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ULTRAVIOLET REFLECTIVITY SPECTRA OF ZnO

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ABSTRACT

Reflectivity measurements at normal incidence were made on ZnO single crystals in the energy region of 3 to 25 eV with linearly polarized light the electric field vector lying perpendicular and parallel to the c-axis. From the reflectivity data the optical constants n and k , the complex dielectric constant $\epsilon = \epsilon_1 + i\epsilon_2$ and the energy loss function $L = -\text{Im } 1/\epsilon$ have been computed by a Kramers-Kronig analysis for both directions of polarization. The profiles of the spectra differ completely from that of other II-VI compounds of the wurtzite structure. The energetic positions and the polarization dependence of the peaks in the reflectivity - and the ϵ_2 - spectra agree well with the results of the first complete band structure calculation accomplished by U. Rössler by the KKR-method.

Mit polarisiertem Licht (Photonenenergie 3 - 25 eV) wurden bei senkrechtem Einfall die Reflexion an ZnO Einkristallen senkrecht und parallel zur c-Achse gemessen und mittels einer Kramers-Kronig-Analyse die optischen Konstanten n und k , die komplexe Dielektrizitätskonstante $\epsilon = \epsilon_1 + i\epsilon_2$ und die Energieverlustfunktion $L = -\text{Im}(1/\epsilon)$ für beide Polarisationsrichtungen berechnet. Die Spektren weichen entscheidend von denen anderer II-VI-Verbindungen mit Wurtzitstruktur ab. Die energetische Lage und die Polarisationsabhängigkeit der Maxima des Reflexions- und des ϵ_2 -Spektrums stimmen jedoch gut mit den Ergebnissen der ersten Bandstrukturberechnungen überein, welche kürzlich von U. Rössler mit der KKR-Methode durchgeführt wurden.

The electrical and optical properties of ZnO crystals have been measured for many years¹. More recently, optical studies in the vicinity of the fundamental absorption edge²⁻⁸ have been intensified due to the complex structure in absorption and reflection and due to the theoretical interest generated by different interpretations of the exciton spectrum^{2,3}.

However, no ultraviolet reflectivity measurements beyond the fundamental absorption edge, which will yield essential information concerning high energy bands, have been reported.

In this paper we report the results of reflectivity measurements in the ultraviolet and the vacuum ultraviolet region. The striking feature of our measurements is that the ultraviolet spectrum is completely different from that of other II-VI-compounds having the wurtzite structure such as CdS, CdSe and ZnS. In the energy region from 3 to 7 eV in contrast to other materials of the wurtzite structure no distinct peaks and structure due to interband transitions are observed.

In this experiment we have tried many crystals grown by different techniques and obtained from different sources⁹ but no differences in the reflectivity spectra were found. The crystals used were of the platelet type, plates and prisms grown from the vapor phase or large bulk crystals grown by the hydrothermal technique. The measurements in the energy region from 3 to 9.5 eV were made with a Hinteregger type discharge lamp, using hydrogen as a source gas and a 0.3 m McPherson vacuum monochromator (Model 218). The reflection chamber contains a

focussing mirror, two LiF plates at Brewster's angle for polarization of light and two photomultipliers coated with sodium salicylate for the detection of both the incident and the reflected light. The angle of incidence was restricted to 10° . By employing two multipliers, incident beam and reflected signal were detected separately, fed through separate amplifiers and divided continuously during the scan. The high energy measurements (9 to 25 eV) have been done at DESY (Deutsches Elektronen-Synchrotron in Hamburg) using the polarized continuum of synchrotron radiation as a light source. The experimental arrangement is described in detail elsewhere¹⁰.

Fig. 1 shows typical reflection spectra of a ZnO crystal for the incident light polarized with the electrical vector parallel and perpendicular to the c-axis of the crystal. Fig. 2 and 3 show the spectra of ϵ_1 and ϵ_2 computed from the reflectivity data by means of a Kramers-Kronig analysis. The peaks at 3.30 eV observed for $E \perp c$ and at 3.34 eV for $E \parallel c$ in the reflectivity curves correspond to transitions at the fundamental absorption edge and can be explained as exciton peaks A,B ($n = 1$) for $E \perp c$ and C ($n = 1$) for $E \parallel c$ in accordance with the low temperature measurements performed by Liang and Yoffe⁴. The energetic distance between the two peaks (0.04 eV) gives the separation of the two valence bands observed at room temperature². On the higher energy side of these two peaks, two broad shoulders are observed at about 3.35 eV for $E \perp c$ and 3.39 eV for $E \parallel c$, which will be discussed later.

Besides these predominant transitions at the edge, reflectivity decreases rather monotonically with increasing photon energy up to about 7 eV. Then, rather weak peaks begin to appear at energies 7.12 and 8.98 eV for $E \parallel c$ and 7.08 eV for $E \perp c$, followed by a well structured reflectivity spectrum for both polarizations from 12 up to 23 eV.

The profiles of these reflectivity spectra are strikingly different from that of other II-VI materials of the wurtzite structure. In CdS¹¹, CdSe¹¹ and ZnS^{11,12}, the transitions at the fundamental absorption edge (E_0) are followed by the predominantly intense peak (E_1). This feature is in very good agreement with the first complete band structure calculations on ZnO by Rössler¹³ (Fig. 4). According to his calculations, carried out by the KKR method, unlike other II-VI materials, the energy bands of ZnO are characterized by the free electron like lowest conduction band, d-bands lying closely below the upper valence bands and p-like conduction bands 17 eV above the valence bands.

Comparing Rössler's band model with our experimental data, the peaks in the reflectivity - and the ϵ_2 -spectra can be correlated to specific band-band transitions as given in the following table:

Reflectivity	ϵ_2	Polarization	Transition	Calculated	Comment
3.30	3.30	\perp	Exciton [†]	adjusted	
3.34	3.34	\parallel	Exciton		
7.12	7.15	\parallel			
7.08	7.42	\perp	d - Γ_1	7.1	
8.98	8.98	\parallel	$U_1 - U_1$	9.0	A
12.60	12.80	\perp	several points in the BZ	12 - 13	B
13.8	13.6	\parallel			
14.0	14.0	\perp			
14.6	14.4	\parallel	d-second group of conduction bands	< 13.6	C
15.2	15.17	\perp			
15.6	15.6	\parallel			
17.1	17.0	\perp			
18.9	19.0	\parallel	p-bonding - p-antibonding		
19.3	19.0	\perp			
20.8	20.9	\perp			

At 11.0 eV another reflection maximum probably exists for $E \parallel c$. It is not included in Fig. 1 and in the results of the Kramers-Kronig-analysis.

Comments A, B and C given by Rössler:

A: The dip in reflectivity for both polarizations at about 10 eV seems to indicate the upper limit of transitions between upper valence bands and lowest conduction bands. The polarization effect can be explained by looking at the limiting band groups which allow only transitions for $E \parallel c$. Other authors have found a similar behavior for CdO^{14,15}.

[†] The calculated position of the band gaps at 4.2 K is given by Liang and Yoffe⁴: 3.448 eV for $E \perp c$ from B-exciton series and 3.487 eV for $E \parallel c$ from C-exciton series and 3.445 from A-exciton series.

- B: The increase of reflectivity for $E \perp c$ above 10 eV with the peak at 12.6 eV might be due to transition from the lower bands of the upper valence band group to the second group of conduction bands. These transitions are allowed for $E \perp c$, e.g. P_1-P_3 , U_1-U_2 , U_1-U_3 .
- C: For an interpretation of transitions, where d-bands are involved, it seems to be necessary to have a refined calculation of the d-bands.

On low temperature measurements (90° K) in the vicinity of the band gap, the broad shoulders, observed at room temperature, became more distinct and an additional peak was seen for each polarization of light as shown in Fig. 5. According to Rössler's band model these peaks cannot be attributed to interband transitions or to excitons connected with a second conduction band². More probably these peaks are due to coupled exciton phonon complexes (EPC) which have been discussed by Liang and Yoffe⁴. These authors have performed low temperature measurements with a higher optical resolution. According to their results, the peaks at 3.41 eV for $E \perp c$ and 3.45 eV for $E \parallel c$ in our measurements could be an overlap of the excited states of the excitons B and C with $n = 2$ and 3, and the EPC transitions L_1a and L_1b [†]. Correspondingly the peaks at 3.50 eV for $E \perp c$ and 3.53 eV for $E \parallel c$ respectively can be explained as L_2 EPC transitions.

Using the ϵ_1 and ϵ_2 data, the energy loss function $L = -\text{Im} \frac{1}{\epsilon}$ has been computed (Fig. 6). The lower peaks in these curves are due to optical transitions. The big maximum at about 18.5 eV can be associated with the

[†] According to the notation of Liang and Yoffe

plasma frequency of ZnO. Electron beam energy loss experiments, accomplished by Hengehold and Pedrotti¹⁶ showed exactly the same result.

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Figure Captions

- Fig. 1 Room temperature reflectance spectra of a ZnO single crystal with $E \perp c$ and $E \parallel c$ at 10° angle of incidence.
- Fig. 2 ϵ_1 -spectra of ZnO for $E \perp c$ and $E \parallel c$ computed by Kramers-Kronig analysis.
- Fig. 3 ϵ_2 -spectra of ZnO for $E \perp c$ and $E \parallel c$ computed by Kramers-Kronig analysis.
- Fig. 4 Band structure of ZnO calculated by Rössler¹³.
- Fig. 5 Reflection of ZnO in the vicinity of the fundamental absorption edge at 90°K at 10° angle of incidence.
- Fig. 6 Energy loss function of ZnO computed by Kramers-Kronig analysis.











