Single and multiple excitation of bulk and surface plasmons on clean ZnO surfaces

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(Received 4 June 1976; in final form 26 July 1976)

Electron energy loss measurements in reflection with primary energies between 80 and 900 eV have been performed on clean cleaved ZnO polar {0001} and nonpolar {1$\bar{1}$00} surfaces in ultrahigh vacuum ($p < 10^{-10}$ Torr). The identification of surface and bulk plasmon loss peaks is possible from the observation of multiple losses and from the dependence of the spectra on primary energy. Surface and bulk plasmon excitation energies are obtained to be at 16 and 18.5 eV, respectively.

PACS numbers: 79.20.Kz, 71.85.Fh

Recently Hengehold and Pedrotti[1] have reported electron energy loss (ELS) measurements on ultrahigh vacuum (UHV) cleaved crystals of ZnO, CdO, and MgO. Contrary to CdO and MgO, where surface and bulk plasmon losses could easily be identified, the dominant structure on ZnO seemed to consist of two or more unresolved losses including bulk and surface plasmon. Because of the lack of unequivocal data for ZnO the present paper is intended to contribute more experimental details to this problem, especially concerning the excitation of the surface plasmon. Measuring second-derivative spectra instead of the undifferentiated spectra of Hengehold and Pedrotti[1] we have looked also for multiple losses that are energetically farther separated than the single losses. Thus bulk and surface plasmons on ZnO could be identified.

The second-derivative loss spectra have been obtained using a standard cylindrical Auger electron analyzer (Varian) with integral gun and lock-in differentiation technique. The energy resolution was about 0.4% for higher primary energies (> 150 eV) and about 0.7 eV for lower energies. The energetic position of the loss features could be obtained within ± 0.2 eV for primary energies below 100 eV. The samples were cleaved in UHV ($p < 10^{-10}$ Torr) using the double wedge technique.

The loss spectra observed on the (000$\bar{1}$) oxygen face and the (1$\bar{1}$00) nonpolar face of ZnO for different primary energies are shown in Figs. 1 and 2, respectively. The structure obtained on the oxygen face for low primary energies is dominated by two excitations at 15.6 and 19.0 eV. With increasing primary energy the height of the 15.6-eV peak decreases drastically as compared to the 19.0-eV loss. At loss energies of 32.6, 36.8, 49.5, and 55.8 eV four more loss peaks could be observed with high amplifier gain. The relative heights of the 32.6- and 49.5-eV losses decrease in comparison to the 36.8- and 55.8-eV losses, respectively, with increasing primary energy. Loss peaks in the energy range $4 < \Delta E < 15$ eV due to interband transitions will be discussed elsewhere,[2] but have been drawn in Figs. 1 and 2 for one primary energy $E_0 = 200$ eV.

Corresponding to the losses at 15.6 and 19.0 eV on the oxygen face, two peaks are observed at 16.1 and 18.8 eV on the nonpolar face (Fig. 2) separated by an additional loss at 17.6 eV. With increasing primary energy the peak at 18.8 eV finally dominates the whole spectrum. At higher loss energies the structure closely resembles that of the oxygen face with losses at 33.0, 36.6, 49.5, and 54.9 eV. The position of the 49.5-eV loss has been derived from the 600-eV primary energy spectrum because the 900-eV spectrum does not reach the zero line in that region thus indicating an overlap of the neighboring peaks. The change of the loss intensities with increasing primary energy agrees with that of the oxygen face. Due to the high amplifier gain used in the 30—40-eV loss range of the 80-eV spectrum in Fig. 2 the relative peak heights were not totally reproducible. This might explain the reversed peak heights of the losses at 33.0 and 36.6 eV.

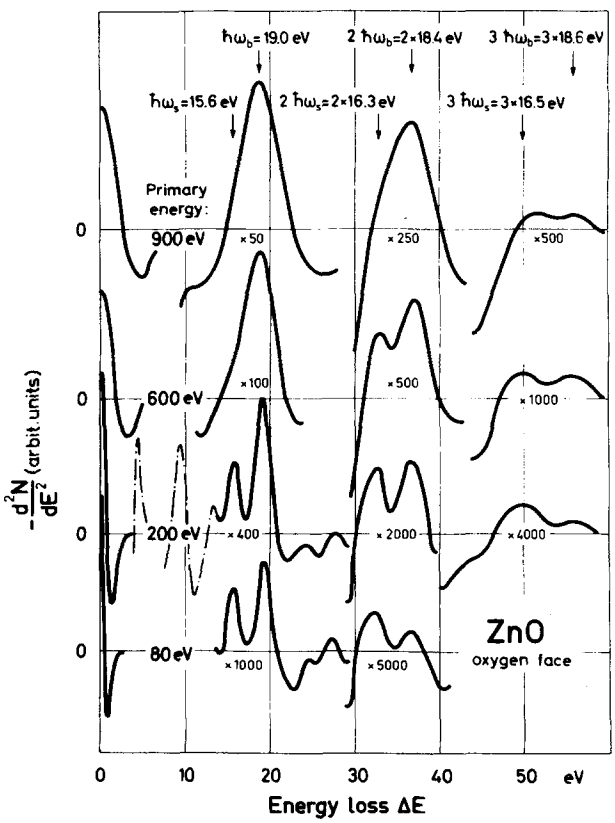

FIG. 1. Second-derivative electron energy loss spectra of the clean (000$\bar{1}$) oxygen face of ZnO for different primary energies. Spectral structure in the loss energy range $3 < \Delta E < 15$ eV has been omitted except for $E_0 = 200$ eV (dashed-dotted line); see Ref. 2.

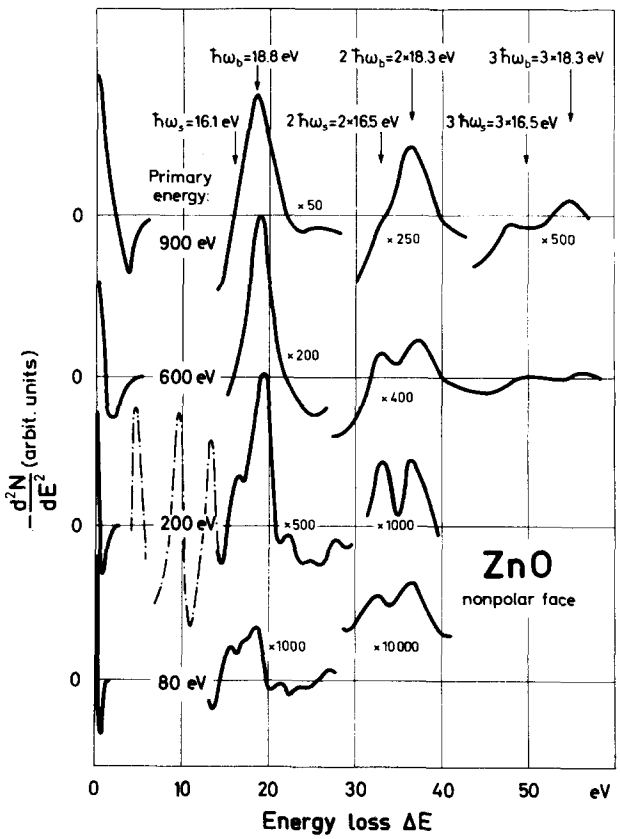

FIG. 2. Second-derivative electron energy loss spectra of the clean $(1\bar{1}00)$ face of ZnO for different primary energies. Spectral structure in the loss energy range $3 < \Delta E < 15$ eV has been omitted except for $E_0 = 200$ eV (dashed-dotted line); see Ref. 2.

In ELS both interband transitions and plasmon excitation can be observed. The concept of plasmon wave excitation loses its simple meaning if interband transitions occur in the energetic range of the bulk and surface plasmon excitation energy. The superimposed variation of $\epsilon(\omega)$ due to interband transitions near the energy of the bulk plasmon ($\epsilon = 0$) and the surface plasmon ($\epsilon = -1$) shifts and/or splits the original bulk and surface plasmon loss peaks. Thus, especially for ZnO whose d-band transitions energetically mix with the plasmon excitation and whose dielectric function $\epsilon(\omega)$ never reaches zero,[3–5] the concept of pure plasmon excitation becomes questionable. Nevertheless the frequencies corresponding to the maximum of the bulk and surface loss functions may be called plasma frequencies and it is in this limited sense that we will use these terms for ZnO.

Among previous publications,[3–5] there is general agreement that the bulk plasmon energy is near 19 eV. This corresponds very well to the two losses at 19 and 18.8 eV we observed on the oxygen face and the nonpolar face, respectively.

Surface losses should only give a small contribution to the dominating bulk losses for the experimental geometry used in previous ELS measurements on ZnO.[6] In a doubly differentiated spectrum this difficulty might be overcome because the peak height is dependent on the slope of the nondifferentiated spectrum. Optical data of Hengehold *et al.*[3] show a maximum of the surface loss function at 16.5 eV, whereas the surface loss function after Freeouf[5] reaches its maximum near 17.5 eV. We observed corresponding losses on both polar and nonpolar faces of ZnO at 15.6 and 16.1 eV, respectively, showing the characteristic primary energy dependence of surface losses.

Another argument for the interpretation of the 15.6 (16.1) eV and 19.0 (18.8) eV loss peaks in terms of the excitation of surface and bulk plasmons is derived from the observation of multiple losses near the corresponding frequencies (Figs. 1 and 2). Slight differences between the calculated (from single excitations) multiple frequencies and the observed loss energies may be explained by a larger angle integration in k space for the multiple losses. Because of more pronounced background structure in the single plasmon region the double differentiation process could also be responsible for energetic differences between single and multiple loss energies.

Contrary to ELS measurements of, e.g., Powell and Swan[7] on aluminum with primary energies between 760 and 2020 eV, in our spectra no mixed multiples of surface and bulk losses could be observed. Nevertheless they might be hidden in the spectra because of a low excitation probability. Another explanation for the lack of mixed multiples might be given according to Ashley and Ritchie,[8] who calculated the probability for "double-plasmon" emission in a free electron gas. From that work one can take as a general feature that with decreasing foil thickness penetrated by the electrons "double-plasmon" excitation (in one event) might become more probable than the excitation of two single plasmons. In the case of a very small foil thickness, therefore, only pure multiples of surface and bulk plasmons should be observable. Experimentally Arnott and Haneman[9] found some evidence for the existence of "double-plasmon" generation on Si. At least from a theoretical point of view, we think, the problem of "pure" and mixed multiple plasmon excitations needs some further investigation.

The authors would like to thank Professor H. Ibach for valuable discussions and Professor G. Heiland for critical reading of the manuscript. The work was financially supported by the Deutsche Forschungsgemeinschaft in the Sonderforschungsbereich 56 (Aachen).

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