

OBSERVATION OF MODIFIED EXCITON-POLARITON BEHAVIOR
NEAR A SEMICONDUCTOR SURFACE

J. Lagois

Max-Planck-Institut für Festkörperforschung
D-7000 Stuttgart 80, Heisenbergstraße 1
Federal Republic of Germany

The experimentally observed change of exciton-polariton resonance-frequencies near a semiconductor surface is reported. Normal-incidence reflection spectra and attenuated-total-reflection (ATR) spectra are measured in the exciton-polariton energy region of ZnO. Excitonic eigen-energies as well as damping obtained from ATR spectra, which probe regions near the surface, were found to considerably exceed those obtained from reflection spectra which probe more deeply into the crystal bulk.

The electrodynamics of excitonic polaritons in semiconductors has been the subject of extensive studies in recent years. These studies concerned the basic physical properties of excitonic polaritons, which are mixed exciton-photon states corresponding to a dielectric polarization in the macroscopic description of dielectrics.

The theoretical problems associated with excitonic polaritons arise mainly from spatial dispersion, i.e., the wave-vector-dependence of the dielectric function of excitons [1]. Various phenomenological theories have been proposed to describe the properties of excitonic polaritons. The theories include the introduction of additional boundary conditions besides those specified by Maxwell's equations. A conclusive description of an exciton approaching the surface is still open to question. Hopfield and Thomas [1] assumed an exciton-free surface layer caused by a repulsive potential seen by the exciton. This potential essentially prevents the exciton from reaching the surface. A comprehensive description of excitonic polaritons approaching the surface has to include the local behavior of the *eigen-energy* of an exciton which senses the surface potential. Only a few authors have incorporated this fundamental property into their theoretical treatment [2]. However, no experimental evidence has so far indicated any modification of excitonic bulk eigen-energies near a semiconductor surface.

This paper reports the experimental observation of exciton-polariton bulk eigen-energies near the crystal surface which deviate from those deep in the crystal bulk. First, normal-incidence reflection spectra are measured, whose structure is determined mainly by crystal bulk properties. Second, attenuated-total-reflection (ATR) spectra are obtained, whose structure is determined, in contrast, primarily by properties of crystal regions close to the surface. A comparison is carried out for excitonic eigen-energies obtained from fitting the experimental spectra measured on the same sample in both arrangements. This comparison leads to the result that the excitonic eigen-energies depend on the exciton's distance from the

crystal surface.

The inset of Fig. (1) shows the experimental arrangement for normal-incidence reflectance. The electric field $\vec{E}$ of the incoming light is polarized perpendicularly to the hexagonal $\vec{c}$ -axis. In this geometry, the light excites the excitons belonging to the upper two valence bands in ZnO (A and B excitons).

The upper part of Fig. (1) exhibits an experimental normal-incidence reflection spectrum of the $A_{n=1}$ and $B_{n=1}$ exciton-polaritons in ZnO (n : main quantum number of a hydrogen-like exciton model). The experimental spectrum is compared with a theoretical one obtained from a best fit to the experiment. The optical properties of the crystal are calculated using the dielectric function $\epsilon(\omega, k)$ of two excitonic transitions A and B and using an exciton-free surface layer. The vanishing of the excitonic contribution to the macroscopic polarization at the surface is chosen as additional boundary condition [3]. The difference between the experimental and theoretical spectra at energies just below B_L (longitudinal B exciton) is known to appear for ZnO, but has not yet been explained. An inter-

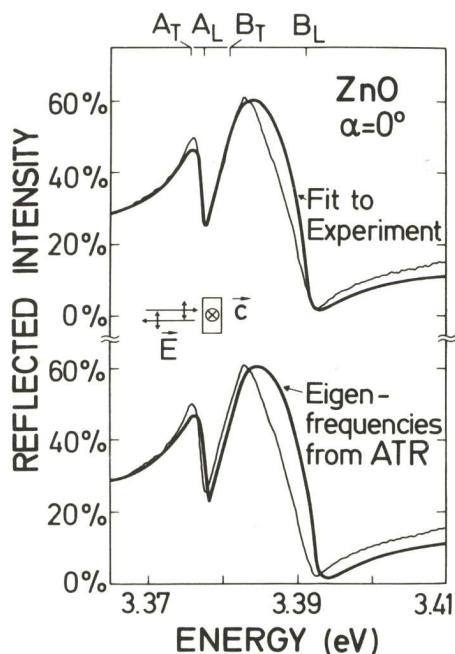


Fig.1 Normal-incidence reflection spectra of the $A_{n=1}$ and $B_{n=1}$ excitonic polaritons in ZnO: Experiment (weak line) at 4.2 K. Upper part: Theory (strong line) with parameters obtained from fit to the experimental reflection spectrum. Lower part: Theory with eigen-energies obtained from fit to the experimental ATR spectrum.

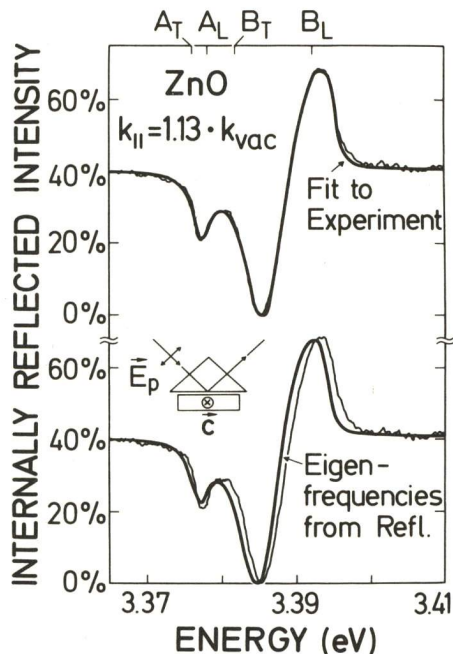


Fig.2 Attenuated-total-reflection spectra of the $A_{n=1}$ and $B_{n=1}$ excitonic polaritons in ZnO: Experiment (weak line) at 4.2 K. Upper part: Theory (strong line) with parameters obtained from fit to the experimental ATR spectrum. Lower part: Theory with eigen-energies obtained from fit to the experimental reflection spectrum.

pretation follows from the results presented in this paper.

The excitonic surface-polariton spectra are taken with an ATR arrangement as shown in the inset of Fig.(2). Light linearly polarized parallel to the plane of incidence is totally reflected inside a prism. An evanescent wave propagating along the prism base excites an excitonic surface-polariton associated with the A and B excitons in ZnO. The excitation in the crystal leads to an outcoupling of intensity from the totally reflected light. This outcoupling is observed as a decrease of the internally reflected intensity in the ATR spectrum. The properties of excitonic surface-polaritons, and thus of the ATR spectra, are determined by the refractive index of the adjacent medium and by $\epsilon(\omega, k)$, the bulk excitation's dielectric function which determines also the reflection spectra [4].

The upper part of Fig.(2) shows an experimental ATR spectrum taken on the same sample as the reflection spectrum of Fig.(1). The experimental spectrum is fitted with a theoretical one of the $A_{n=1}$ and $B_{n=1}$ excitonic surface-polaritons in ZnO.

A comparison of the parameters obtained from fits to reflection and to ATR spectra shows two striking results. First, the empirical damping constant Γ used in the dielectric function differs by a factor of about three. Second, the excitonic eigen-energies obtained by fitting ATR spectra are considerably higher than those obtained by fitting reflection spectra, although both theoretical spectra

are determined by the same dielectric function containing the excitonic eigen-energies of the crystal bulk. This deviation amounts to about 10 percent of the splitting between the transverse and the longitudinal eigen-energies. The deviation is conspicuous in the lower parts of Figs.(1) and (2) where the reflection spectrum is calculated with eigen-energies obtained from the ATR fit, and the ATR spectrum with those obtained from the reflection fit. These theoretical spectra are compared with the same experimental spectra as in the upper parts of Figs.(1) and (2), respectively.

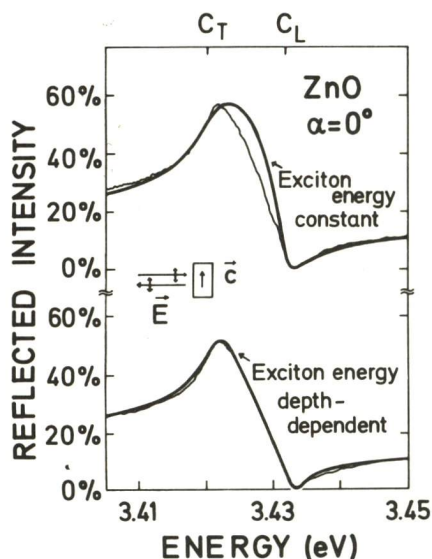


Fig.3 Normal-incidence-reflection spectra of the $C_{n=1}$ excitonic polaritons in ZnO. Experiment (weak line) at 4.2 K. Upper part: Theory (strong line) with constant eigen-energies. Lower part: Theory with depth-dependent eigen-energies.

The results turn out to be almost independent of the choice of the additional boundary condition. Vanishing excitonic polarization as well as vanishing spatial derivative of the excitonic polarization at the surface are used, either with the longitudinal exciton branch being excited, or alternatively this branch not being excited. These conditions indeed reveal different behavior of the excitons, but the findings reported above are found to be nearly unaffected.

The deviations of the obtained parameters can be explained by considering the penetration depths of excitonic polaritons. An ATR experiment probes spatial regions close to the crystal surface, whereas a reflection experiment probes deeper into the crystal bulk. Therefore, the results yield an increased damping of excitonic polaritons close to the crystal surface, and above all, a considerable increase of excitonic eigen-energies in near-surface crystal regions.

This spatial behavior of the excitonic eigen-energies should be included in model calculations. As a first step, I approximated a continuous dependence by a four-step model consisting of an exciton-free surface layer and of three layers with modified exciton eigen-energies on top of the crystal bulk. The three layers contained excitons with spatial dispersion. Continuous excitonic polarization was chosen as additional boundary condition. The excitonic eigen-energies decreased from the bulk value by 1 meV and increased near the crystal surface to 4 meV above the bulk value. This behavior is in agreement with calculations for excitons in an electric field [5]. The electric field originates from surface charges.

The calculations have been performed for the $C_{n=1}$ exciton resonance in ZnO. This exciton behaves very similar to the $B_{n=1}$ exciton. The upper part of Fig.(3) shows for comparison an experimental normal-incidence reflection spectrum of the $C_{n=1}$ exciton and a theoretical one calculated with the model used in Fig.(1). The lower part of Fig.(3) exhibits the same experimental spectrum compared with a theoretical one calculated with the model described above. The excellent agreement especially at energies just below C_L gives strong support for a spatial dependence of the excitonic eigen-energies near the crystal surface.

In conclusion, this paper reported the result of experiments which manifested the modified properties of excitons near a semiconductor surface. This modification is verified by measurements of normal-incidence reflection and attenuated-total-reflection spectra of excitonic $n=1$ transitions in the semiconductor ZnO.

I thank R.Helbig (Erlangen, Germany) for supplying the samples used in this investigation. I am also grateful to H.J.Queisser, B. Fischer, F.Stern, R.Zeyher, and H.Venghaus for many helpful discussions, and to H.G.Fischer for technical assistance. I was supported by the Deutsche Forschungsgemeinschaft.

- 1) J.J.Hopfield and D.G.Thomas: Phys.Rev. 132, 563 (1963).
- 2) M.F.Deigen and M.D.Glinchuk: Fiz.Tverd.Tela 5, 3250 (1963) [Sov.Phys.Solid State 5, 2377 (1964)];
S.Sakoda: J.Phys.Soc.Japan 40, 152 (1976);
I.Balslev: phys.stat.sol.(b) 88, 155 (1978);
J.Gallardo and D.Mattis: phys.stat.sol.(b) 93, 229 (1979);
V.A.Kiselev: Fiz.Tverd.Tela 21, 1069 (1979) [Sov.Phys.Solid State 21, 621 (1979)].
- 3) S.I.Pekar: Zh.Eksp.Teor.Fiz. 33, 1022 (1957) [Sov.Phys.-JETP 6, 785 (1958)]; J.Phys.Chem.Solids 5, 11 (1958).
- 4) J.Lagois and B.Fischer: in *Festkörperprobleme - Advances in Solid State Physics*, Vol.XVIII, p.197, ed.by J.Treusch (Vieweg, Braunschweig, 1978);
B.Fischer and J.Lagois: in *Topics in Current Physics*, Vol.14, p.183, ed.by K.Cho (Springer, Heidelberg, 1979).
- 5) D.F.Blossey: Phys.Rev.B 3, 1382 (1971).