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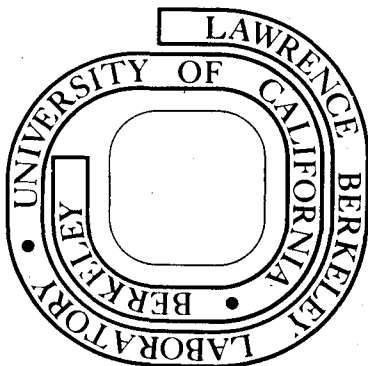
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STUDY OF SURFACE POLARITONS IN GaP
BY OPTICAL FOUR-WAVE MIXING

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ABSTRACT

We demonstrate experimentally that optical four-wave mixing can
be used to study surface polaritons in solids. The dispersion charac-
teristics 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 coherently excite and 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 follow closely the notations of Ref.6. The surface polaritons exist in the restrahlen band of the crystal. Their complex wave vector $K_x = K_x' + i K_x''$ along the surface satisfies the dispersion relation $K_x^2 = (\omega/c)^2 \, \varepsilon/(1+\varepsilon)$, 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 $\vec{k}_1$ amd $\vec{k}_2$ 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 much

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]

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

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

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

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

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 $\Delta k_x = 0$, e.e.,

$k_x = K_x'$ on the dispersion curve of the surface polaritons. The atten-

uation coefficient K_x'' of the surface polaritons is measured by the

Lorentzian halfwidth.

Our experimental setup of four-wave mixing is shown in Fig. 1. It

is similar to the one reported earlier in Ref. 5. A Q-switched ruby laser

with a 30-nsec pulsewidth provided a beam at $\omega_1 = 14403$ 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 13333 cm^{-1} while ω_2

was tuned in the range between 14006 and 14035 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 out-

put at ω_4 around the phase-matched direction for four-wave mixing was then

collected by a lens and analyzed by a double monochromator with an RCA

C31025 C photomultiplier. For each given $\omega = \omega_1 - \omega_2$, we measured $I(\omega_4)$ as

a function of k_x around $\Delta k_x = 0$. 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 $\hat{x}$, $\hat{y}$, and $\hat{z}$ as the crystal axes along the three [100] directions;

$\hat{x}$ and $\hat{y}$ were at 45° with respect to the slab normal $\hat{z}$ and $\hat{z}$ was along $\hat{y}$

lying on the slab surface. The three incoming fields were polarized as

follows: $\vec{E}(\omega_1) = \hat{z} E_1$, $\vec{E}(\omega_2) = \hat{x} E_{2x} + \hat{y} E_{2y}$ with $E_{2x} \approx -E_{2y}$, and $E(\omega_3) = \hat{z} E_3$. Then, because the only nonvanishing elements of $\overleftrightarrow{\chi}^{(2)}$ for GaP are $\chi_{ijk}^{(2)}$ with $i \neq j \neq k$, we had

$$\vec{P}^{NL}(\omega) = \chi_{xyz}^{(2)}(\omega = \omega_1 - \omega_2)[\hat{x} E_1 E_{2y}^{*} + \hat{y} E_1 E_{2x}^{*}] \tag{3}$$

which was nearly along $\hat{X}$ since $E_{2x} \approx -E_{2y}$. 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 $\hat{X}$ and $\hat{y}$. Consequently, the nonlinear polarization resulting from optical mixing of $\vec{E}^{(b)}(\omega)$ and $\vec{E}(\omega_3)$ was given by

$$\vec{P}^{NL}(\omega_4) = \chi_{xyz}^{(2)}(\omega_4 = \omega_3 - \omega)[\hat{x} E_3 E_y^{(b)*} + \hat{y} E_3 E_x^{(b)*}] \tag{4}$$

Thus, the scattered field $\vec{E}(\omega_4)$ should be polarized in the $\hat{x} - \hat{y}$ 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 $\vec{P}^{NL}(\omega_4, E^{(p)}) = \overleftrightarrow{\chi}^{(2)}(\omega_4 = \omega_3 - \omega): \vec{E}(\omega_3) \vec{E}^{(p)}(\omega)^{*}$. The other is a direct third-order process due to electronic contribution which gives rise to[10]

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

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 sur-face polaritons. They contribute only to the background of the $I(\omega_4, \Delta k_x)$ versus Δk_x curve. 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 fit 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 dis-persion relation for surface polaritons.

$$(K_x' + i\ K_x'')^2 = (\omega/c)^2\ \epsilon/(1 + \epsilon) \qquad (6)$$

where[12] $\epsilon(\omega) = \epsilon_\infty + \omega_p^2/[\omega_T^2 - \omega^2 - i\ \omega_T\Gamma]$, with $\epsilon_\infty = 9.091$, $\omega_T = 367.3\ \mathrm{cm}^{-1}$, $\omega_p^2 = 1.859\ \omega_T^2$, and $\Gamma = 1.28\ \mathrm{cm}^{-1}$. 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 deviate 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 $I(\omega_4)$

versus Δk_x curve 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 multi-oscillator theory for the lattice modes of GaP. In Fig. 3, we have also plotted the dashed theoretical curves calculated from this multi-oscillator 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 ω_4. 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.

FOOTNOTES AND REFERENCES

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FIGURE CAPTIONS

Fig. 1. Experimental setup. The inset shows the wave-vector diagram

for the four-wave mixing process.

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.

(O ——— K_x' versus ω; Δ ——— $2K_x''$ versus ω). The solid

curves are calculated from the single-oscillator model using

Eq. (5). The dashed curves are calculated from the multi-oscillator

model of Ref. 13.

Fig. 1

XBL 764-6740

Fig. 2

XBL 764 - 6741

Fig. 3

XBL 764-6739

00 0 0 0 4 3 0 0 4 1 7

00 0 0 4 3 0 0 4 1 7