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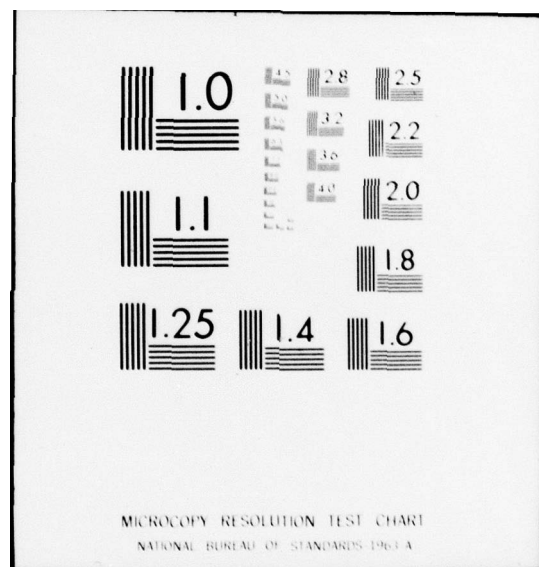
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Final Report

For the period from 15 March 1975 to 15 March 1978

SURFACE STATES ASSOCIATED WITH CHEMISORBED SPECIES

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Prepared for:

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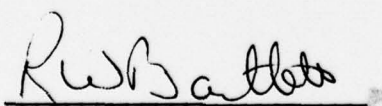
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M. Landstrass (Graduate Student at Stanford)  
K. Frese (Visiting Scientist)

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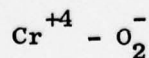
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REVIEW OF PROGRAM, SURFACE STATES  
ASSOCIATED WITH CHEMISORBED SPECIES

During the three year period covered by this final report, two areas of interest were investigated, first, surface states on semiconducting powders, and second, states associated with defects in passivating oxide films, emphasizing  $\text{SiO}_2$  on Si.

In the studies of surface states on semiconducting powders, the program was viewed to some extent as the basic research phase of a development of gas sensors. Thus, the particular systems studies were chosen with the concept in mind of investigating gas/surface state interaction. For example, the interaction of gaseous bases with acid sites on solids<sup>1\*</sup> was studied. In this study we were able to show that in many cases sites on an oxide surface play a dual role, acting both as acid sites and as surface states. Because of this dual role, the adsorption of gaseous bases on these sites causes electrical changes in the semiconductor. In a separate study<sup>2</sup> of the important catalyst chromia,  $\text{Cr}_2\text{O}_3$ , we were able to show that unoccupied adsorption sites behave as surface states. Specifically coordinatively unsaturated  $\text{Cr}^{+3}$  ions at the surface that act in  $\pi$  bonding CO or that act as sites for oxygen adsorption as  $\text{O}_2^-$  or  $\text{O}^-$  are, when no adsorbed gas is bonded to them, donor surface states. The physical picture of a surface state donor and the chemical picture of a donor-acceptor complex:



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\* For references, see Publications.

are thus directly reconcilable. Of interest also is the observation that the surface donor level of the  $\text{Cr}^{+3}$  was found to be 0.3 eV higher than the bulk  $\text{Cr}^{+3}$  levels (the valence band) and the surface ion is thus highly reactive with adsorbing gaseous oxidizing agents.

Our studies of silica on silicon had two objectives, one to examine flaws in the silica, the other to study surface states on the silica. To date only the first has been pursued. In particular, we have examined oxygen ion vacancies ( $\text{Si}^{+3}$  sites) introduced by high-temperature treatment of the grown  $\text{SiO}_2$  film in vacuum. The  $\text{SiO}_2$  prepared in this way behaves as if the defects form a conducting impurity band, and the  $\text{SiO}_2$ -covered silicon becomes an active and reproducible electrode exchanging electrons with many ions in solution.

This study has not yet been submitted for publication--the impurity band interpretation and the interpretation of the electrode processes that follows is a substantial divergence from normal electrochemical models, so must be strongly supported by experimental evidence. In our next series of experiments we will vary the defect concentration at constant oxide thickness (vary the temperature of the vacuum treatment) to define the model more accurately. Independent of the final model, however, this unusual "glass electrode" with its electronic conductance mechanism, will be of great interest.

#### Appendix

##### Publications During the Period Covered by this Report

1. Surface States Associated with Acid Sites on Solids, Surface Sci. 50, 329 (1975).
2. Surface States on a Chromia Catalyst, J. Catalysis 47, 69 (1977).
3. The Study of Semiconductor Using Electrochemical Techniques, to be published in Proc. 5th Conf. on the Physics of Compound Semiconductor Surfaces, Los Angeles, 1978.

4. Dislocations in ZnO as Channels for Electron Transfer from Surface Species, Nat. Bu. Standards Special Public. 455, "Electrocatalysis on Non-Metallic Surfaces," ed. A. D. Franklin, November 1976.
5. U.S. Patent No. 4,039,941, Gas Sensor, issued August 2, 1977.

Review Articles and Books During this Period. These were not directly sponsored by ARO, but drew heavily on the background of our ARO research:

1. Semiconductor Surfaces, p. 203 of "Treatise on Solid State Chemistry" Vol. 6B, ed. N. B. Hannay (Plenum, New York, 1976).
2. Theory of Adsorption, p. 221 of "Surface Physics of Phosphors and Semiconductors," ed. E. G. Scott and C. E. Reed (Academic, London, 1975).
3. "Catalysis-on Top of Semiconductors" Chemtech 7, 570 (1977).
4. "The Chemical Physics of Surfaces" (Plenum, New York 1977).