Raman Scattering from Surface Polaritons in a GaAs Film*

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We have observed the Raman scattering from surface polaritons in a thin film (≈ 2500 Å thick) of GaAs on a sapphire substrate. The mode frequency varies as a function of the scattering angle from the TO phonon frequency of GaAs, $\omega_{\mathrm{TO}} = 270\ \mathrm{cm}^{-1}$, corresponding to forward scattering, to the asymptotic value of $283\ \mathrm{cm}^{-1}$, corresponding to a large scattering angle. The dispersion of the mode frequency was found to be appropriate for the surface polariton of a GaAs film bounded by a sapphire substrate on one side and by air on the other side.

In recent years, considerable interest has developed in the surface polaritons of infrared-active optical phonons in crystals. Surface polaritons are admixtures of optical phonons and photons and, like the bulk polaritons, show strong dispersion in the long-wavelength limit. Several theoretical studies on this subject have appeared in the literature in the past few years.[1,2] Experimentally, surface polaritons with frequencies in the infrared have been observed by the attenuated total reflection (ATR) method[3-5] and by the low-energy electron-diffraction (LEED) method.[6] Since bulk optical phonons in opaque semiconductors and metals can be observed by the surface-reflection Raman scattering (SRRS) method,[7,8] which samples only the optical penetration region of several hundred angstroms, and since the surface-polariton fields extend deeper into a crystal surface than a typical optical penetration depth, we have been convinced that surface polaritons should be observable by means of Raman scattering.

In this Letter, we report the first measurement of the dispersion of surface polaritons by Raman scattering. The Raman spectra of a thin film (≈ 2500 Å) of GaAs on a sapphire substrate were measured for different scattering angles, and the dispersion curve of the surface polaritons of the GaAs film was obtained. Comparison of the experimental dispersion curve with the theory of Mills and Maradudin[9] shows that the modes observed in our experiment correspond to the surface polaritons of a layered structure composed of vacuum-GaAs-sapphire.

In Fig. 1, for the purpose of comparison, we show three dispersion curves for surface polaritons: *a*, at a GaAs-vacuum interface; *b*, at a GaAs-sapphire interface; and *c*, in a vacuum-GaAs-sapphire layered structure. Curve *a* was obtained from the dispersion relation[2]

$$c^2 q_{\parallel}^2/\omega^2 = \epsilon(\omega)/[1+\epsilon(\omega)] \qquad (1)$$

for a vacuum-GaAs interface, where $q_{\parallel}$ is the component of the surface-polariton wave vector parallel to the surface, $\epsilon(\omega)$ is the frequency-dependent dielectric function of GaAs, and c is the speed of light in vacuum. The dielectric function $\epsilon(\omega)$ for GaAs has the form

$$\epsilon(\omega) = \epsilon_{\infty} + (\epsilon_0 - \epsilon_{\infty})\omega_{\mathrm{TO}}^2/(\omega_{\mathrm{TO}}^2 - \omega^2), \qquad (2)$$

where $\epsilon_{\infty} = 11.1$, $\epsilon_0 = 13.1$, and $\omega_{\mathrm{TO}} = 270\ \mathrm{cm}^{-1}$. The dispersion curve *b* for the film-substrate interface, when the substrate is a (0001) sapphire surface, is given by[10,11]

$$\frac{c^2 q_{\parallel}^2}{\omega^2} = \frac{\epsilon_{\parallel}\epsilon(\omega)[\epsilon(\omega) - \epsilon_{\perp}]}{\epsilon^2(\omega) - \epsilon_{\perp}\epsilon_{\parallel}}, \qquad (3)$$

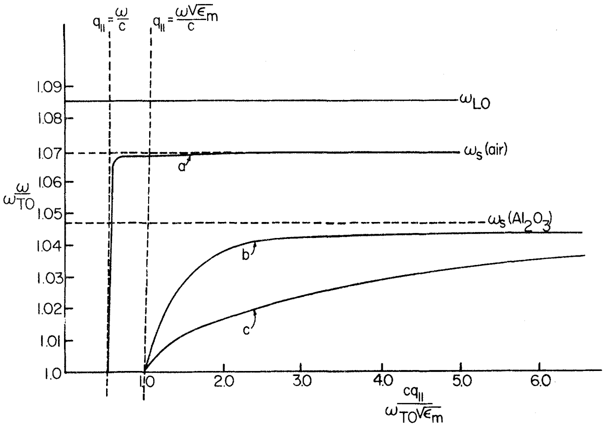

FIG. 1. Dispersion curves for surface polaritons: *a*, at a GaAs-vacuum interface; *b*, at a GaAs-sapphire interface; and *c*, in a vacuum-GaAs-sapphire layer structure. The vertical axis is the dimensionless variable $\omega/\omega_{\mathrm{TO}}$ ($\omega_{\mathrm{TO}} = 270\ \mathrm{cm}^{-1}$), and the horizontal axis is the dimensionless variable $cq_{\parallel}/\omega_{\mathrm{TO}}\sqrt{\epsilon_M}$ [$\epsilon_M = (\epsilon_{\parallel}\epsilon_{\perp})^{1/2} = 10.4$].

where $\epsilon_\parallel$ and $\epsilon_\perp$ are the static dielectric constants of sapphire parallel and perpendicular, respectively, to the c axis. The numerical values of these constants are $\epsilon_\parallel = 11.6$ and $\epsilon_\perp = 9.35$.[12] Curve c for a layered structure was obtained using the dispersion equation recently derived by Mills and Maradudin[9]:

$$\left[1+\frac{\alpha_0}{\alpha_1}\epsilon(\omega)\right]\left[1+\frac{\alpha_2}{\alpha_1}\frac{\epsilon(\omega)}{\epsilon_\perp}\right]-\exp(-2\alpha_1 d)\left[1-\frac{\alpha_0}{\alpha_1}\epsilon(\omega)\right]\left[1-\frac{\alpha_2}{\alpha_1}\frac{\epsilon(\omega)}{\epsilon_\perp}\right]=0, \tag{4}$$

where d is the thickness of the film, and α_0, α_1, and α_2 are defined by

$$\alpha_0 = (q_\parallel{}^2 - \omega^2/c^2)^{1/2},$$
$$\alpha_1 = [q_\parallel{}^2 - \epsilon(\omega)\omega^2/c^2]^{1/2},$$
$$\alpha_2 = [(\epsilon_\perp/\epsilon_\parallel)(q_\parallel{}^2 - \epsilon_\parallel\omega^2/c^2)]^{1/2}.$$

Equation (4) was derived by solving Maxwell's equations in the three regions and applying appropriate boundary conditions at the film-vacuum and film-substrate interfaces. In addition to curve c in Fig. 1, Eq. (4) has the additional dispersion solution for a surface polariton originating at $\omega_{\rm LO}$ for small $q_\parallel$ values and decreasing with increasing $q_\parallel$ to the asymptotic value 288 cm^{-1}.

The film we studied was prepared by Manasevit.[13] The GaAs was grown epitaxially with a (111) orientation on a (0001) surface of a sapphire substrate, and the film thickness was estimated to be approximately 2500 Å. Hall-effect measurements showed that the film was nearly intrinsic.[14] Raman-scattering measurements were made at room temperature using the 4880-Å line of an argon ion laser (≈ 400 mW cw) as an exciting source. The incident light was polarized perpendicular to the scattering plane and the scattered light was not analyzed. The scattered light was collected with a 10-cm focal-length converging lens and was spectrally analyzed by a Spex 1400 double-grating spectrometer. The signal was detected by an ITT FW130 photomultiplier with an S-20 cathode, and the number of photon counts was digitally recorded by a computer-controlled data accumulation system.[15] Typical integration time per data point was about 90 sec. Although GaAs is opaque at 4880 Å ($n \cong 4.4$ and $\kappa \cong 0.4$),[16] we could make near-forward scattering measurements, because the film thickness (≈ 2500 Å) was comparable to the optical penetration depth (≈ 900 Å). The incident laser beam was always kept normal to the film surface, and the scattering angle ψ in the GaAs was varied to obtain the dispersion curve. Wave-vector conservation parallel to the surface requires

$$|\vec{q}_\parallel| = |\vec{k}_s| \sin\psi, \tag{5}$$

where $\vec{q}_\parallel$ is the wave vector of the surface polariton parallel to the surface, and $\vec{k}_s$ is the wave vector of the scattered light.

Figure 2 shows typical spectra measured at various near-forward angles. The bulk TO and LO phonons were observed at the frequencies appropriate to GaAs: $\omega_{\rm TO} = 270$ cm^{-1} and $\omega_{\rm LO} = 292$ cm^{-1}. (The lowest-frequency optical phonon of sapphire is at 378 cm^{-1},[17] so no scattering peak due to the sapphire substrate is expected in the frequency range of interest here.) We note that both the LO and TO phonon peaks are narrow, indicating that the film is crystalline and free from inhomogeneous strains at the interface with sapphire.[18,19] These two peaks are stationary when the scattering angle ψ is changed. In addition to the TO and LO phonon peaks, we see a smaller peak whose frequency changes with the scattering angle. Its asymptotic frequency for large angles ($\psi > 10°$) is 283 cm^{-1}, and it merges with the TO phonon line for near-forward scattering ($\psi \approx 0°$). The linewidth of this peak is comparable to those of the TO and LO phonon peaks. In Fig. 3, we show the dispersion of this peak as a function of $q_\parallel$ calculated using Eq. (5). The solid curve in

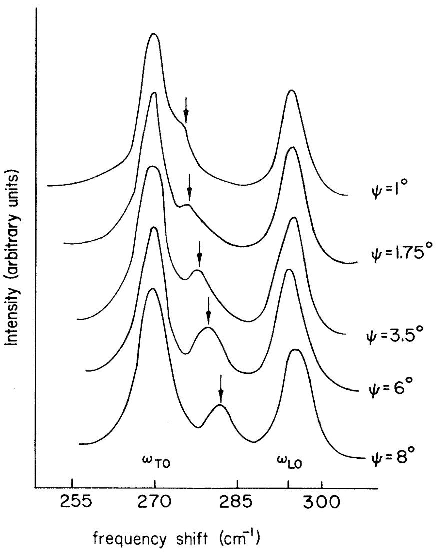

FIG. 2. Typical Raman spectra for different scattering angles ψ. The arrow indicates the peak position of the surface polariton in the GaAs film. Spectrometer resolution is about 2 cm^{-1}.

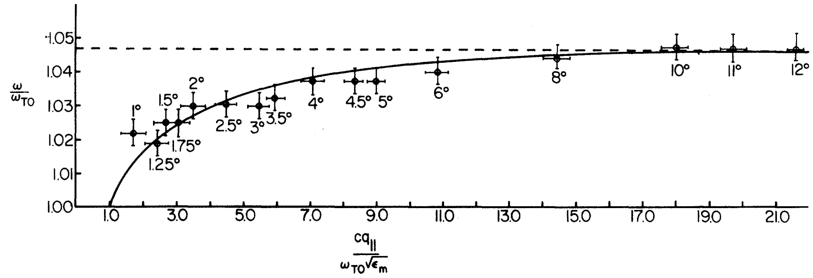

FIG. 3. Dispersion of surface polariton in a vacuum-GaAs-sapphire layer structure. The error bars indicate the uncertainty in determining the polariton frequency and wave vector. The solid curve is obtained from Eq. (4) using the value $d = 2500$ Å.

Fig. 3 was obtained from Eq. (4) for $d = 2500$ Å. We see that the data points fall very closely on the solid curve corresponding to the dispersion of the surface polaritons in a vacuum-GaAs-sapphire layered structure. The agreement between the data and the theory is essentially perfect except at very small scattering angles. In this region, the peak location is not well defined because it merges with the TO phonon line. We note that the frequency scale in Fig. 3 is enlarged from that of Fig. 1 in order to exhibit the details, and that 0.01 on the dimensionless frequency scale corresponds to 2.7 cm^{-1}. Thus on the basis of its asymptotic frequency and its dispersion characteristics, we conclude that the third peak observed in Fig. 2 is due to the surface polaritons of a layered structure, vacuum-GaAs-sapphire.

We did not observe the scattering from the upper branch predicted by Eq. (4) (not plotted in Fig. 1). It was not expected to be observable, because its frequency at all $q_{\|}$ values stays within the linewidth of the LO phonon frequency.

At this point it is interesting to re-examine Fig. 1 and consider why the surface-polariton dispersion was not observed in Raman scattering in earlier efforts. One notices that the surface-polariton dispersion curve *a* for the vacuum-crystal interface stays very close to the LO phonon frequency until it approaches the vacuum light line and then suddenly drops to ω_{TO}. Thus for most scattering angles used in SRRS, the value of $q_{\|}$ is such that the surface-polariton scattering peak is within the linewidth of the LO phonon peak. We believe that this is the reason why the surface polaritons were not observed in SRRS, although they scatter light as strongly as the bulk phonons within the penetration depth of the incident laser light. On the other hand, if a material of high dielectric constant in the far infrared is placed against a crystal surface (curve *b*), the surface-polariton dispersion curve becomes depressed far enough below the LO phonon frequency at relatively large values of $q_{\|}$, so that a separate peak for the surface polaritons can be observed in Raman scattering. Moreover, the strongly dispersive portion of the ω versus $q_{\|}$ curve moves farther out in $q_{\|}$ value, and the dispersion of the mode frequency can be obtained for experimentally practical values of the scattering angles. In the present experiment the film thickness was comparable to the wavelengths of the surface polaritons, so we observed the modes of a layered structure. However, by placing a liquid with an appropriate dielectric constant against a crystal surface, one should be able to observe the surface polaritons of a semi-infinite crystal by SRRS at the liquid-crystal interface. Such an experiment should open up a new way of measuring the dispersion of surface polaritons by Raman scattering.

Since the dispersion of surface polaritons in a film depends on its thickness, the fact that the linewidths of the observed surface-polariton peaks are comparable to those of the bulk modes indicates high uniformity of the film thickness and the sharpness of the interfaces. Measurement of the surface-polariton linewidths and dispersion relations may prove to be an effective way of evaluating thin-film qualities.

In conclusion, we observed a strongly dispersive mode in a GaAs film on a sapphire substrate by means of Raman scattering, and identified this mode to be the surface polaritons of a layered structure, vacuum-GaAs-sapphire, from its dispersion characteristics. The main factor which enabled us to observe the surface-polariton dispersion was the presence of a dielectric substrate in contact with the sample surface.

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Properties of Surface Polaritons in Layered Structures

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We present the theory of surface polaritons which propagate in a film of a surface-active material placed on a substrate. The theory provides a description of the new mode observed recently by Evans, Ushioda, and McMullen in the Raman spectrum of a GaAs film placed on a sapphire substrate.

Quite recently, Evans, Ushioda, and McMullen (EUM)[1] have observed a new mode in the Raman spectrum of visible light scattered from a GaAs film grown on a sapphire substrate. The mode lies between the LO and TO frequencies of the GaAs film, where its dielectric constant is negative. This suggests that the mode is a surface polariton, since the wave vector $k_{\parallel}$ of the mode lies to the right of the light line appropriate to the vacuum or the sapphire substrate. This paper presents the theory of the mode responsible for the feature observed by EUM, and examines its properties. We begin by deriving the dispersion relation of the mode.

The geometry is illustrated in Fig. 1. Region I ($z>0$) is the vacuum, region II ($0>z>-d$) is a thin dielectric film with isotropic dielectric constant $\epsilon(\omega)$, and region III ($-d>z>-\infty$) is an anisotropic substrate described by a dielectric tensor whose only nonzero elements are $\epsilon_{xx}=\epsilon_{yy}$

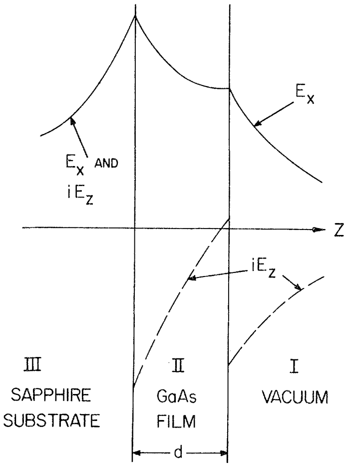

FIG. 1. The geometry employed in the EUM experiment. We have superimposed on the figure the electric field components associated with the lower branch of the dispersion curve with $k_{\parallel}=8\omega_T\epsilon_{\parallel}^{1/2}/c$.