delta k_z''$ arises from attenuation factors rather than from wave-vector uncertainties and that, in forward scattering, it is given by the difference $k_{iz}'' - k_{sz}''$ and not by the sum $k_{iz}'' + k_{sz}''$.) The two terms within the curly brackets determine the contributions of the 3-1 and 2-1 interface-mode parts to the scattering efficiency of the surface modes. Although $S_{312}^{(F,B)}(\Omega_\pm)$ exhibits an $\exp(i\Delta k_z'd)$ oscillatory dependence, its amplitude is small (since in backward scattering $\Delta k_z''d > 1$ and in forward scattering $\Delta k_z'd \ll 1$) and can be neglected for present purposes.

The expression for $S_{213}^{(F,B)}(\Omega_+)$, the scattering efficiency of the surface modes when the radiation is incident at the 2-1 (air-semiconductor) interface, has the identical form as that for $S_{312}^{(F,B)}(\Omega_+)$ except for the interchange of the subscripts 3-1 and 2-1. We note that when $\alpha_1 d$ is greater than 1, $S_{213}^{B}(\Omega_+)$ is appreciably greater than $S_{312}^{B}(\Omega_+)$, and $S_{312}^{B}(\Omega_-)$ is appreciably greater than $S_{213}^{B}(\Omega_-)$. On the other hand, $S_{213}^{F}(\Omega)$ and $S_{312}^{F}(\Omega)$ are within 10% of one another.

The expressions for backward scattering efficiency of the volume modes of the slab have, apart from small oscillatory dependence on d, the same form as that given in Eq. (1) for a single interface, with g replaced by $g^B(d)$ and Γ replaced by $\Gamma(d)$. Since $\Delta k_z'd \gg 1$, only one of the superposed plane waves of the volume modes participates in backward scattering. On the other hand, the expressions for the forward-scattering efficiency of the volume modes, which involve contributions from the $\exp(iq_z'z)$ and the $\exp(-iq_z'z)$ plane waves, have the same basic form as Eq. (4) before integration over q_z'. After integrating over q_z', one obtains an effective forward-scattering length for the volume modes given by $l_v(d) = d^*\exp(-2k_{sz}''d)$, where $d^* \approx 2d$.

As in the case of the single-interface configurations, the backward scattering efficiency of the surface modes in the two-interface configuration is very small because of the presence of the large $\Delta k_z'$ term in the denominator. On the other hand, $\Delta k_z'$ and $\Delta k_z''$ are both small in forward scattering and, as a consequence, the forward-scattering efficiency of the surface modes can be sizable.

We infer, from the absence of any minimum in the observed scattering intensity of the Ω_- surface modes on frequency[1] and from data on the relative backward scattering intensities of the TO and LO phonons,[8] that the atomic displacement and electro-optic contributions have the same sign. We estimate the ratio of the electro-optic and atomic displacement contributions to the Raman tensor of LO phonons to be ~0.3. The corresponding ratio for the surface modes is $\sim 0.3(\omega_T^2 - \Omega^2)/(\omega_T^2 - \omega_L^2)$.

Using the appropriate components of the Raman tensor for a (111) slab and neglecting the small difference in the frequencies of the surface and volume modes, we have calculated the scattering efficiencies of the Ω_+ and Ω_- surface modes relative to that of the volume TO phonon modes at 4880 Å.

The key results are summarized in Table I for various Θ, together with the experimental values for the corresponding scattering intensities of

TABLE I. Relative scattering efficiency at 4880 Å of the surface and volume modes of an air-GaAs-Al_2O_3 slab (d = 2500 Å). Calculations based on $\omega_T = 270.0$ cm^{-1}; $\omega_L = 293.3$; $\epsilon_\infty = 11.1$ for GaAs; $\epsilon_c = 11.6$ and $\epsilon_a = 9.35$ for Al_2O_3 at $\omega \approx 270$ cm^{-1}.

Θ_1	1°	1.75°	3.5°	6°	8°
Ω_- (cm^{-1})	273.5	276.1	279.6	281.4	281.9
$\alpha_1 d$	0.42	0.45	0.81	1.4	2.0
α^*/α_1	1.1	1.1	1.0	1.0	1.0
$S^F(\Omega_-)/S^F(\omega_T)$	0.24	0.27	0.29	0.26	0.21
$I^F(\Omega_-)/I^F(\omega_T)$	0.18	0.19	0.27	0.32	0.26
$S_{312}{}^B/S^B(\omega_T)$	0.002	0.002	0.003	0.005	0.006
Ω_+ (cm^{-1})	292.9	292.6	292.0	291.6	291.5
$\alpha_1 d$	0.23	0.38	0.79	1.4	2.0
α^*/α_1	1.6	1.3	1.1	1.0	1.0
$S^F(\Omega_+)/S^F(\omega_T)$	0.21	0.22	0.24	0.24	0.23
$S_{213}{}^B/S^B(\omega_T)$	0.003	0.003	0.004	0.006	0.008

the Ω_- surface modes, $I^F(\Omega_-)/I^F(\omega_T)$, taken from the data of Evans, Ushioda, and McMullen.[1] We see from the table that the theoretical estimates of the relative forward-scattering efficiencies of the Ω_- surface modes, $S^F(\Omega_-)/S^F(\omega_T)$, are in reasonable agreement with the experimental values of $I^F(\Omega_-)/I^F(\omega_T)$. We see furthermore that the relative forward-scattering efficiencies of the Ω_+ surface modes $S^F(\Omega_+)/S^F(\omega_T)$ are comparable in magnitude to $S^F(\Omega_-)/S^F(\omega_T)$. Finally we see that the relative backward-scattering efficiency of the Ω_+ and Ω_- surface modes is very small, i.e., $S_{312}{}^B(\Omega_-)/S^B(\omega_T) \approx S_{213}{}^B(\Omega_+)/S^B(\omega_T) \leq 10^{-2}$, as in the case of single interfaces.

In conclusion, we note that it is now possible on the basis of the theoretical formulation presented here, to specify the conditions for observing Raman scattering by surface polaritons. They are as follows: (i) forward scattering at a two-interface (slab) configuration; (ii) excitation frequency at which scattering is strongly resonance enhanced and scattering by TO and LO phonons is observable when $\Delta k_z'' = 1/\delta_{EM} \approx \alpha_1$; (iii) thickness of the slab comparable to δ_{EM}.

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[1]D. J. Evans, S. Ushioda, and J. D. McMullen, Phys. Rev. Lett. 31, 369 (1973).

[2]D. L. Mills and A. A. Maradudin, Phys. Rev. Lett. 31, 372 (1973).

[3]R. Ruppin and R. Englman, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer, Berlin, 1969), p. 157.

[4]V. M. Agranovich and V. L. Ginzburg, Zh. Eksp. Teor. Fiz. 61, 1243 (1972) [Sov. Phys. JETP 34, 662 (1972)].

[5]D. L. Mills, A. A. Maradudin, and E. Burnstein, Ann. Phys. (New York) 56, 504 (1970).

[6]Since the surface polaritons are macroscopic modes, their atomic displacement and electro-optical Raman tensors $\underline{a}$ and $\underline{b}$ are the same as those of the volume modes. The extension to wave-vector—dependent or electric-field—dependent Raman scattering is straightforward.

[7]K. L. Kliewer and R. Fuchs, Phys. Rev. 144, 495 (1966), and 150, 573 (1966).

[8]J.-Y. Prieur and S. Ushioda, Phys. Rev. Lett. 34, 1012 (1975).