THIN FILMS

a conference report

By ***J. C. Fisher***

LAKE George is a body of very clear water surrounded by tree-covered granite mountains in the southeastern part of New York State's gigantic Adirondack State Park. Much of its shoreline is state land, maintained in its wild condition, but some is privately owned and dotted with summer camps, motels, and hotels to serve the various requirements of summer visitors. On Labor Day week end, most of these visitors fade away, not to return until the following summer. Their absence makes available fine accommodations at reduced rates, and the still-warm water is most inviting. These factors, plus easy accessibility, drew the International Conference on Structure and Properties of Thin Films to the Sagamore Hotel, Bolton Landing, Lake George, for the three-day period September 9–11, 1959.

The conference was sponsored jointly by the Air Force Office of Scientific Research, Air Research and Development Command, and the General Electric Research Laboratory. Participants included about twenty overseas visitors from the United Kingdom, France, West Germany, The Netherlands, and Japan; and about twenty from US industry, twenty from US universities, and ten from US government agencies. Their backgrounds were diverse, and it was the hope of D. A. Vermilyea (GE Research Laboratory), the conference organizer and chairman, that the exchange of a broad range of views through review papers, current research papers, and informal discussion, would be of value to all.

Vermilyea's hope was realized in large measure. Many improved techniques for the formation and study of thin metallic films and surfaces, known only to one or another handful of conferees, became known to all as the conference proceeded. These techniques included ultrahigh vacuum, improved electron diffraction and electron microscope observations, field ion microscopy, rotational hysteresis, single-crystal films, and Moiré patterns. Description of each improved technique elicited reactions ranging from joy to dismay as its consequences were recognized by various members of the audience. There is no doubt that the sharing of these techniques was one of the most important results of the conference, leading as it must to a discontinuous increase in the effectiveness of thin-film research. By the end of the conference, the initial reserve that is natural among a group of near strangers had given way to the comradery of a group of colleagues who have shared a valuable and stimulating experience.

The technical program was divided into six sessions, Wednesday morning and evening, Thursday morning and evening, Friday morning and afternoon, chaired by Vermilyea, J. W. Beams (University of Virginia), L. Marton (National Bureau of Standards), C. S. Smith (University of Chicago), F. C. Tompkins (Imperial College), and J. C. Fisher (GE Research Laboratory), respectively. Save for the first session, which began with introductory remarks by J. W. Mitchell (University of Virginia), who emphasized the strong differences between films laid down in the three temperature ranges $\sim 4°K$, $\sim 70°K$, $\sim 400°K$, and the last, which began with a panel discussion, each session began with an hour-long review paper and finished with a half-dozen current research papers.

John C. Fisher is a physicist in the Metallurgy and Ceramics Research Department of the General Electric Research Laboratory in Schenectady, N. Y. The proceedings of this conference have recently been published (John Wiley & Sons) under the title *Thin Films*, with C. A. Neugebauer, J. B. Newkirk, and D. A. Vermilyea as editors.

Participants in the International Conference on Structure and Properties of Thin Films. *First row* (left to right): J. B. Newkirk, R. Schmidt, V. L. Newhouse, P. E. Tannenwald, H. Levenstein, H. Ehrenreich, D. O. Smith, N. Cabrera; *second row:* J. Vaumoron, L. Apker, L. Marton, D. D. Eley, F. C. Tompkins, D. A. Vermilyea, J. C. Fisher, J. W. Mitchell, W. Shockley, W. Buckel, D. W. Pashley, C. A. Neugebauer; *third row:* R. D. Heidenreich, J. J. Lander, R. B. Nicholson, O. S. Heavens, J. W. Beams, A. Colombani, P. Huet, M. J. Whelan, H. E. Farnsworth, G. Ehrlich, C. Herring, C. P. Bean, H. Mayer; *fourth row:* E. Pugh, H. J. Juretschke, H. J. Mueller, E. H. Layer, E. B. Henschke, E. W. Müller, L. L. Van Reijen, H. Hashimoto, M. M. Wachtel, R. Suhrmann, E. Burstein, B. M. Siegel, P. W. Selwood, R. W. Hoffman, E. C. Crittenden, Jr., S. M. Rubens; *fifth row:* M. Tinkham, F. Leonhard, M. P. Givens, H. G. F. Wilsdorf, C. Kemball, J. W. Menter, V. Heine, J. N. Wilson, L. G. Schulz, L. Pensak, J. A. Bennett, H. W. Schleuning, T. N. Rhodin, C. S. Smith, H. Fowler, R. M. Burger.

Formation of thin films (in particular, the problem of epitaxy, or the formation of oriented films by deposition upon single-crystal substrates) was reviewed by D. W. Pashley (Tube Investments Research Laboratories). He discussed the range of application of Frank and Van der Merwe's theory of epitaxy, and described the results of electron-diffraction and electron-microscope observations of thin-film formation. Many vapor-deposited films whose average thickness was a few atomic layers proved, upon observation, to consist of widely separated islands of thicker material. Visually, these "films" appeared to resemble spatters; or when thicker, oil droplets on the surface of stirred soup. Some nuclei seemed to form nearly at random on crystalline substrates and others to form at cleavage steps or other preferred sites.

Mechanical properties of thin films were discussed by J. W. Menter (Tube Investments Research Laboratories). Owing either to the inherently poor mechanical properties of most thin films, or to the difficulty of applying loads that do not stress the relatively weak film edges, strengths approaching the theoretical values, such as have been obtained with single-crystal "whiskers", have not as yet been achieved with certainty in films.

H. Mayer (Bergakademie Clausthal) reviewed the conduction phenomena in thin films, insofar as thin films could be utilized to throw new light upon electrical conductivity of metals. Because the film thickness is known and controllable, it is possible to deduce electron mean free paths in the bulk material and thereby to deduce further properties of the electron gas in interaction with the crystal. Mayer discussed primarily the properties of thin films of potassium deposited slowly upon glass, in a vacuum below 10^{-9} mm Hg. Although he believes these films to be continuous, surface roughness makes them difficult to use for mean free path measurements when their thicknesses are below 100A. Resistivity, Hall coefficient, thermoelectric power, and photoemissivity measurements led to conclusions relating to electron effective mass, number of electrons per atom, and mean free paths of electrons.

Work on the magnetization of thin films and surface anisotropy was reviewed by C. P. Bean (GE Research Laboratory), who pointed out the divergence of observations with respect to the saturation magnetization and Curie temperatures of thin films, where some measurements suggest that they decrease with decreasing film thickness and others suggest that they remain constant down to 20A. Bean suggested that more measurements of magnetization as a function of magnetic field, and more work with clean films, single crystals, and materials such as gadolinium and ferrites better suited to theoretical analysis, would be of value. He also reviewed Néel's concept of surface anisotropy, which reflects the tendency of magnetism to lie parallel or perpendicular to external or internal surfaces.

G. Ehrlich (GE Research Laboratory) commented upon molecular processes at the gas-solid interface—in particular, the sticking probability of molecules and the surface mobilities and lifetimes of adsorbed species. Theory and experiment are in reasonable agreement for the adsorption of rare gases on ionic crystals, and are becoming so for the adsorption of rare gases on metals.

TURNING now to the current research papers, several investigators pointed out that thin films often are not what they seem. Mitchell reported that the surface area of copper films deposited at $-183°C$ was proportional to the mass of the film, indicating a sponge-like structure. C. Kemball (Queen's University of Belfast) found that the catalytic activity of thin films tended to be proportional to their weight, lending support to this conclusion. B. M. Siegel (Cornell University) found that very thin films of copper deposited on carbon were not continuous, in agreement with Pashley's results as already described.

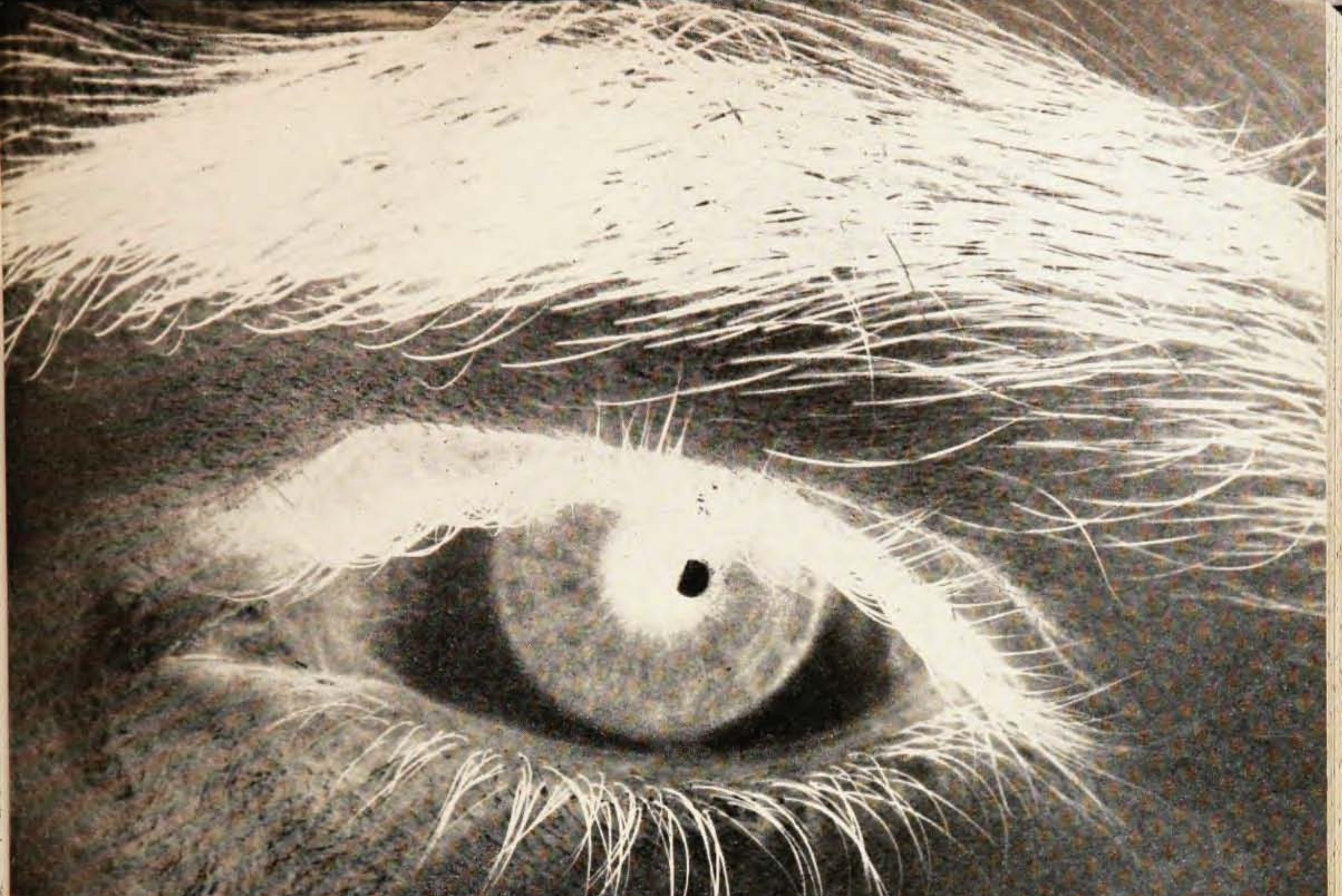
A number of investigators are using thin films in order to study bulk properties of crystals by techniques that are particularly appropriate to very thin samples. The electron microscope played a particularly important role in studying thin films by transmission. H. G. F. Wilsdorf (The Franklin Institute) has observed the motion of individual dislocations in stainless steel films formed by chemical polishing, and finds that dislocations come from low-angle grain boundaries, inclusions, and Frank-Read sources within the grains. M. J. Whelan (University of Cambridge) has observed the formation and growth of 200A diameter prismatic dislocation loops formed by vacancy condensation in quenched aluminum. In thin films these loops shrink as vacancies diffuse from them to the film surface, whereas in bulk samples they coarsen. R. B. Nicholson (University of Cambridge) has studied thin aluminum-silver alloys, and has observed prismatic loops, helical dislocations, and hexagonal loops surrounding a region of stacking fault. Pashley reported on observations of ordering and the arrangement of domains of order in CuAu I and CuAu II. In CuAu I alternate 002 planes are Cu and Au, and antiphase boundaries were observed to terminate on dislocations. In CuAu II a periodic domain structure is formed with antiphase domain boundaries separated by about 5 atom layers, and can be observed clearly.

Electron diffraction also played an important role in studying the structure of thin films. W. Buckel (University of Göttingen) found crystallites in thin films of Al, Zn, Pb, and Hg formed at liquid He and H_2 temperatures, and followed their growth on heating. He also showed that Bi and Ga gave liquid-like diffraction patterns as deposited at 2°K, but transformed to crystallites at about 15°K. Gallium transforms to a non-equilibrium form, and reverts to the equilibrium form around 70°K. H. Hashimoto (Kyoto Technical University) showed electron microscope motion pictures of the growth of thin plates and needles of WO_3 and MoO_3, their structure being followed by electron diffraction. R. D. Heidenreich (Bell Telephone Laboratories) used both diffraction and microscope techniques for investigating the structure of thin magnetic films, particularly those with directional anisotropy. In many instances he was able to find evidence of structural elements aligned with the axis of easy magnetization.

Chemical reactions at solid surfaces were discussed at some length. J. A. Bennett (British Scientific Instrument Research Association) discussed experiments designed to measure the heat of adsorption of gold on aluminum oxide and bismuth oxide films. T. N. Rhodin (Cornell University) reported investigations of the nucleation of oxide films on magnesium, wherein the oxygen consumption of a freshly evaporated surface was determined. He found the sticking probability of oxygen to vary with time. H. E. Farnsworth (Brown University) reported on his studies of the chemisorption of oxygen on nickel. Mitchell described his work in which the adsorption of oxygen strongly affected the decay of resistivity of copper films. P. W. Selwood (Northwestern University) discussed chemisorption of various organic materials on superparamagnetic nickel particles, the formation of bonds between hydrogen and the nickel tying up electrons and reducing the magnetic moments of the particles. He was able to deduce some of the steps in several catalytic processes. D. D. Eley (University of Nottingham) reported on the kinetics of oxidation of vapor-deposited aluminum films under low oxygen pressures, and was able to show that several processes were involved in forming films as thick as 20A.

Dissolved gases were found to affect thin film properties. Hydrogen in palladium produced pronounced resistivity effects, as reported by R. Suhrmann (Technische Hochschule Hanover), leading to interpretations of the solution process. L. Pensak (RCA Research Laboratories) found that dissolved gases affected the high-voltage photovoltaic effect.

Considerable work was reported bearing upon the



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Discussion at the dinner table. Clockwise: Mrs. E. B. Henschke, E. B. Henschke, C. Herring, D. W. Pashley, J. W. Menter, E. Pugh, D. O. Smith, C. S. Smith, J. B. Newkirk.

Discussion during a coffee break. H. Fowler, R. B. Nicholson, M. J. Whelan, H. G. F. Wilsdorf at blackboard.

magnetic properties of thin films of ferromagnetic materials. C. A. Neugebauer (GE Research Laboratory) reported measurements of the saturation magnetization and Curie temperatures of thin nickel films below 100A in thickness, and found them to be independent of thickness and equal to the bulk values for thicknesses down to 20A. R. W. Hoffman (Case Institute of Technology) reported measurements of the saturation magnetization of thin iron films and found it to be reduced to about two-thirds the bulk value in 100A films, and to increase with temperature for films less than 100A in thickness. The discrepancy between the measurements on nickel and iron was not resolved in the discussion. D. O. Smith (Lincoln Laboratory, MIT) discussed the anisotropy of Permalloy films, which could be produced by the application of a magnetic field during deposition or by depositing at an angle to the normal to the surface. He found structural elements oriented perpendicular to the easy direction of magnetization. P. E. Tannenwald (Lincoln Laboratory, MIT) discussed spin waves in thin films and showed how they could be used to determine the exchange stiffness. A. Colombani and J. Vaumoron (both University of Caen) discussed Hall effect measurements in thin nickel films, and Hall effect and magnetoresistance effects in bismuth films. H. J. Juretschke (Brooklyn Polytechnic Institute) also discussed Hall effect observations in thin ferromagnetic films and was able to explain some odd variations with magnetization in films magnetized slightly out of line with the easy direction. O. S. Heavens (Royal Holloway College) described measurements of Faraday rotation in thin epitaxially grown single-crystal films of nickel.

Superconducting properties of thin films were discussed. E. C. Crittenden, Jr. (US Naval Postgraduate School) described measurements of critical currents in superconducting films, and found them proportional to film width and to the square root of film thickness. V. L. Newhouse (GE Research Laboratory) emphasized the point that heating effects often were important in determining the limiting currents. M. Tinkham (University of California) described a means for determining the energy gap in superconductors by measuring infrared transmission in 20A films of Pb, Sn, In.

A NUMBER of other subjects were considered at the conference. Beams discussed the mechanical properties of thin films tested by the bulge method, which has been highly refined. W. Shockley (Shockley Transistor Corporation) discussed several properties of the internal interfaces in semiconductors: diffusion of phosphorus along dislocations and grain boundaries, the influence of decorated dislocations on the properties of *p-n* junctions they penetrate, and possible means of measuring the phonon mean free path by means of phonon-drag effects across a *p-n* junction.

To my mind, the most fascinating report of the conference was given by E. W. Müller (Pennsylvania State University) who used field ion microscope studies to reveal the individual atoms in crystalline tungsten needle points. He showed individual atoms, individual dislocations, impurity atoms, lattice vacancies, and the atomic displacements produced by irradiation damage. By counting the lattice vacancies in 71 layers containing a total of about 10 000 atoms, he found a fraction of vacancies in agreement with the number others have derived by indirect means. He studied the surface corrosion caused by a poor vacuum, and found it to extend several atom layers into the tip. The atomic displacements caused by the impingement of a single α-particle were shown.

The final session of the conference was given over to a panel discussion of the theory of surfaces. C. Herring (Bell Telephone Laboratories) chaired the panel, the other members being N. Cabrerra (University of Virginia), V. Heine (University of Cambridge), Juretschke, and Shockley. An hour's spirited questioning and discussion followed the panel's presentation, and the conference closed with a five-minute summary by Fisher, necessarily shorter than this one.