oxide serves to decouple the surface electron energy levels from the band structure of the bulk copper. It is interesting to note that the tube axis is not shielded from the field produced by passing an axial current through the walls of the tube. A search is now in progress for a theoretical model for this dramatic shielding effect.[16]

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Nonlinear Optical Excitation of Surface Exciton Polaritons in ZnO

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Dispersion and damping characteristics of surface exciton polaritons in ZnO have been measured by nonlinear optical technique. Optical mixing was used to excite surface exciton polaritons while surface roughness was used to couple the surface waves out. The results were used to deduce characteristic parameters of bulk excitons in ZnO.

The surface exciton polariton has long been a subject of extensive theoretical studies.[1] Experimental research on the subject has however been very rare. So far as we know, Lagois and Fischer[2] have conducted the only measurement of exciton polariton dispersion in ZnO using the method of attenuated total reflection (ATR). The difficulty lies in the fact that excitons usually exist at low temperatures and the ATR method is not easily applicable to surface polaritons with relatively short wavelengths. We have recently proposed that surface polaritons can be investigated by nonlinear optical techniques.[3-5] In this Letter, we report the first experiment on nonlinear optical excitation of surface exciton polaritons. We show that the surface exciton polariton waves are radiative because of surface roughness,[6] and detection of the radiative surface waves enables us to measure both dispersion and damping of the surface exciton polaritons.

Surface polaritons only exist in the reststrahlen band of a crystal. For a semi-infinite anisotropic crystal b bounded by an isotropic medium a, the dispersion relation for polaritons is given[7]

(using the notations of Ref. 4) by

$$K_x^2 = (K_x' + iK_x'')^2 = \left(\frac{\omega}{c}\right)^2 \frac{\epsilon_a \epsilon_{bz}(\epsilon_{bx} - \epsilon_a)}{\epsilon_{bx}\epsilon_{bz} - \epsilon_a^2}, \quad (1)$$

where ϵ_{bx} and ϵ_{bz} are respectively the dielectric constants of the crystal along the surface-wave propagation direction $\hat{x}$ and along the surface normal $\hat{z}$. Surface polaritons only exist when $\epsilon_{bx} < 0$ and $\epsilon_{bz} > \epsilon_a$ or $\epsilon_{bz} < 0$.

As shown in Ref. 4, if the crystal lacks inversion symmetry, optical mixing of two laser beams at ω_1 and ω_2 can induce a nonlinear polarization $\vec{P}^{(2)}(\omega = \omega_1 + \omega_2) = \vec{\chi}^{(2)}: \vec{E}(\omega_1)\vec{E}(\omega_2)$ at $\vec{k} = \vec{k}_1 + \vec{k}_2$, which may generate a bulk electromagnetic wave at ω in the crystal. No such propagating bulk wave can however be generated if ω falls into the reststrahlung band; instead, if $k_x' \sim K_x'$ is larger than $k_a'(\omega)$ and $k_b'(\omega)$, a surface transverse-magnetic wave can be excited. When sufficiently strong damping is present, the excited surface wave in the crystal is given (assuming $P_z^{(2)} = 0$) by

$$\vec{E}^{(b)}(\omega) = \frac{A}{(k_x - K_x') - iK_x''}(\hat{x}k_{bz} + \hat{z}k_x)P_x^{(2)} \times \exp[i(k_x x - \omega t) + ik_{bz} z], \quad (2)$$

where A and k's are defined in Ref. 4. A surface-polariton wave propagating on a smooth surface is of course nonradiative. In the presence of surface roughness, it can however be coupled out into a radiative mode. The radiative output should be proportional to the power of the excited surface wave:

$$I(\omega, k_x) \propto \int |E^{(b)}(\omega)|^2 dx\, dy \propto \frac{|\vec{\chi}^{(2)}: \vec{E}(\omega_1)\vec{E}(\omega_2)|_x^2}{(k_x - K_x')^2 + K_x''^2}. \quad (3)$$

We notice that the output $I(\omega)$ versus k_x is a Lorentzian. Its maximum appears at the point where the phase matching condition $k_x = k_{1x} + k_{2x} = K_x'$ is satisfied. This corresponds to resonant excitation of the surface wave at $K_x'(\omega)$. The Lorentzian half-width on the other hand is described by the damping constant K_x'' of the surface-polariton wave.

We were interested in studying surface exciton polaritons in ZnO by the nonlinear excitation method described above. We chose $\omega_1 = \omega_2$ in our experiment so that only one exciting laser beam was needed. Our experimental setup is shown in Fig. 1. A Q-switched ruby laser was used to pump a dye laser generating a tunable laser beam

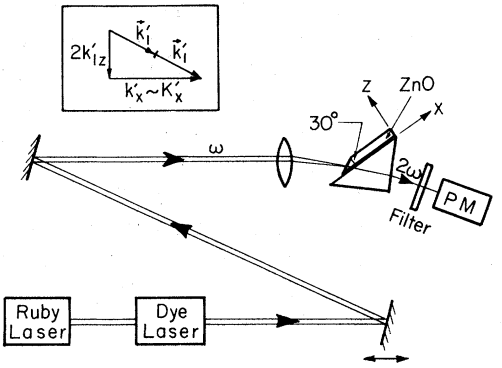

FIG. 1. Experimental setup. The inset shows the wave-vector relation.

at ω_1 around 1.712 eV. The laser beam had a linewidth less than 1.5 cm^{-1}, a beam diameter of about 8 mm, a pulse width of 30 nsec, and a peak power of about 50 kW. It was focused onto the plane surface of ZnO by an $f = 25$ cm lens through the wedged side of the crystal. For a given ω_1, the wave vector k_{1x} could be varied by varying the incidence angle θ with respect to surface normal. This was achieved by translating the incoming laser beam parallel to the lens axis. The angular resolution was limited to approximately 0.5°.

The crystal was immersed in superfluid liquid helium at 2.0°K. The radiation output at $\omega = 2\omega_1$ was monitored through the roof-top prism placed on top of the crystal. The prism was supposed to couple out the nonradiative surface wave into a directional beam. Then the output should depend strongly on the spacing between the surfaces of the prism and the crystal—decreasing exponentially with increasing spacing if the spacing is appreciably larger than the wavelength. We found, however, that the output was independent of the spacing and was spread over a large solid angle. We have therefore concluded that surface roughness of the crystal was responsible for our observation. The crystal surface was first optically polished and then chemically etched in order to remove the exciton-free layer.[2,8] This surface treatment produced pits of several hundred angstroms in size. They should be very effective in coupling out the surface polaritons into radiative modes.[6] Unfortunately, limited by our apparatus, we were not able to measure quantitatively the angular distribution and polarization dependence of the radiative output.

The output was monitored by a photomultiplier after filtering out the fundamental laser light.

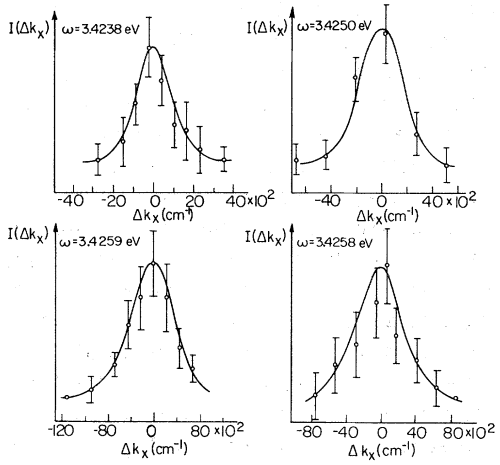

FIG. 2. Experimental results of normalized $I(\omega, \Delta k_x)$ vs Δk_x at four output frequencies. The solid curves are Lorentzian used to fit the data points.

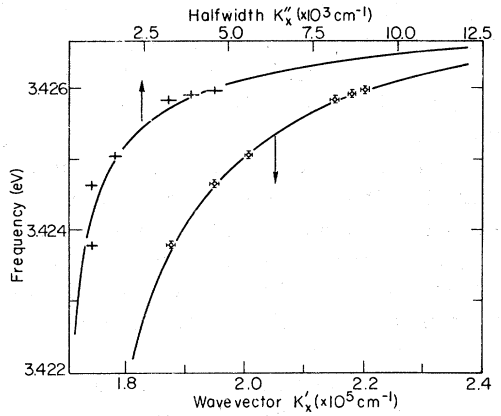

FIG. 3. Measured dispersion and damping characteristics of surface exciton polaritons in ZnO. (Circles with bars, K_x' vs ω; plus signs, K_x'' vs ω.) The solid curves are calculated from Eqs. (1) and (2) using $\epsilon_\infty = 6.15$, $\epsilon_0 = 6.172$, $\omega_T = 3.421$ eV, and $\Gamma = 0.25$ meV.

Actually, in our experiment, the incidence angle of the laser beam on the crystal surface was larger than the total reflection angle, so that only scattered laser light could leak through the surface under investigation. For each given $\omega = 2\omega_1$, we measured the output $I(\omega)$ as a function of $k_x = 2k_{1x}$. Each datum point was taken by averaging the signals from ~10 laser shots. Some examples are shown in Fig. 2.

The ZnO crystal had its c axis along $\hat{x}$ in the direction of the surface-wave propagation. We studied only the surface polaritons associated with the c exciton in ZnO. The dipole matrix element for the c excitonic transition is allowed only for polarization parallel to the c axis. Therefore, using the single-oscillator model to describe the contribution of the c exciton to the dielectric constant, we have

$$\epsilon_{bx} = \epsilon_\infty - (\epsilon_0 - \epsilon_\infty)\omega_T^2[(\omega^2 - \omega_T^2) + i\omega\Gamma]^{-1}, \qquad \epsilon_{bz} = \epsilon_\infty, \tag{4}$$

where ω_T is the transverse exciton frequency, Γ is the damping constant, $(\epsilon_0 - \epsilon_\infty)$ is proportional to the oscillator strength of the excitonic transition, and $\epsilon_\infty > 0$ is the background contribution to the dielectric constant. We have neglected the anisotropy in ϵ_∞ ($|\epsilon_{\infty x} - \epsilon_{\infty z}|/\epsilon_\infty < 2\%$). With the incoming laser beam polarized in the plane of incidence (the x-z plane), the induced nonlinear polarization was dominated by the $\hat{x}$ component

$$P_x^{(2)}(\omega) = \chi_{31}^{(2)} E_z^2(\omega_1) + \chi_{33}^{(2)} E_x^2(\omega_1).$$

With the incoming laser beam polarized along $\hat{y}$, the induced nonlinear polarization had only the $\hat{x}$ component

$$P_x^{(2)}(\omega) = \chi_{31}^{(2)} E_y^2(\omega_1).$$

In both cases, with $\chi_{31}^{(2)} \sim 2.9 \times 10^{-8}$ esu and $\chi_{33}^{(2)} \sim 8.7 \times 10^{-8}$ esu,[9] we estimated a maximum output at ω of $\sim 10^8$ photons per pulse if the crystal surface was smooth and if the prism with a spacing of the order of a wavelength was used to couple out the excited surface polaritons. We observed, however, only $\sim 10^4$ photons per pulse. This further supports our conviction that the observed output was the result of surface roughness.

For each ω, our experimental results of $I(\omega)$ versus k_x could be fitted by a Lorentzian curve as shown in Fig. 2. We could then deduce $K_x'(\omega)$ and $K_x''(\omega)$ for the surface polaritons from the peak positions and the half-widths of the curves, respectively, with very good accuracy. The results are shown in Fig. 3 in comparison with the theoretical curves calculated from the dispersion relation of Eq. (1) and ϵ_{bx} and ϵ_{bz} given by Eq. (4). We found that the dispersion curve K_x' vs ω was rather insensitive to Γ in the range between 0 and 5 meV, but that K_x'' vs ω was a strong function of Γ. By least-squares fitting the experimental data points in Fig. 3 with the theoretical curves, we obtained $\epsilon_\infty = 6.15 \pm 0.01$, $\omega_T = 3.421 \pm 0.0001$ eV, $\epsilon_0 = 6.172 \pm 001$, and $\Gamma = 0.25 \pm 0.05$ meV. As shown in Fig. 3, the theoretical curves agree well with the experimental data except that close to ω_T the observed K_x'' was pre-

sumably dominated by the angular spread of the focused laser beam. Compared with $\epsilon_\infty = 6.15$, $\omega_T = 3.4213$ eV, $\epsilon_0 = 6.188$, and $\Gamma = 0.5$ meV reported in the literature,[8] the only serious discrepancy appears to be that our value of $(\epsilon_0 - \epsilon_\infty)$ is a factor of 1.7 lower. The larger value of $(\epsilon_0 - \epsilon_\infty)$ has the effect of shifting the dispersion curve upward by about 1 meV. We present in the following a discussion on the possible causes of our discrepancy even though we may question the accuracy of $(\epsilon_0 - \epsilon_\infty)$ determined earlier by the linear reflection method.[8]

(1) Surface roughness responsible for the radiation damping of surface polaritons may lead to a downward shift of the dispersion curve. This has been shown theoretically and experimentally for surface plasmons.[6] The shift can be of the order of 1 meV for surface pits with a mean size of a few hundred angstroms. Since surface roughness was instrumental in our observation of surface polaritons, it could be the major cause of our discrepancy. (2) Surface contamination also leads to a downward shift of the dispersion curve. However, we believe our etched sample surface was not sufficiently contaminated to cause any appreciable shift.

Our measured dispersion curve is also about 2 meV lower than the one measured by Lagois and Fischer using the ATR method.[2] We have not been able to find any good way to resolve the discrepancy. It is somewhat difficult to deduce from their report the accuracy of their K_x' measurement. We are also not sure whether they have taken the anisotropy of ϵ into account in their theoretical calculation. Uncertainty in the gap thickness between the prism and the crystal in their case might shift the data points, but it cannot explain the discrepancy. Their sample was in cold helium gas at ~8°K while our sample was immersed in liquid helium at 2°K. Since the dielectric constant of liquid helium is 1.058,[10] our surface-polariton dispersion curve should be down-shifted from theirs by ~1 meV, but not as 2 meV. Finally, we expect that surface roughness would shift the dispersion curve as much in their case as in our case since their surface treatment of the sample was similar to ours. More work with controlled surface roughness is needed to resolve this discrepancy.

In conclusion, we have demonstrated here that nonlinear optical excitation can be used to study surface exciton polaritons. This is the first time the damping parameters of surface exciton polaritons were directly measured. The results enable us to deduce also the properties of bulk exciton polaritons. Compared with other methods, ours is more straightforward and yields direct information. Surface roughness was responsible for our present observation. With controlled surface conditions, one should be able to use this technique to study the surface effects on surface exciton polaritons in quantitative detail.

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