

# Observation of a series of surface excitons in ZnO associated with intrinsic two-dimensional surface subbands

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The reflection spectra of ZnO single crystals reveal a series of lines due to surface excitons. The number and energies of these lines vary with the height of the surface potential and the distance over which it decays. The surface excitons observed are related to intrinsic two-dimensional surface subbands.

We have studied the reflection spectra at the interface between ZnO and an electrolyte, where it is possible to continuously change the surface potential without resorting to metal coatings, in an effort to determine the nature of the surface excitons in ZnO crystals. An ohmic contact is deposited on the ZnO surface opposite that being studied. This contact is used as an electrode and is immersed into the electrolyte along with a second metal electrode. A static external voltage  $V_{ex}$  is applied between these electrodes. The resistance of the (*n*-type) ZnO wafer and of the electrolyte is chosen less than  $10^3 \Omega$ , so that  $V_{ex}$  falls primarily across the ZnO surface layer. In the course of the experiments we monitor the optically polished surface of the sample and the reproducibility of all the experimental results.

Figure 1 shows reflection spectra of ZnO at the  $(10\bar{1}0)$  face obtained at various values of  $V_{ex}$  with linearly polarized light. The reflection peaks on curve 2 in Fig. 1, a and b, are due to *A* and *C* volume excitons which have a binding energy of 60.8 meV, as determined from the reflection spectra<sup>1</sup> and electroreflection.<sup>2</sup> The energy distance between peaks *A* and *C* is  $\sim 40$  meV and is due to a hexagonal splitting of the valence band. At  $V_{ex}$  approximately equal to  $-0.5$  V, the energy bands straighten out near the ZnO surface, and the reflection spectra are dominated by the *A* and *C* volume excitons, which at 300 K are the narrowest of the reflection lines shown in Fig. 1. As  $V_{ex}$  is varied, we observe a pronounced weakening of the lines of the volume excitons and the appearance of new lines (*K*, *L*, and *M*) in a definite sequence.

An increase  $V_{ex}$  from 0 to 16 V simultaneously raises the height of the surface potential and the distance over which it falls, giving rise to, initially, lines  $K_{\perp}$  and  $K_{\parallel}$  (curve 3 in Fig. 1), a shift of these lines in the long-wave direction (curves 4–9), and their disappearance (curve 10). The inset in the upper part of Fig. 1 shows how the relative intensities and the position of the peak of the  $K_{\parallel}$  line vary on curves 3–9 for various values of  $V_{ex}$ . Only after the shift of the  $K_{\perp}$  and  $K_{\parallel}$  lines by a certain amount do the lines  $L_{\perp}$  and  $L_{\parallel}$  appear, at energies slightly below the corresponding widths of the energy gaps,  $E_{g\perp}$  and  $E_{g\parallel}$  (Figs. 1 and 2). With increasing  $V_{ex}$ , the shift of the *L* lines in the long-wave direction increases, and their relative intensities vary by analogy with that of line  $K_{\parallel}$ . In the same fashion, a third peak appears in the reflection spectra,  $M_{\perp}$  and  $M_{\parallel}$  (curves 7–10), and this process continues (the line  $N_{\parallel}$  appears on curve 10;

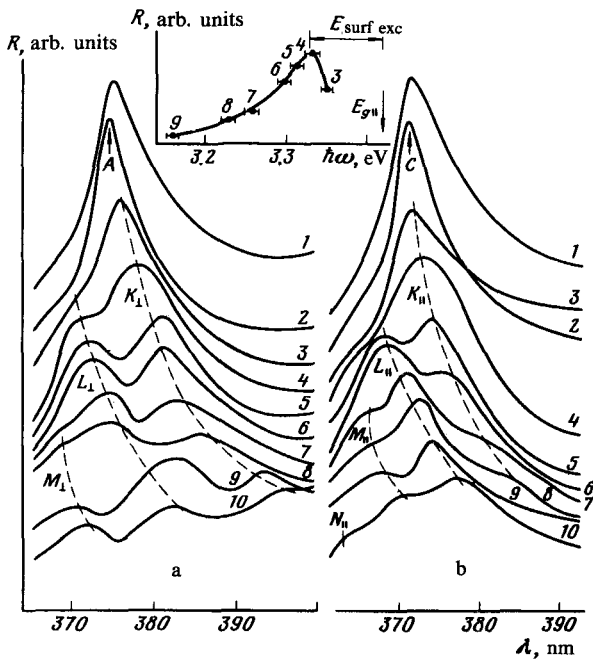


FIG. 1. Reflection spectra of ZnO at 300 K for polarized light. a— $E \parallel C$ ; b— $E \parallel L$ . The static external voltage  $V_{ex}$  (V) is: 1—1.5; 2—0.5; 3—0; 4—1; 5—2; 6—3; 7—6; 8—8; 9—12; 10—16. The dashed lines show the direction in which the  $K$ ,  $L$ , and  $M$  lines move. The inset at the top shows the relative intensities and positions of the peaks of the  $K_{\parallel}$  versus  $V_{ex}$ , according to curves 3–9.

Fig. 1b) as the surface potential is changed further.

Figure 2 shows that the lines  $K_{\parallel}$ ,  $L_{\parallel}$ , and  $M_{\parallel}$  lie  $\sim 40$  meV away from  $K_{\perp}$ ,  $L_{\perp}$ , and  $M_{\perp}$ , respectively, and that the curves describing the shift of the lines of the two polarizations remain parallel over nearly the entire range of the surface potential

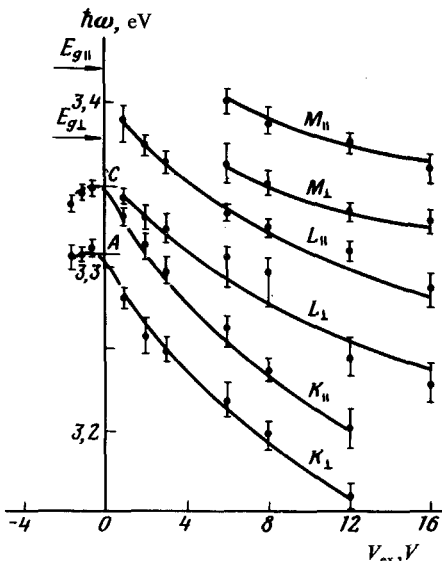


FIG. 2. The energy positions of the  $K$ ,  $L$ , and  $M$  lines in the reflection spectra versus the static external voltage for  $E \parallel C$  and  $E \parallel L$ .

achieved in these experiments. The rates at which the  $K$ ,  $L$ , and  $M$  lines shift, however, are significantly different.

The lines in the reflection spectra remain clearly defined, and all the features described above persist, up to donor-impurity densities  $\sim 10^{18} \text{ cm}^{-3}$ , where the length of the space-charge region is  $\sim 10^{-6} \text{ cm}$ . With a heavier doping of the ZnO (e.g., at doping with Fe to  $\sim 10^{20} \text{ cm}^{-3}$ ), the reflection spectra become blurred, and the number of peaks decreases. This behavior is also observed in the electroreflection spectra. Certain versions of these lines in the reflection spectra are also observed for an interference between ZnO and air, when it is possible to change the surface potential by means of a surface treatment.

Certain aspects of the behavior which we have observed can, in principle, be explained by means of known mechanisms for the formation of surface excitons,<sup>3,4</sup> but, in our opinion, the entire set of results reported here can be explained in a qualitative way by assuming that there exists yet another surface-exciton mechanism, associated with intrinsic two-dimensional surface subbands. Under the actual conditions prevailing at a surface, these intrinsic surface states are distributed with peaks near the edges of the energy gap (Ref. 5, for example). A change in the height of the surface potential and the distance over it decays has strong effects on the position of the intrinsic two-dimensional surface subbands and the number of these subbands in the energy gap of the semiconductor.<sup>6</sup> When light is absorbed by the semiconductor, an electron can migrate from, for example, one of the filled intrinsic two-dimensional surface subbands,  $E_s$ , into the conduction band,  $E_c$  (or from the filled valence band into a free intrinsic two-dimensional surface subband). Such transitions can contribute significantly to the overall absorption coefficient if the intrinsic two-dimensional surface subbands are close to, for example, the lower edge of the energy gap,<sup>7</sup> in which case the electron localization radius at the surface state is comparable to or greater than the wavelength of the light. In our case, the latter condition does not hold, so that the band responsible for this absorption, which lies in the region  $\hbar\omega > E_c - E_s$ , cannot be observed. In the region  $\hbar\omega < E_c - E_s$ , however, absorption lines can be seen with a relatively large oscillator strength, due to excitons associated with intrinsic two-dimensional surface subbands. Since the continuously varying surface potential allows the appearance of more than one intrinsic two-dimensional surface subband,<sup>6</sup> there is a surface exciton associated with each. We attribute these lines in the reflection spectra to such surface excitons.

An increase in the applied voltage increases the height of the surface potential and the distance over which it falls, leading to the appearance of intrinsic two-dimensional surface subbands, beginning at quasi-steady-state values in the region of the volume energy spectrum. The intrinsic two-dimensional surface subbands subsequently intersect the edge of the volume band,  $E_v$ , and rise into the volume energy gap. This process is accompanied by a decrease in the distribution density of surface states because of a random potential at the surface.<sup>5</sup> This mechanism explains the appearance of a surface-exciton line on both the short-wave and long-wave sides of the volume-exciton line. It is clear from these arguments that the relative intensities of the lines of the surface excitons will have a maximum (see the inset in Fig. 1) when the edge of the intrinsic two-dimensional surface subbands intersects the edge of the vol-

ume band, so that the energy distance from the edge of the volume band to this maximum gives us the binding energy of a surface exciton. From this figure we find the estimate  $E_{surf\ exc} \sim 100$  meV for the  $K_{\parallel}$  surface exciton. A further change in the height for the surface potential and the distance over which it falls leads to the appearance and motion into the energy gap of second, third, etc., intrinsic two-dimensional surface subbands. In this way we can explain the appearance and motion of a series of peaks in the reflection spectra (Figs. 1 and 2) due to corresponding surface excitons as  $V_{ex}$  is varied.

<sup>1</sup>D. M. Kolb and H. J. Schulz, *Curr. Top. Matter. Sci.* (Amsterdam) **7**, 227 (1981).

<sup>2</sup>M. Cardona, *Modulation Spectroscopy*, Academic, New York, 1969 (Russ. transl. Mir, Moscow, 1972, p. 416).

<sup>3</sup>V. A. Kiselev, *Fiz. Tverd. Tela* (Leningrad) **20**, 2173 (1978) [*Sov. Phys. Solid State* **20**, 1255 (1978)].

<sup>4</sup>Yu. E. Lozovik and V. N. Nishanov, *Fiz. Tverd. Tela* (Leningrad) **18**, 3267 (1976) [*Sov. Phys. Solid State* **18**, 1905 (1976)].

<sup>5</sup>A. A. Vardanyan, V. M. Gasparyan, and Z. A. Kasamanyan, *Izv. Vyssh. Uchebn. Zaved., Fiz.* No. 6, 123 (1979); Deposited article #1515-79, All-Union Institute for Scientific and Technical Information.

<sup>6</sup>A. A. Vardanyan and Z. A. Kasamanyan, *Izv. Akad. Nauk ArmSSR, Ser. Fiz.* **12**, 129 (1977).

<sup>7</sup>S. Kh. Barsegyan and Z. A. Kasamanyan, *Izv. Akad. Nauk ArmSSR, Ser. Fiz* **13**, 25 (1978).

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