

IV. PHOTOEMISSION SPECTROSCOPY

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1. INVESTIGATIONS OF MOLECULAR CHEMISORPTION ON SEMICONDUCTORS BY ANGLE-RESOLVED PHOTOEMISSION SPECTROSCOPY

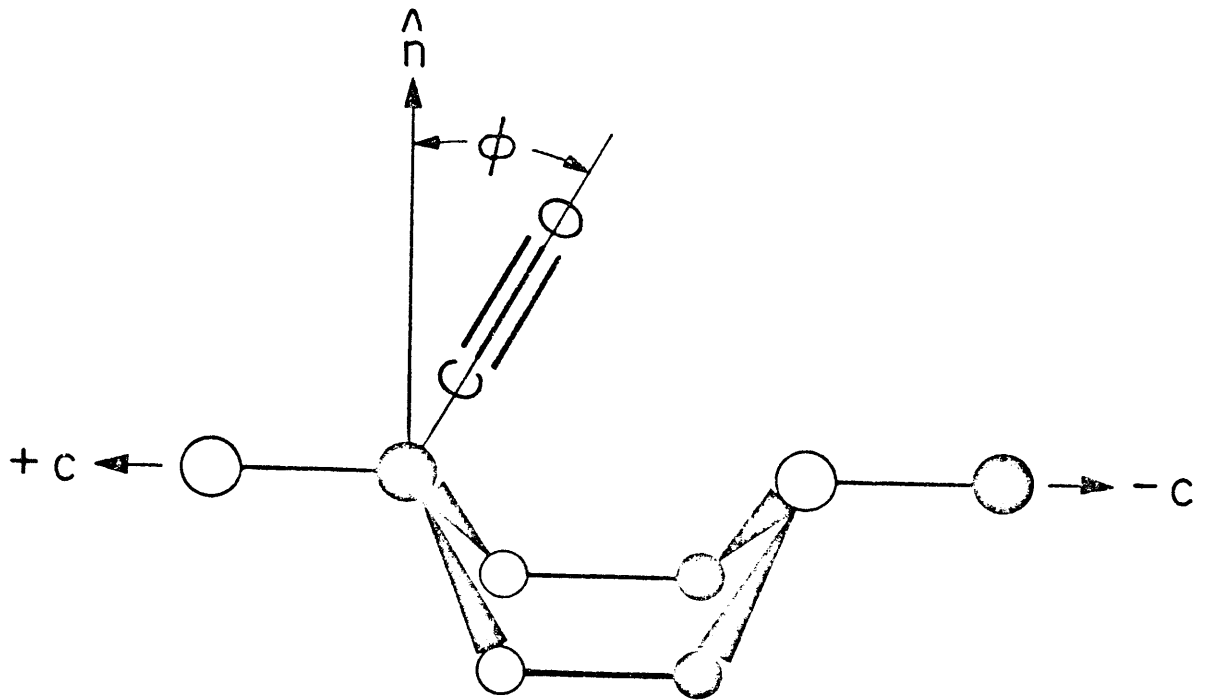
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During the past year this project has progressed from the stage of instrument development to a fully operational experimental effort. The first experiment undertaken with our spectrometer was a study of the chemisorption site geometry for CO bound to ZnO $10\bar{1}0$ surfaces.

Despite the importance of molecular chemisorption processes in modifying surface electronic properties, and in participating in reactions both with the surface (e.g., etching) and on the surface (e.g., catalytic reactions), studies of the fundamental nature of molecular bonding to the surfaces of these materials have lagged far behind corresponding efforts to understand chemisorption on metals.

In many respects, this system is an extremely attractive one to study. Zinc oxide serves as a practical catalyst for the synthesis of methanol from CO and H₂, and the CO-ZnO system has served as a prototype for the study of surface photo-oxidation reactions. A detailed mechanistic understanding of both of these important processes clearly requires a knowledge of the bonding mechanism of CO to the surface. In addition, the intrinsic surfaces of ZnO (the nonpolar $10\bar{1}0$ and $11\bar{2}0$); and the polar 0001 and $000\bar{1}$ faces) have been very well characterized by LEED. These results demonstrate that the surface is substantially unreconstructed, with the $10\bar{1}0$ surface, in particular, also exhibiting a (1×1) unit mesh with ~ 0.5 Å zinc ion displacements from their ideal positions. Thus our information on molecular



Zn \equiv 
 O \equiv 

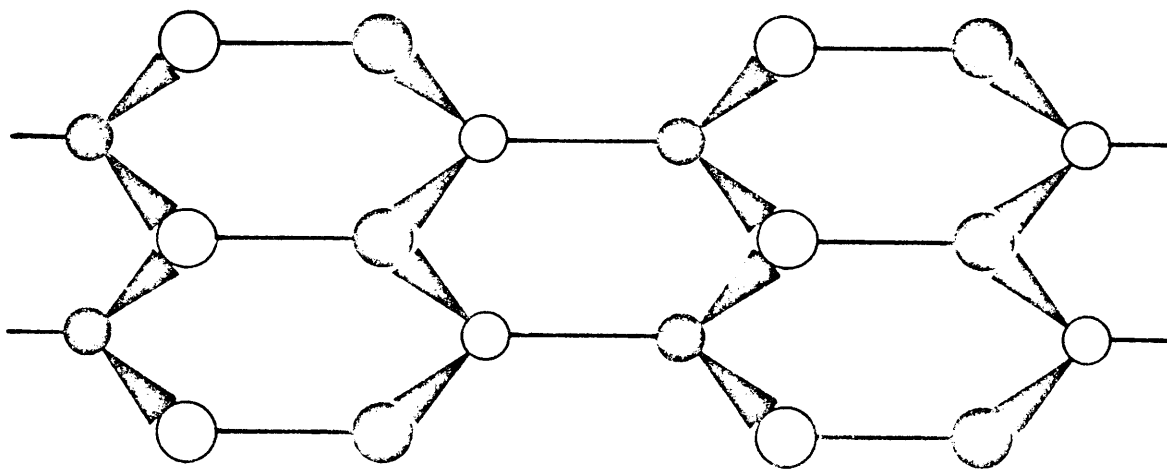


Fig. IV-1.

(IV. PHOTOEMISSION SPECTROSCOPY)

orientation can be related to a surface geometry which is both simple and accurately known. In addition, extensive angle-integrated photoemission studies of CO chemisorption on ZnO by Solomon and co-workers (with whom we collaborated on this project), performed at the Lincoln Laboratory, had elucidated the thermodynamics of the adsorption process and methods of crystal preparation, which greatly facilitated this work.

Our results, shown in Fig. IV-1, indicated that the carbon monoxide is bound to the surface zinc atom, by means of a dative bond from the CO 5σ molecular orbital. The molecules were found to be oriented at an angle of $\phi \approx 30^\circ$ from the surface. As the position of the "missing" oxygen atom on this surface would be $\phi = 19^\circ$, the carbon monoxide molecule is thus acting as a substitute ligand. However, since the CO-Zn bond is rather weak, the molecule is bent from 19° to 30° as a result of an electrostatic interaction with the rest of the surface, particularly the nearest oxygen atom.

Current work involves extending this study to other crystal faces of ZnO, particularly the polar faces where bonding to defects may be important. During the coming year we will be extending studies of this type to the less ionic groups IV and III-V surfaces.

2. STUDIES OF SEMICONDUCTOR SURFACE REACTIVITY

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Preparations have been made during the past year for experiments studying the surface chemistry of semiconductor etching processes (e.g., plasma etching). A combination of photoemission and electron-energy-loss spectroscopy will be used for this purpose.

