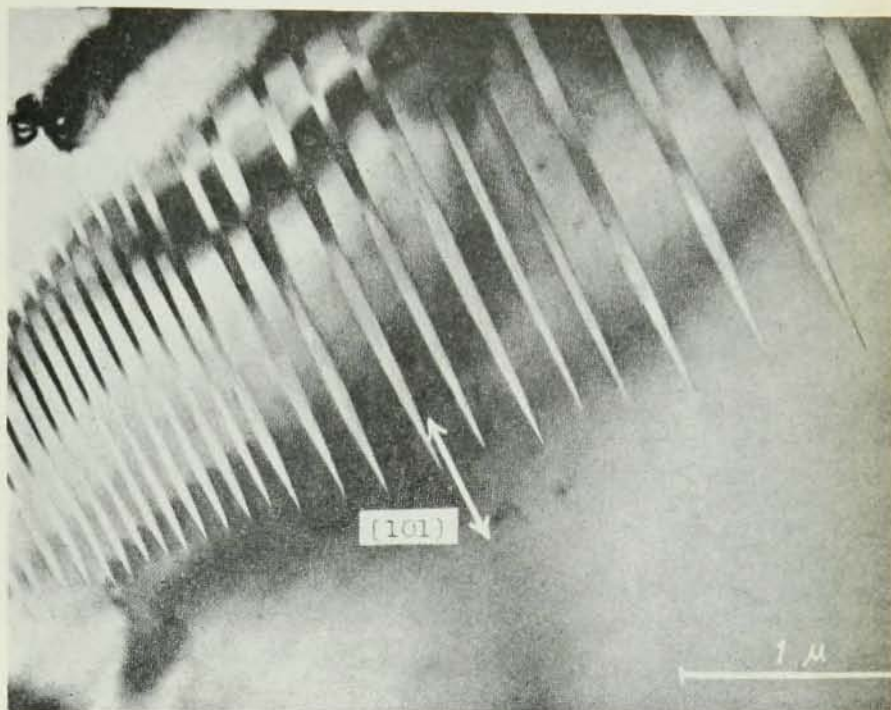


CRYSTALS

Slim Slender Single

A report on a conference on single-crystal films that took place last May at the Philco Scientific Laboratory in Blue Bell, Pa.

By O. S. Heavens



Electron micrograph of film of barium titanate

SOME years ago I found it impossible to refute the irreverent comments of a colleague to the effect that thin films should be considered as belonging to the liquid state, such was their condition of disorder, rather than to the solid state. One had of necessity to admit that the grim reality of the early experimenters' films, deposited at an uncertain rate, in a dirty vacuum (or sputtered), on a substrate of uncertain properties, bore but little

resemblance to the theoretician's concept, deftly represented by two parallel straight lines, of a homogeneous, isotropic, parallel-sided slab of material with nice, well-behaved physical properties. The development of the electron microscope soon enabled one to see just how different was the harsh reality, revealing a depressingly complex system, sensitive alike to method of preparation and nature of substrate, in which particle size, particle shape, crystallographic orientation, and form of grain boundaries represent but a few of the variable factors in the field. The phenomenon of epitaxy is by no means new, having been discussed as far back as 1836. Interest in the phenomenon received a fillip when electron diffraction was discovered in the late twenties. On my last count, as of some six months back, there were 674 distinct examples of epitaxy in films condensed from the vapor phase on to a monocrystalline substrate. Despite this large number, the detailed mechanism underlying the process remains unclear. Quite apart from the interest in epitaxy as a crystal-growth phenomenon, the possibility arises of using the process (even though we may not understand it) as a means of



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Electron diffraction pattern of Au-Ni alloy film grown epitaxially on (100) NaCl inclined several degrees to [001]-zone axis. Extra spots were caused by twin lattices and double diffraction.

A number of scientists from over laboratories presented papers at conference. Among them were (Honjo of the Tokyo Institute of Technology, C. Paparoditis of the Laboratory of Magnetism and Physics of Solids in Bellevue, M. Blackman of the Imperial College of Science and Technology at the University London, and J. H. van der Merwe of the University of Pretoria in South Africa.

producing films which more closely approach the theoretician's delight of a well-behaved, ordered film. It was to bring together those interested in this area of thin-film physics—those dedicated to the belief that such systems *can* possess a state of order justifying their inclusion in the field of solid-state physics—that a meeting was held at the Philco Scientific Laboratory, Blue Bell, Pennsylvania, from May 13 through 15, 1963. Sponsored jointly by the Office of Naval Research, Philco Corporation, Princeton University, and the University of Pennsylvania, the conference, entitled "Single-Crystal Films", was held under the chairmanship of Roman Smoluchowski. The meeting was ably organized by Carlo Bocciarelli and Maurice Francombe in a manner that combined informality with efficiency. Some 150 people attended, thus obviating the need for parallel sessions (in which the two papers which *you* want to hear invariably coincide) and insuring a large enough collision cross section so that one had no difficulty in capturing anyone at some stage.

The conference is the first one to be devoted entirely to single-crystal films; discussions ranged over a wide field, covering the fundamentals of film formation, dependence of film structures on deposition conditions, and the role of dislocations, in addition to reports of studies of the physical prop-

erties of the films formed by the epitaxial process. Electrical, magnetic, and optical properties were reported, on mainly metallic and semiconducting films, and some work on oxidation was described.

Blackman's continuous association with the field of electron diffraction since its inception made him the logical choice for an introductory speaker; his comprehensive review of the background to the subject, with adequate reminders of the many unsolved problems, set the stage admirably for the discussion to follow. In spite of the reminder of the cinefilm results of Bassett, Menter, and Pashley, which show the dramatic mobility of large nuclei during film formation, this feature was unhappily rather quickly forgotten in many of the ensuing discussions. The present state of nucleation theories was presented by Pound in a vein of optimism which was less enthusiastically shared by many of the audience. The tongue-in-cheek (or was it?) provocation in the claim that nucleation theory essentially provides all the answers stung some investigators to defend those experimental results which obstinately refuse to fit into the theoretical picture. One of the difficulties is concerned with the use of microscopic concepts, such as the angle of contact, for an assumed liquid-like drop nucleus, in discussing nuclei consisting of only small numbers of atoms. Except in the case of very high su-

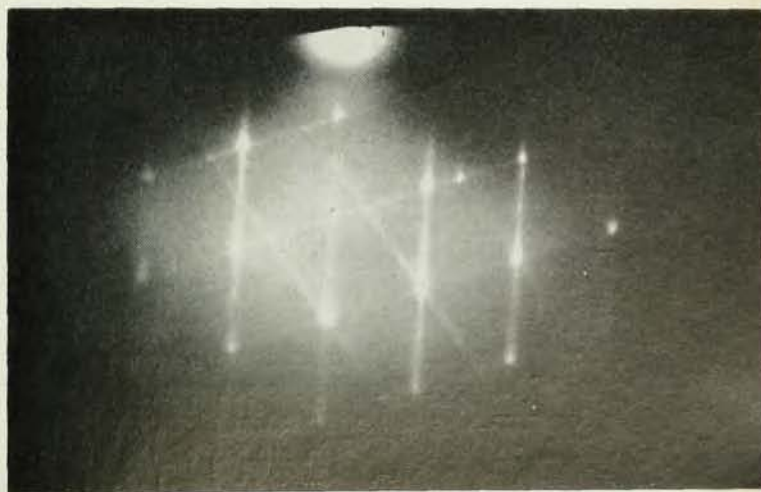


persaturation, such small nuclei may be expected to be the rule in the initial stages of film growth. One of the difficulties associated with the theory of homogeneous nucleation is that this form of nucleation is rare and is believed not to occur in most observed cases of epitaxy. A theory of homogeneous nucleation does, however, form a useful basis of a description of heterogeneous nucleation. The role of the substrate in nucleation, with particular reference to crystallographic registry and interfacial energy, was discussed by Rhodin, who considered the stability of single atoms and of clusters of atoms on the substrate surface. On the basis that nucleation, rather than growth effects, are dominant in determining the orientation observed, it is reasonable to assume that the orientation will be characteristic of that of the most stable group configuration of atoms on the surface. A striking result of Rhodin's analysis is that different configurations of nuclei are stable over different temperature ranges, so that a plot of nucleation rate vs. $1/T$ exhibits a discontinuous change of slope. For Ag on NaCl, the change of slope occurs at a temperature in the neighborhood of the epitaxial temperature, suggesting a possible significance for this sometimes somewhat nebulous quantity. The effects of surface defects on growth are taken into account by the fact that different degrees of supersaturation are required for condensation on different types of defect sites.

Reports on the growth of oriented films on various substrates included the disturbing one from Vook, Schoening, and Witt which revealed a difference in the defect structures of copper films, grown on glass at 2×10^{-9} torr, depending on whether tungsten or tantalum was used as a source-supporting material. Striking features in films of silver telluride, reported by Paparoditis included an almost exact repetitiveness in the detailed crystal form of separate patches of film formed by deposition through an electron microscope grid. A further important feature of these films, which is shared by the results of Zemel and Jensen on PbS,

PbTe, and SnTe, is that the mobilities observed approach those of the bulk material. The latter films were prepared on alkali-halide substrates. One feature of promise in these layers is the feasibility of obtaining layers sufficiently thick for possible application in interferometric devices at wavelengths well beyond the absorption edge. The method of flash evaporation, hitherto generally applied to the evaporation of simple binary materials of which the individual constituents evaporate selectively, has been applied to more complex materials, and Richards, Muller, and Hart report the successful evaporation by this technique of titanates and niobates. In addition, single-crystal films of mixtures of GaAs and GaP may be formed by this process.

The use of decoration techniques as a means of studying nucleation has been in use for some time past. The results of Trillat and Sella show dramatically different decoration patterns between surfaces, depending on whether they have or have not been exposed to air. The temperature at which growth on vacuum-cleaved crystals occurs is found to be significantly lower, by some 200°C , than that for crystals cleaved in air. Similar results were



Indium phosphide grown epitaxially on germanium (111) showing twinning and faulting along (111) axes



Gallium-arsenide film sputtered on germanium substrate

given by Honjo in a paper which showed the remarkable sophistication of Japanese work in the field of electron diffraction, both of a practical and theoretical nature.

The method of preparing films by sputtering has now become quite respectable, as shown by the experiments of Francombe and Khan. From studies of the resistivity of Au-Ni alloys, produced by sputtering and subsequently oxidized, it is seen that the nickel diffuses entirely out of the gold, leaving behind a gold layer of conductivity equal to that of the bulk material. Epitaxial growth of the NiO is observed. In the sputtering of germanium films on to a variety of monocrystalline substrates, the effects of substrate temperature and rate of deposition, investigated by Krikorian, exhibit a triple-point, separating regions of amorphous, polycrystalline, and single-crystal growth, a feature likely to be of considerable interest both from the theoretical and experimental standpoints.

Further development of earlier theoretical work with Frank was discussed by van der Merwe, of Pretoria, in which the role of bonding to the substrate and the effects of stress on the film orientation were considered. Direct experimental evidence of the effects of dislocations on the behavior of diffused films of Au-Pd were given by Matthews. The use of diffused films enables a controllable amount of misfit to be introduced between the upper and lower portions of the substrate.

A remarkable use of epitaxial film techniques is that discussed by Sato in studies of the long period superlattice structures observed in certain alloys. Au-Cu is one of the best known examples of this behavior, which can exist in a form in which

a 40-Å periodicity exists in the "b" direction of the crystal. The influence of varying concentrations of free electrons on the structure has been examined by alloying the film with a variety of materials. The domain size is found to increase as the electron/atom ratio decreases, giving the feasibility of producing an alloy with a predetermined periodicity of superlattice at will. These experiments are made possible only by the fact that, in thin epitaxial film form, the specimen may be produced, with its appropriate additive, in a reasonably short space of time.

In discussions of the electrical and magnetic properties of films (Neugebauer, Heavens, Chopra, Sato) the differences between island structures and continuous films were brought out. In the case of electrical properties, the question arises of whether diffuse or specular reflection occurs at the film boundaries and the available experimental evidence suggests that either (or both) can be expected. Since essentially bulk conductivity can be observed even in films of thickness much less than the mean free path, a high degree of specular reflection is indicated. In annealed polycrystalline films, however, the results generally follow the Fuchs-Sondheimer theory on the basis of diffuse reflection.

In the case of magnetic-properties, a marked dependence is observed on the film structure and many apparently anomalous properties of very thin layers can be ascribed to the discontinuous structure obtained at small thicknesses. The saturation magnetization and Curie temperature of continuous films are found to be independent of thickness (above ~ 100 Å) and the Faraday rotation per unit thickness is likewise independent of film thickness. Measurement on different epitaxial films enables measurements of this type to be carried out in specific crystallographic directions. Progress on the experimental side in this area is steady now that some earlier difficulties, associated with uncertainties in film structure, have been overcome.

There are signs that the realm of thin films, once rudely consigned to that of the liquid state, is one in which substantial progress is being made. For the first time we have the necessary experimental facilities to produce films under controllable, known, clean conditions and can, with the help of epitaxy, make them in specific crystallographic orientations. The means of examination—by electron diffraction and microscopy—enable precise information on structure to be obtained. The highly successful meeting at the Philco Laboratories served to bring out the considerable interest in this rapidly growing field.