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The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

1. Photoemission
2. Photoemission Spectroscopy
3. Surface States
4. Surface Reconstruction
5. Amorphous Semiconductor
6. Core Shift
7. Oxygen Adsorption
8. Germanium
9. Silicon
10. Tin
11. Tin Oxide
12. $SrTiO_3$
13. ZnO
14. Cesium
15. Cesium adsorption

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The surface electronic structure and certain aspects of the surface chemistry of amorphous and crystalline Si and Ge as well as crystalline $SrTiO_3$, and Sn have been studied using photoemission spectroscopy and Auger electron spectroscopy. By examining the surface, valence, and core states a more detailed picture of the surface electronic structure and chemistry could be obtained

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20. (Continued)

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STUDIES OF THE SURFACE ELECTRONIC STRUCTURE AND CHEMISTRY OF Si, Ge, AND OTHER SOLIDS

FINAL REPORT

Professor W. E. Spicer

January 30, 1978

U.S. ARMY RESEARCH OFFICE
RESEARCH AGREEMENT DAHC04-74-G-0215

Stanford Electronics Laboratories
Stanford University
Stanford, CA 94305

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ABSTRACT

The surface electronic structure and certain aspects of the surface chemistry of amorphous and crystalline Si and Ge as well as crystalline $SrTiO_3$ ZnO, and Sn have been studied using photoemission spectroscopy and Auger electron spectroscopy. By examining the surface, valence, and core states a more detailed picture of the surface electronic structure and chemistry could be obtained than has been generally possible in the past. Of particular importance has been the use of Stanford Synchrotron Radiation Laboratory which has provided continuously tunable radiation from 10 to 300 eV. Using this capability, it is possible ~~we are able~~, for example, to examine the surface states and core levels as a gas is adsorbed. It has been ~~Very strikingly, we have~~ found it possible to adsorb oxygen on Si in such a way that the surface states are removed but the usual shift in the Si 2p core level associated with chemical bonding is missing. This indicates a new type of "covalent" bonding, previously unexpected. These results can give new insight into the kinetics of oxygen takeup on Si. Three other stages of oxygen uptake have been observed by means of the core shifts. These are assigned to silicons bonded to increasing numbers of oxygen atoms. For amorphous Ge and Si, no filled surface states appear in the band gap in contrast to the case for the crystalline forms of these materials. This is believed to be due to the fact that the surface atoms on amorphous Ge and Si have more opportunity to relax and thus lower the surface state energy as in GaAs. In opposition to theoretical predictions, no surface states were found on $SrTiO_3$. It was found easy to clean ZnO and apply a Cs monolayer to reduce its work function. It was found that oxygen adsorbed on Sn tended to go beneath the surface leaving a metallic surface layer. This last result is of interest because of SnO cold cathodes.

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I. STATEMENT OF PROBLEM STUDIED

The major emphasis in this study was on the surface electronic structure and surface chemistry of crystalline and amorphous Si. To study the surface chemistry, oxygen was used as a test gas. It has been possible to add important new dimensions to these studies by use of synchrotron radiation and, to a lesser extent, by application of new sophisticated sputter - Auger equipment obtained under other support.

Another emphasis has been on the oxidation of metals and on the search for surface states on metal oxides such as $SrTiO_3$ (where they had, in some cases, been predicted theoretically) and in the details of oxygen uptake on metals such as Sn. This work was partially stimulated by a study (also sponsored by ARO) of tin oxide and tin-indium-oxide cold cathodes where understanding of the oxidation and reduction processes was of critical importance. It was also stimulated by fundamental interest in these problems.

II. MOST IMPORTANT RESULTS

- It was found (see Item 14 on publication list) that, under certain specified conditions, molecular oxygen can be adsorbed on the surface of (111) Si removing all surface states but not forming a chemical bond requiring sufficient electron transfer from the Si to O_2 to produce a Si 2p chemical shift. This surprising result suggests a new "covalent bond" between O_2 and the Si surface. The "covalently" bonded O_2 could be disassociate into atomically adsorbed oxygen by striking the surface with an electron beam. Further details are given in Publication #14.

- Four distinct steps in the takeup of oxygen on Si and Ge have been identified. Details will be given for the Si case. The first stage possible is that of "covalently" bound O_2 described above. Under certain exposure procedures, outlined in Publications 14, 15, and 16, this step could be eliminated or reduced and atomically adsorbed oxygen observed with a chemical shift of 2.0 eV by exposures at higher pressure (10^{-6} rather than 10^{-8} torr). This is the second stage of adsorption. The third stage produces a chemical Si 2p shift of 2.6 eV. We speculate that this is an Si atom bonded to two oxygen atoms. In the fourth stage, the clearly defined state is SiO_2 with each Si bonded to four oxygen. This produces a 3.8 eV chemical shift. Other intermediate shifts may be present but only the above can be claimed to be clearly resolved. In particular, another broad peak is seen at 3.3 eV which may be due to the 3.8 eV plus a second unresolved peak lying below 3.3 eV. This latter peak would then, logically, seem to be assigned to an oxygen coordinated to the oxygens. However, all of the assignments of 2p core shifts to detailed atomic configuration must be considered tentative. More work is clearly and urgently needed in this area.

- On crystalline Si and Ge (111) surfaces filled surface states centered below the valence band maximum but extending into the band gap are clearly seen. No corresponding states are seen for amorphous layers of these materials formed by evaporation. Rather, no evidence has been found for filled surface extending into the forbidden gap. It is suggested that the relaxation of the surface atoms (as in, e.g., GaAs) moves the surface states below the valence band maximum. (See Items 10 and 17 on Publications list.)

- Morin and Wolfram (Phys. Rev. Letter 30, 1214 (1973) had predicted surface states on the $SiTiO_3$ surface due to the empty Ti d-bands. Further, they had predicted very special surface catalytic properties due to these states. We searched carefully for these surface states and found no evidence for them. It now appears that surface states can be induced by departures from stochiometry on the surface but that no states exist of the type predicted by Morin and Wolfrom (see Item 6 on Publications list).

- It was found that oxygen tended to move below the surface of Sn leaving a metallic surface layer. (See Item 11 on Publications list.)

This is of significance to SnO cold cathode work as well as of fundamental importance.

We found that ZnO powders could be cleaned relatively easily by heating to 500°C and that Cs adsorbed on the clean surface reduced the electron affinity by about 3 eV. (See Item 12 on the Publications list.)

III. LIST OF PUBLICATIONS UNDER ARO SPONSORSHIP UNDER THIS CONTRACT

1. "Surface States and the Oxidation of Amorphous Ge and Si", W.E. Spicer, B.A. Orlowski, A.D. Baer, C.R. Helms, V. Pereskokov and T.M. Donovan, in Tetrahedrally Bonded Amorphous Semiconductors (AIP Conference Proceedings No. 20), page 53, American Institute of Physics, N.Y. 1974.

2. "Effect of Angle of Evaporation on Amorphous Ge Films", B. Orlowski, W.E.Spicer, and A.D. Baer, in Tetrahedrally Bonded Amorphous Semiconductors (AIP Conference Proceedings No. 20), page 241, American Institute of Physics, N.Y. 1974.

3. "Photoemission Spectroscopy and the Electronic Structure of Amorphous Materials--Studies of Ge and Si", W.E. Spicer, Proc. of 5th International Conf. of Amorphous and Liquid Semiconductors (1974), page 499, Taylor and Francis Ltd., London. (Invited Paper)

4. "X-ray and Ultraviolet Photoemission Studies of the Electronic Structure of the Amorphous Ge_xTe_{1-x} Systems", G.B. Fisher, I. Lindau, B.A. Orlowski, W.E. Spicer, Y. Verhelle and H.E. Weaver, Proc. of 5th International Conf. of Amorphous and Liquid Semiconductors (1974), page 621, Taylor and Francis Ltd., London.

5. "Phase Separation in Silicon Oxides As Seen By Auger Electron Spectroscopy", J.S. Johannessen, W.E. Spicer, and Y.E. Strausser (Varian Associates), Appl. Phys. Letter 27, 452 (1975) (also supported by ARPA).

6. "Photoemission Investigation of Surface States on $SrTiO_3$", R.A. Powell and W.E. Spicer, Phys. Rev. B6, 2601 (1976).

7. "Study of Chemisorption of Oxygen on Al", K.Y. Yu, J.N. Miller, P. Chye and W.E. Spicer, Phys. Rev. 14, 1446 (1976), also supported by NSF.

8. "Bulk and Surface Ultraviolet Photoemission Spectroscopy", W.E. Spicer, Chap. 12 in Book, Optical Properties of Solids: New Developments, B.O. Seraphin, Ed., p. 633, North-Holland, Amsterdam (1976).

9. "Ultraviolet-Photoemission Studies of TlCl, S.F. Lin, W.E. Spicer, Phys. Rev. B14, 4559 (1976), (also supported by NASA and NSF).

10. "Photoemission Studies of Surface States and Oxidation of Group IV Semiconductors", G.M. Garner, I. Lindau, J.N. Miller, P. Pianetta, and W.E. Spicer, J. Vac. Sci. and Tech., 14, Jan./Feb. 1977.

11. "Photoemission Study of Oxygen Chemisorption on Tin," R.A. Powell and W.E. Spicer, Surface Science, 55, 681 (1976).

12. "Photoemission Study of Cesiation of ZnO, R.A. Powell and W.E. Spicer, Jour. of Appl. Phys., 48, October 1977, pp. 4311-4314.

13. "High-Resolution Auger Spectroscopy of Oxygen Chemisorbed on Sn", R.A. Powell, submitted for publication.

14. "New Phenomena in the Adsorption of Oxygen on Si", C.M. Garner, I. Lindau, C.Y. Su, P. Pianetta, J.N. Miller, and W.E. Spicer, Phys. Rev. Letters scheduled for Feb. 6, 1978 issue.

15. "Bonding States of Oxygen on Si", C.M. Garner, I. Lindau, C.Y. Su, P. Pianetta, and W.E. Spicer, Jour. of Vac. Sci. and Technology, scheduled for Vol. 15, #4, July/Aug. 1978.

16. "New Studies of Oxygen Adsorption and Surface States of Si", C.M. Garner, I. Lindau, C.Y. Su, P. Pianetta, J.N. Miller, and W.E. Spicer, in preparation.

17. "Photoemission Studies of Bulk and Surface Electronic Structure of Amorphous and Crystalline Ge and Si", J.N. Miller, I. Lindau, D.T. Ling, and W.E. Spicer, in preparation.