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Study of Surface Polaritons in GaP by Optical Four-Wave Mixing

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We demonstrate experimentally that optical four-wave mixing can be used to study surface polaritons in solids. The dispersion characteristics of surface polaritons in GaP are measured and compared with theoretical calculations.

Stimulated by the recent development in surface physics, there has been rapidly growing activity in the field of surface polaritons and plasmons. A large number of reports on the subject exist in the literature dealing with experimental investigation using various methods: inelastic electron diffraction,[1] attenuated total reflection,[2] grating coupling,[3] spontaneous Raman scattering,[4,5] etc. Studies of surface polaritons and plasmas can lead to information about oxide or molecular overlayers on semiconductor and metal surfaces.[5] Recently, two of us have proposed that the method of nonlinear excitation by optical mixing of laser beams can also be used to study surface polaritons and plasmons.[6] We have now succeeded in demonstrating experimentally the feasibility of the method in our laboratory. We used the four-wave mixing scheme[7,8] to excite coherently and to detect the surface polaritons in GaP and to measure their dispersion characteristics. In this Letter, we report the preliminary results of our experiment.

Before we venture into the experimental details, let us first briefly review the theory. We shall fol-

low closely the notations of Ref. 6. The surface polaritons exist in the reststrahlen band of the crystal. Their complex wave vector $K_x = K_x' + K_x''$ along the surface satisfies the dispersion relation $K_x^2 = (\omega/c)^2\epsilon/(1+\epsilon)$, where ϵ is the linear dielectric constant of the crystal which sits in air. Consider two intense laser beams $\vec{E}_1$ and $\vec{E}_2$ with frequencies ω_1 and ω_2 and wave vectors $\vec{k}_1$ and $\vec{k}_2$ falling on the crystal. Optical mixing of the two beams in the crystal induces a nonlinear polarization $P_x^{NL}(\omega)$ at $\omega = \omega_1 - \omega_2$ and $\vec{k}_s = \vec{k}_1 - \vec{k}_2$. If $k_{sx} \equiv k_x \sim K_x'(\omega)$, then a surface electromagnetic wave is resonantly excited. A bulk driven wave is simultaneously created, but is far weaker in amplitude. The excited surface wave actually consists of a free wave and a driven wave. In usual cases, however, the free-wave contribution can be neglected. Then the excited surface wave in the crystal can be written as[9]

$$\vec{E}^{(b)}(\omega) = A \frac{1}{\Delta k_x - iK_x''} (\hat{x}k_{bz} + \hat{z}k_x) P_x^{NL}(\omega) \exp[i(k_x x - \omega t) + ik_{bz} z], \tag{1}$$

where

$$A = -[2\pi(k_{bz} - \epsilon k_{az})/K_x'\epsilon(1-\epsilon^2)(k_s^2 - k_b^2)](\epsilon k_{az} k_{sz} - k_{bz}^2),$$

$$\Delta k_x = k_x - K_x',$$

$$k_a^2 = k_x^2 + k_{az}^2 = \omega^2/c^2,$$

$$k_b^2 = k_x^2 + k_{bz}^2 = \omega^2\epsilon/c^2.$$

Note that k_{bz} following the definition in Ref. 6 is a negative pure imaginary quantity for a lossless surface wave. Equation (1) shows that excitation of surface polaritons as a function of k_x has its maximum at phase matching, $\Delta k_x = 0$.

One can use a third laser beam $\vec{E}(\vec{k}_3, \omega_3)$ to probe the excited surface wave. Optical mixing of this probing field with the surface wave induces a nonlinear polarization $\vec{P}^{NL}(\omega_4 = \omega_3 - \omega)$ which in turn generates a new coherent wave $\vec{E}(\omega_4)$. The output at ω_4 has its phase-matched peak at $\vec{k}_4$ determined by $k_x = k_{1x} - k_{2x} = k_{3x} - k_{4x}$ and has its intensity given by

$$I(\omega_4, \Delta k_x) \propto |\vec{P}^{NL}(\omega_4)|^2 = |\vec{\chi}^{(2)}(\omega_4 = \omega_3 - \omega) : \vec{E}(\omega_3)\vec{E}^{(b)}(\omega)^*|^2$$

$$\propto \frac{|A|^2}{\Delta k_x^2 + K_x''^2} |\vec{\chi}^{(2)}(\omega_4 = \omega) : \vec{E}(\omega_3)\vec{\chi}^{(2)*}(\omega = \omega_1 - \omega_2) : \vec{E}^*(\omega_1)\vec{E}(\omega_2)|^2. \tag{2}$$

The above equation shows that $I(\omega_4, \Delta k_x)$ versus Δk_x from this four-wave mixing process is a Lorentzian with its peak located at $\Delta k_x = 0$, i.e., $k_x = K_x'$ on the dispersion curve of the surface polaritons. The attenuation coefficient K_x'' of the surface polaritons is measured by the Lorentzian half-width.

Our experimental setup of four-wave mixing is shown in Fig. 1. It is similar to the one reported earlier in Ref. 7. A Q-switched ruby laser with a 30-nsec pulsewidth provided a beam at $\omega_1 = 14\,403$ cm^{-1}. It was also used to pump simultaneously two dye lasers emitting two tunable laser beams at ω_2 and ω_3 with a linewidth of ~ 1.5 cm^{-1}. In the experiment, ω_3 was held fixed at 13 333 cm^{-1} while ω_2 was tuned in the range between 14 006 and 14 035 cm^{-1} so that optical mixing of ω_1 and ω_2 beams could excite surface polaritons in the range between 368 and 397 cm^{-1}. Part of the ruby laser beam and the two dye laser beams were focused by a common achromatic lens with a 20-cm focal length on the surface of a 2-mm GaP slab. Small diaphrams were used in front of the lens to reduce the convergence angle of each beam at the crystal to about 4 mrad. The focal spot size was about 0.5 mm. The output at ω_4 around the phase-matched direction for four-

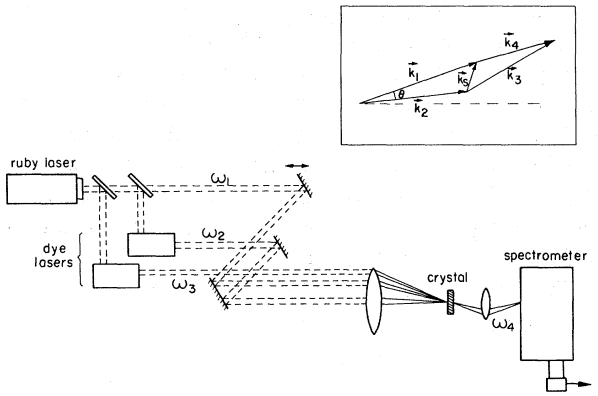

FIG. 1. Experimental setup. The inset shows the wave-vector diagram for the four-wave mixing process.

wave mixing was then collected by a lens and analyzed by a double monochromator with an RCA C31025C photomultiplier. For each given $\omega = \omega_1 - \omega_2$, we measured $I(\omega_4)$ as a function of $k_x = 0$. The value of k_x was adjusted by varying the $\vec{k}_1$ direction and hence varying the angle θ between $\vec{k}_1$ and $\vec{k}_2$. Some examples are shown in Fig. 2.

The GaP crystal slab had its surface parallel to the (110) plane. We choose $\hat{\bar{x}}$, $\hat{\bar{y}}$, and $\hat{\bar{z}}$ as the crystal axes along the three [100] directions; $\hat{\bar{x}}$ and $\hat{\bar{y}}$ were at 45° with respect to the slab normal $\hat{z}$ and $\hat{\bar{z}}$ was along $\hat{y}$ lying on the slab surface. The three incoming fields were polarized as follows: $\vec{E}(\omega_1) = \hat{\bar{z}}E_1$, $\vec{E}(\omega_2) = \hat{\bar{x}}E_{2\bar{x}} + \hat{\bar{y}}E_{2\bar{y}}$ with $E_{2\bar{x}} \approx -E_{2\bar{y}}$, and $\vec{E}(\omega_3) = \hat{\bar{z}}E_3$. Then, because the only nonvanishing elements of $\vec{\vec{\chi}}^{(2)}$ for GaP are $\chi_{ijk}^{(2)}$ with $i \neq j \neq k$, we had

$$\vec{P}^{NL}(\omega) = \chi_{\bar{x}\bar{y}\bar{z}}^{(2)}(\omega = \omega_1 - \omega_2)(\hat{\bar{x}}E_1E_{2\bar{y}}^* + \hat{\bar{y}}E_1E_{2\bar{x}}^*), \tag{3}$$

which was nearly along $\hat{x}$ since $E_{2\bar{x}} \approx -E_{2\bar{y}}$. As seen from Eq. (1), the excited surface polariton wave $\vec{E}^{(b)}(\omega)$ should now have components along $\hat{x}$ and $\hat{z}$ or $\hat{\bar{x}}$ and $\hat{\bar{y}}$. Consequently, the nonlinear polarization resulting from optical mixing of $\vec{E}^{(b)}(\omega)$ and $E(\omega_3)$ was given by

$$\vec{P}^{NL}(\omega_4) = \chi_{\bar{x}\bar{y}\bar{z}}^{(2)}(\omega_4 = \omega_3 - \omega)[\hat{\bar{x}}E_3E_{\bar{y}}^{(b)*} + \hat{\bar{y}}E_3E_{\bar{x}}^{(b)*}]. \tag{4}$$

Thus, the scattered field $\vec{E}(\omega_4)$ should be polarized in the $\hat{\bar{x}}$-$\hat{\bar{y}}$ or $\hat{x}$-$\hat{z}$ plane. This was indeed the case we found experimentally. All waves were propagating in the $\hat{x}$-$\hat{z}$ plane. The wave vector diagram for this four-wave mixing process is shown in the inset of Fig. 1.

We note that $\vec{P}^{NL}(\omega_4)$ in Eq. (4) is actually created by a two-step process, i.e., optical mixing of $\vec{E}(\omega_1)$ and $\vec{E}(\omega_2)$ first generates $\vec{E}^{(b)}(\omega)$, and then mixing of $\vec{E}^{(b)}(\omega)$ with $\vec{E}(\omega_2)$ creates $\vec{P}^{NL}(\omega_4)$. In general, however, there are two other processes which also contribute to $\vec{P}^{NL}(\omega_4)$. One is a two-step process involving a driven bulk wave $\vec{E}^{(p)}(\omega)$ generated by optical mixing of $\vec{E}(\omega_1)$ and $\vec{E}(\omega_2)$[6]: We have $\vec{P}^{NL}(\omega_4, E^{(p)}) = \vec{\vec{\chi}}^{(2)}(\omega_4 = \omega_3 - \omega) : \vec{E}(\omega_3)\vec{E}^{(p)}(\omega)^*$. The other is a direct third-order process due to electronic contribution which gives rise to[10]

$$\vec{P}^{(3)}(\omega_4) = \chi_{\bar{x}\bar{z}\bar{x}\bar{z}}^{(3)}[\hat{\bar{x}}E_1^*E_{2\bar{x}}E_3 + \hat{\bar{y}}E_1^*E_{2\bar{y}}E_3], \tag{5}$$

where $\chi^{(3)}$ is the third-order nonlinear susceptibility. Both $\vec{P}^{NL}(\omega_4, E^{(p)})$ and $\vec{P}^{(3)}(\omega_4)$ are not affected by resonant excitation of surface polaritons. They contribute only to the background of the curve of $I(\omega_4, \Delta k_x)$ versus Δk_x. Knowing $\chi^{(2)}$ and $\chi^{(3)}$ for GaP,[11] we can estimate $P^{NL}(\omega_4, E^{(p)})$ and $P^{(3)}(\omega_4)$. We found that they were at least one order of magnitude smaller than $P^{NL}(\omega_4)$ of Eq. (4). Our experimental results on $I(\omega_4, \Delta k_x)$ versus Δk_x in Fig. 2 exhibit no appreciable background away from the peak. This is partly due to small $P^{NL}(\omega_4, E^{(p)})$ and partly due to a small phase mismatch $\vec{k}_3 - \vec{k}_4 \neq \vec{k}_s = \vec{k}_1 - \vec{k}_2$.

Figure 2 shows that at each ω, the experimental results $I(\omega_4, \Delta k_x)$ versus Δk_x can be fitted by a Lorentzian curve. From the peak positions and widths of the Lorentzian curves, we can then deduce $K_x'(\omega)$ for the surface polaritons. The results are presented in Fig. 3. We have also plotted in Fig. 3 the theoretical curves of $K_x'(\omega)$ and $K_x''(\omega)$ calculated from the dispersion relation for surface polaritons,

$$(K_x' + iK_x'')^2 = (\omega/c)^2\epsilon/(1+\epsilon), \tag{6}$$

where[12] $\epsilon(\omega) = \epsilon_\infty + \omega_p^2/(\omega_T^2 - \omega^2 - i\omega_T\Gamma)$, with $\epsilon_\infty = 9.091$, $\omega_T = 367.3$ cm^{-1}, $\omega_P^2 = 1.859\omega_T^2$, and $\Gamma = 1.28$ cm^{-1}. The agreement between theory and experiment for K_x' is good. The agreement for K_x'' is satisfactory at larger ω, but the experimental K_x'' approaches a constant and deviates

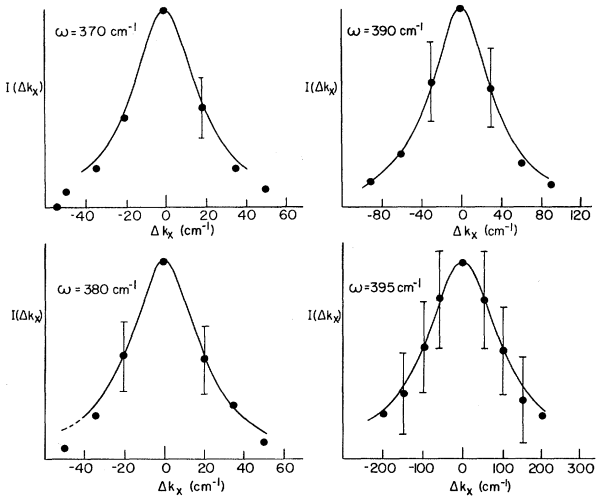

FIG. 2. Experimental results of normalized $I(\omega_4, \Delta k_x)$ versus Δk_x at $\omega = 370$, 380, 390, and 395 cm^{-1}. The solid curves are Lorentzian used to fit the data points.

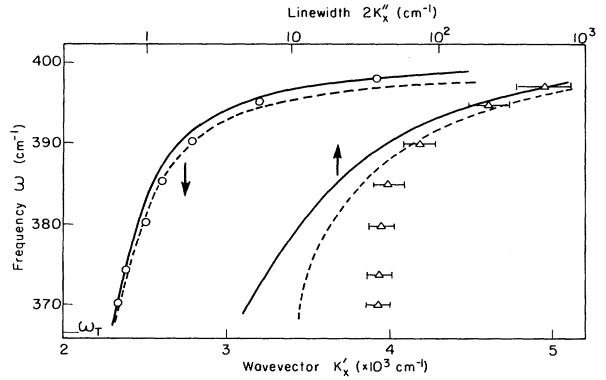

FIG. 3. Measured dispersion characteristics of surface polaritons in GaP (circles, K_x' versus ω; triangles, $2K_x''$ versus ω). The solid curves are calculated from the single-oscillator model using Eq. (5). The dashed curves are calculated from the multioscillator model of Ref. 13.

from the theoretical curve as ω decreases towards ω_T. This is because we used focused beams in the experiment so that at small K_x'', the observed width of the curve of $I(\omega_4)$ versus Δk_x was dominated by the spread of $\vec{k}$ of the focused beams. As K_x'' increases with increasing ω, this latter effect becomes less important and then the experimental result approaches the theoretical prediction. Equation (6) is the result obtained from a single-oscillator model. Barker[13] has developed a multioscillator theory for the lattice modes of GaP. In Fig. 3, we have also plotted the dashed theoretical curves calculated from this multioscillator model.

With a 50-KW peak power in each of the three incident laser beams, we detected a resonant output peak power of about 0.1 μW at $\omega_4 = 380$ cm^{-1}. This was in good agreement with the predicted output of 0.27 μW calculated from Eq. (9) of Ref. 6.

In conclusion, we have demonstrated the feasibility of using optical four-wave mixing to study surface polaritons. This technique has the following advantages: (1) The surface polariton wave is coherently excited; (2) both k_x and ω of the driven surface polaritons can be independently varied; (3) the dispersion characteristics of the surface polaritons can be measured directly. With small beam size and short (picosecond) laser pulses, the technique can also be used to measure directly the decay length and lifetime of the surface polaritons.

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