ide, diamond and hexagonal closed-packed structures has been produced. The preparation of surfaces in high vacuum, the examination by electron microscopy of metal films evaporated on to glass, and the effects of bombarding gold with inert gas atoms have been studied. The oxygen adsorption on, and possible solution in, a clean silver surface at about 200° C, in the range 10^{-3} – 5×10^{-2} mm of mercury pressure was measured and the quantity related to the surface area of the silver determined by the adsorption of krypton at –195° C. The quantity of oxygen sorbed per unit area and the shape of the isotherm depended markedly on the surface to volume ratio of the evaporated film. The surface appeared to be covered with a monolayer at approximately 5×10^{-3} mm of mercury pressure and the amount of oxygen adsorbed at that pressure corresponded to one oxygen atom for every krypton atom absorbed.

For the preparation of metal specimens for X-ray and electron microscope measurements a spark erosion machine was developed and the amount and depth of the damage produced by the machine on nickel was studied. Other investigations included the effects of surface, temperature

and strain rate on the Bauschinger effect and cyclic work-hardening in copper single crystals; the measurement of the electrical resistivity of dislocations; the formation of point defects in plastically deformed metals and the dislocation rearrangements during recovery; and martensite transformations in steel. For the Divisions of Textile Physics and Protein Chemistry proton resonance studies of the kinetics of the absorption of water by wool and the exchange of deuterium for hydrogen in a particular wool-water system were made, and in conjunction with the Division of Applied Mineralogy the properties of inter-layer water in vermiculite crystals were investigated.

The annual report includes details of the publications by the members of staff of the Division and a list of the names of the senior members of staff. Dr. L. M. Clareborough, Dr. M. E. Hargreaves and Mr. M. H. Loretto received the David Syme Research Prize for their work on imperfections in metal crystals and Dr. A. K. Head was visiting professor at Brown University, Rhode Island. Prof. P. P. Ewald, president of the International Union of Crystallography, visited the Division in October 1961.

S. WEINTROUB

CLEAN SURFACES AND SURFACE PHENOMENA IN SEMICONDUCTORS

A RECENT issue of the *Annals of the New York Academy of Sciences* contains the series of papers presented at the conference entitled "Clean Surfaces" held by the Academy during April 5–7, 1962, and, as a supplement, the papers of the symposium on "Surface Phenomena in Semiconductors" held by the American Chemical Society during March 21–29, 1962*.

The conference was divided into four parts, the first of six papers dealing mainly with electron diffraction and the electronic properties of clean surfaces; the second of six papers with cleaved and etched surfaces; the third of three papers with adsorption; and the fourth of six papers with nucleation. E. W. Müller gave a survey of field emission microscopy of clean surfaces with electrons and positive ions. He stressed that the field ion microscope is a research tool for the investigation of clean surfaces, and of the defect structure in the interior of metal crystals exposed at the surface by field evaporation. More detailed information on adsorption can be expected by the operation of the microscope with gases of lower ionization energy, but this will require ultra-pure imaging gases, and the lower field strength will reduce the resolution of the microscope. L. H. Germer discussed the very recent applications of the diffraction of slow electrons to the investigation of surfaces and the new science of two-dimensional crystallography. Experiments described by H. E. Farnsworth of low-energy electron diffraction from a cleaved germanium surface have established that crystal faces other than that desired by cleavage were present, and that a cleaved surface had a larger area of undesired crystal facets than a surface prepared by cutting the crystal with a diamond wheel, ground, etched chemically, and cleaned *in vacuo* by argon ion bombardment and subsequent annealing.

The symposium on "Surface Phenomena in Semiconductors" was suggested and organized by H. van Olphen, the chairman of the division of colloid and surface chemistry of the American Chemical Society. The object was to stimulate discussion among surface chemists and research scientists in the semiconductor surface field. The symposium was tutorial in character and the fourteen papers presented comprise a series of review or tutorial papers each devoted to a particular area of specialization.

* *Annals of the New York Academy of Sciences*, 101, Article 3: *Conference on Clean Surfaces*, with Supplement: *Surface Phenomena in Semiconductors* (Symposium). By F. G. Allen *et al.* Pp. 583–1014. (New York: New York Academy of Sciences, 1963).

The introductory review by W. R. Savage (Texas Instruments Inc.) covers the general field of the properties of semiconductor surfaces. J. N. Zemel (United States Naval Ordnance Laboratory) describes several fundamental physical measurements used in semiconductor surface research and their connexion with some of the main streams of contemporary work. He mentions that the properties of surface states on only five materials (germanium, silicon, zinc oxide, lead sulphide and indium antimonide) have been studied to any extent. The investigation of a clean semiconductor surface is a difficult and challenging pursuit, because whereas a metal surface with a hundredth of a monolayer is considered acceptably clean for thermionic work, such a density of contamination on a semiconductor would produce, if diffused in 10^{-4} cm, a degenerate layer of width equal to the surface space charge region. It is not surprising, therefore, that he concludes that though there is a great deal known about the surfaces of semiconductors, there is little understanding. Field emission as a tool, and the grain boundary as a system, for the study of surfaces are discussed by F. G. Allen (Bell Telephone Laboratories Inc.) and P. Handler (University of Illinois) respectively. Lifetime and conductivity measurements on clean germanium surfaces are reviewed by Y. Margoninski (Raytheon Research Division) and the pulsed field effect method of investigation of surface states on semiconductors by G. Rupprecht (Tyco Laboratories Inc.).

Several papers deal with aspects of surface chemistry and electrochemistry. M. Green (University of Pennsylvania), in a paper entitled "The Configuration of Complexes on Semiconductor Surfaces", discusses a new approach to the problem of the equilibrium configuration of surface layers which should be useful in problems of chemisorption, film nucleation and related phenomena. The reaction between heated germanium and oxygen, and between water and methyl alcohol is reported on by M. J. Sparnay (Philips Research Laboratories), and H. C. Gatos and M. C. Lavine (Massachusetts Institute of Technology) discuss the process of formation of thermal etch figures on germanium single crystals when heated to temperatures of 700°–925° C in the presence of argon-oxygen mixtures.

An interesting and instructive paper of the series, though it did not produce any comment in the final panel discussion session of the symposium, was that of N. J.

Harrick (Philips Laboratories) on total internal reflexion and its application to surface studies. The absorption of infra-red radiation in semiconductors has been used successfully to study bulk properties of semiconductors, but through the use of multiple total internal reflexion, the space-charge region can be probed and the properties of the carriers in the space charge region can be measured. Because of the special characteristics peculiar to total internal reflexion, both the outside and the inside of the surface can be studied. After a clear description of the process of internal reflexion and of some of the well-

known, but nowadays rather neglected, beautiful optical demonstrations of fundamental phenomena associated with internal reflexion, Harrick discusses the application to surface studies. The experimental arrangement and preparation of the samples are described, and details are given of the results of investigations by various workers on chemisorbed molecules, oxide growth and thin films. Finally, various possible experimental studies, using infra-red radiation to obtain information concerning the space charge region on semiconductors are suggested and outlined.

S. WEINTROUB

ELECTRON-PROBE MICROANALYSIS OF ANODIC OXIDE FILMS ON ALUMINIUM ALLOYS

By DR. G. C. WOOD, V. J. J. MARRON and B. W. LAMBERT

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IN view of the successful application of electron-probe microanalysis to the qualitative and quantitative analysis of oxide scales on alloys^{1,2}, it appeared desirable to examine the possibilities of the technique when applied to the examination of corrosion products obtained in aqueous media. In particular, the field of the formation, transformation and dissolution of anodic films, and indeed of the reactions between all types of semi-conducting films and electrolytes, is extremely important and likely to receive increasing attention. Anodic oxide films on aluminium alloys were chosen for preliminary studies because they are readily reproducible, their general properties are sufficiently well documented to enable comparisons to be made and metallographic preparation for the micro-analyser is simple. In addition, it was felt that further useful information about their formation, dyeing, sealing and corrosion properties could be obtained.

Consequently, six small sheet specimens of an aluminium-magnesium alloy (magnesium 5.00, manganese 0.25, copper 0.01, iron 0.24, silicon 0.01, wt. per cent) were chemically polished and anodized at 25 m.amp/cm² in stirred 15 per cent w/v sulphuric acid at 15° C for 60 min. Individual specimens were then subjected to one of the following treatments: (1) dabbed with filter paper to remove surplus surface acid; (2) washed for 1 min in running distilled water; (3) washed for 24 h by rotation in distilled water; (4) sealed in potassium dichromate solution (50 g/l.) at 95° C for 1 h; (5) sealed in a conventional nickel acetate solution (nickel acetate 6 g/l., boric acid 8 g/l.) at 95° C followed by smudge removal with a clean dry rag; (6) sealed in concentrated nickel acetate solution (nickel acetate 60 g/l., boric acid 80 g/l.) at 95° C with subsequent smudge removal.

A further specimen was prepared under similar anodizing conditions at 30° C and washed for 1 min.

The specimens were then set in small electrically conducting mounts and cross-sections prepared metallographically in a conventional manner, finishing on 1 μ diamond suspension. Optical examination showed that films formed at 15° C were 45–48 μ thick, indicating very little dissolution at the outer surface during formation, whereas the film produced at 30° C was only 30 μ thick because a third of it had been completely dissolved. Static probe measurements of aluminium, magnesium and sulphur concentrations, and of nickel and chromium concentrations where appropriate, were made at short intervals in the films along lines of traverse normal to the metal/oxide interface using a Cambridge 'Microscan' microanalyser. The apparent percentages of the elements were determined by comparison with appropriate standards, the results being corrected for background radiation and dead-time but not generally for absorption because of the complex and uncertain nature of the X-ray source

in the specimens. Some of the more important trends are illustrated in Figs. 1–3.

The distributions of aluminium across films formed at 15° C and 30° C respectively, followed by washing for 1 min, are compared in Fig. 1. For the former specimen the aluminium concentration is virtually constant with a slight hint of lower values towards the outer interface, although this trend is masked by the scatter. Clearly there is little extra dissolution in the pores or at the outer surface in this case. The aluminium content of the unwashed specimen (not shown on the diagram) was slightly higher, probably due to Al³⁺ ions in the liquid in the pores, but for the other washed and sealed specimens was very similar. On the other hand, the partly dissolved film formed at 30° C shows a pronounced reduction of apparent aluminium content from 30 wt. per cent near the alloy to 11 wt. per cent near the solution, indicating extra dissolution in the pores. These results support the view that the truncated-cone pore model³ must be largely due to extra dissolution rather than inherent in the mechanism of film growth. The apparent aluminium contents are somewhat low when compared with the figure of 37 per cent aluminium given for a typical anodic film⁴. This is

Fig. 1. Influence of anodizing temperature on aluminium distribution