a decade of progress in

VACUUM TECHNOLOGY

By H. L. Caswell, W. J. Lange, and L. E. Preuss

The Tenth National Vacuum Symposium, sponsored by the American Vacuum Society, was held on October 16 to 18 in the Statler-Hilton Hotel in Boston. The technical meeting, completing a decade of such symposia, was attended by fifteen hundred scientists, engineers, and related technical people. An additional eight hundred others visited the technical exhibits. The size of this meeting was a far cry from the first such assemblage at Asbury Park, which was sponsored by the originating Committee on Vacuum Techniques. In the intervening ten years since Asbury Park, this symposium has grown about tenfold in size, and the group has become an affiliate of the American Institute of Physics. The national symposium is the one meeting in which the technology of and phenomena associated with vacuum are brought together, reviewed, and the most recent advances discussed.

The 1963 program reflected the current intense growth of interest in the subject. The program could accommodate less than half of the total manuscripts submitted. Over one hundred papers were presented. Special sessions of invited papers were presented on phenomena of sputtering, friction at ultra-high vacuum, freeze-drying, and semiconductor films. The balance of the twelve sessions (contributed papers) dealt with such topics as gauges, sputtering, getter and ion pumps, systems, thin films (preparation and properties), sorption pumping, and cryopumping.

Gauges

The emphasis in the session on gauges was on measurement at very low pressures. Erroneous high pressures can be indicated by Bayard-Alpert ionization gauges under certain conditions, in particular with or following oxygen exposure. An understanding of some of the sources of such anomalies was presented, although complete agreement on relative importance was not yet achieved. The Washington State University group (D. R. Denison, H. F. Winters, E. E. Donaldson) showed that emission of alkali-metal positive ions from the filament can cause an important error in pressure determination in such gauges. The University of Illinois group (W. C. Schuemann, J. L. de Segovia, D. Alpert) attribute the spurious ion-collector currents to ionization and release of gas chemisorbed on the grid or electron collector, a phenomenon which has been studied in some detail by others. W. H. Hayward, R. L. Jepsen (Varian Associates), and P. A. Redhead (Canadian National Research Council) reported on a variation of the relatively old anomaly, the x-ray effect. This effect in ion gauges is due to soft x rays emitted from the electron collector, with the x rays then releasing photoelectrons from the ion collector. These authors described experiments with gauges having conducting walls. In this case, it was shown that indiscriminate choice of ion-collector potential relative to the wall potential can result in photoelectrons from the wall reaching the ion collector. However, proper choice of potentials can lead to a cancellation of the two photoelectron currents, thereby extending the useful range of the gauge. H. I. Smith, Jr. (Air Force Cambridge) reported measurement of sticking times of 500 to 1000 sec for molecules pumped ionically in Bayard-Alpert gauges. Three papers were concerned with gauge calibration. J. C. Simons, Jr. discussed problems associated with establishing calibration standards; F. Feakes and F. L. Torney, Jr. (NRC) compared responses of gauges; and W. D. Davis (GE) re-

---

The authors: H. L. Caswell is a physicist at the IBM Research Center in Yorktown Heights, N. Y.; W. J. Lange is a physicist at the Westinghouse Research Laboratories in Pittsburgh; L. E. Preuss is with the Henry Ford Hospital in Detroit.

The papers presented at the 1963 National Vacuum Symposium have been published in the tenth and last of a series of transactions recording the proceedings of the symposia. Beginning in September, a refereed journal of the American Vacuum Society will be published bimonthly through the American Institute of Physics and will contain many of the papers which, in the past, would have appeared in the transactions.

ported a calibration in the ultrahigh vacuum region based on calculation of pressure using known conductance orifices and MacLeod gauge readings.

A paper by J. R. Young and F. P. Hession (GE) described a cold-cathode gauge for use over the pressure range 10^{-3} to 10^{-14} torr with fairly high sensitivity, yet with ionic pumping speed comparable to the Bayard-Alpert gauge. The gauge utilizes a Penning-type discharge with a filament operated only to initiate the discharge at low pressure. The application of Bayard-Alpert and Redhead-type gauges to measurements in space (aboard Explorer XVII) was reported by G. P. Newton, D. T. Pelz, G. E. Miller, R. Horowitz (NASA). The response of these gauges was most interesting, since the satellite speed was even greater than molecular velocities of the gas being sampled. H. H. Atkinson (Rutherford Lab, England) described a gauge utilizing neutralization of electron space charge by positive ions. The time response of this gauge was shown to be comparatively rapid: e.g., 10^{-4} seconds are required to measure a pressure of 10^{-6} torr.

Pumps and components

The increased use of ionic pumping and gettering in the past few years has given rise to an effort by the manufacturers to gain a better understanding of pumping mechanisms. This was evident from the papers describing experiments aimed at improving pumping characteristics at low pressure, S. L. Rutherford (Varian Associates), increasing speed by incorporation of reactive-metal film gettering, C. F. Brothers, T. Tom, D. F. Munro (Ultek Corporation), improved magnetic field configuration for ion pumps, W. J. Kearns (GE), and understanding of the Penning discharge, W. Knauer and E. R. Stack (Hughes). A paper by H. S. Maddix and M. A. Allen (Microwave Associates) described the removal of inert gases at a quartz surface in an electrodeless discharge at pressures in the 1–10-torr range.

Increased interest in space simulation and hydrocarbon-free pumping systems was reflected in the attention being given to removal of gas by means of sorption. In the case of space simulators, this type of pumping occurs as an added benefit because of the inclusion of cryogenically cooled shrouds in order to simulate radiation conditions in space. J. Hengevoss and E. A. Trendelenburg (Bendix-Balzers) reported measuring removal rates of hydrogen and helium from the gas phase by trapping in or burial under argon simultaneously condensing on a surface at 4.2°K. The maximum rate for hydrogen removal was found to be almost one hydrogen molecule removed per condensing argon atom, while the rate for helium was much less. Two papers were concerned with analytical representation of cryosorption. W. W. Stickney and B. B. Dayton (CVC) analyzed a particular test system which included a 10.2°K surface and compared calculations with experimentally determined pressures. S. M. Kindall (Arnold Air Force Station) presented empirical relationships based on his earlier experimental data.

In hydrocarbon-free pumping systems, sorption pumps are used in place of mechanical fore pumps. In general, liquid-nitrogen-cooled material, such as artificial zeolite, is used. Y. Murakami and H. Okamoto (Tokyo Shibaura Electrical Company) described the use of such molecular-sieve material in connection with analysis of residual gas. By warming the sorbent slowly from −195°C to 300°C, they were able to identify the gases previously sorbed by noting the temperatures at which gas was released. For example, nitrogen was released at a lower temperature than carbon monoxide.

The components session was weighted heavily toward diffusion pumps and performance of systems so pumped. W. M. Langdon and E. G. Fochtman (ITT Research Institute) described backstreaming measurements with baffled oil pumps using a variety of baffle temperatures and pumping fluids. D. L. Stevenson (CVC), on the other hand, was concerned with the effect of nozzle design upon the rate and distribution of backstreaming of oil diffusion pumps. The importance of individual design of successive stages for maximum speed and forepressure tolerance was shown by W. Baechler, R. Clary, and H. Forth (Leybold) if one is to obtain optimum resultant speed and forepressure tolerance in a multistage diffusion pump. B. D. Power, N. T. M. Dennis, and L. de Csernatony (Edwards) reported on results obtained with bakeable systems of somewhat unusual design employing mercury and oil diffusion pumps. M. H. Hablanian and P. L. Vitkus (NRC) presented residual gas analyses for a bakeable six-inch diffusion-pumped system. While the conductance to the mass spectrometer was not ideal, extended time tests did reveal mass peaks characteristic of the pump fluid being used at total pressures of approximately 10^{-9} torr. Two papers from the Princeton Plasma Physics Lab dealt with components peculiar to the requirements of the C Stellarator. G. Lewin and D. Mullaney described a fast-acting valve for admitting a burst of gas into the Stellarator which gives the desired time-spatial distribution of gas. Another requirement of this machine is that the donut be electrically "open". K. Kirchner (Princeton) reported how the large (19-inch diameter, 42-inch long) ceramic section was made. T. H. Batzer and J. F. Ryan (Lawrence Radiation Lab) discussed the performance of a primarily aluminum-alloy ultrahigh-vacuum system. The demountable joints employed common aluminum foil between deformable flanges designed to give high stored energy. The most thorough study of metal gasket seals to date was presented by W. R. Wheeler (Varian Associates). He reported results and comparisons of several designs currently in use, concluding that "capturing" or containment of gasket material is desirable.

Thin films

A special session at the 1963 AVS symposium was devoted to sputtering techniques and the characteristics of sputtered films. Historically, sputtering has been a popular method for depositing thin films because of the simple apparatus required to sputter a wide variety of materials fairly uniformly over large substrates. A minimum of vacuum equipment can be used since the sputtering discharge is normally operated at the "very high" pressure, in terms of today's vacuum standards, of 10^{-2} to 10^{-1} torr. However, the characteristics of films deposited under these minimal conditions have, in general, been nonreproducible and have varied significantly from the results predicted on the basis of bulk data. In recent years, the necessity for precise control of deposition parameters in sputtering experiments has been realized. For example, film contamination caused by active residual gases has been minimized by employing ultrahigh-vacuum techniques which provide a base chamber pressure as low as 10^{-10} torr. Ultrahigh-purity argon is then admitted to a pressure of 10^{-2} to 10^{-1} torr and sputtering performed in an environment free of oxygen and water vapor within an estimated part per million. With improved techniques, the purity of sputtered films has improved rather dramatically as illustrated by the systematic reduction in the room-temperature resistivity of sputtered tantalum films from early values of 50 000 $\mu\Omega$ cm to values near the bulk resistivity of 15 $\mu\Omega$ cm. Even superconducting tantalum films can be prepared which were unheard of several years ago. The old adage that sputtered films are inferior to evaporated films has been disproved as reviewed by M. H. Francombe (Philco). He has found the thickness dependence and substrate temperature dependence of the coercive force in sputtered permalloy films to be similar to that of permalloy films thermally evaporated in ultrahigh vacuum. In some instances, the higher energy (typically 10 eV) of sputtered material may offer an advantage over the lower energy (typically 0.1 eV) of thermally evaporated material. This is particularly true of epitaxial film growth where appreciable substrate mobility is desirable. In fact, high-quality, single-crystal films of germanium and gold have been prepared by sputtering.

One advantage of sputtering is that a variety of materials may be deposited as a thin film which would be difficult to prepare by other techniques. Thus, alloys and compounds can be sputtered without distillation or dissociation; multiple cathodes can be used to sputter simultaneously two or more elements; and films of various compounds can be deposited by sputtering a selected metal in a reactive gas. For example, with the addition of small quantities of nitrogen to the argon sputtering atmosphere, various tantalum nitrides can be formed, as was reviewed by N. Schwartz (BTL). Of interest was the observation that tantalum carbide rather than tantalum oxide is formed upon sputtering tantalum in carbon monoxide. Thermodynamically, the carbide would be expected only at temperatures in excess of 1500°C. This implies that the effective cathode or substrate surface temperature may be very hot, although their nominal temperature is near room temperature.

The momentum-transfer explanation for sputtering as proposed some time ago by Wehner appears to be on very firm ground. His observation that sputtered material from single-crystal targets is ejected preferentially along close-packed directions in the crystal lattice has been verified in several laboratories. Precise measurements are being made on the sputtering threshold energy, velocity of ejected particles, and sputtering yield to provide additional information on the sputtering mechanism, as was indicated by S. P. Wolsky (Mallory). The threshold energy quoted has more often been representative of the measuring technique rather than the material. Thus, as sensitivity has been improved by utilizing spectroscopic and microbalance techniques, values for the sputtering threshold have decreased by a factor of two or more. The decisive experiment is difficult to perform in sputtering because of the large number of variables which must be controlled. But these are precisely the experiments which are required to improve our understanding of the mechanism.

A second subject which received special attention at the symposium was the structure and properties of films formed from semiconductors. There is appreciable interest at the present time in CdS films, both for their semiconducting properties in field-effect and rectifying devices and their photovoltaic properties in optical arrays. This interest was reflected by several papers which dealt with the improvement in film structure and film properties achieved by heat treating polycrystalline CdS films. For example, heat treatment results in a resistivity increase of five orders of magnitude because of crystal growth and reorientation.

R. R. Addiss, Jr. (RCA) reported on his investigations of the intriguing technique due originally to Gilles and Van Cakenberghe for obtaining single-crystal CdS films on noncrystalline substrates. Single-crystal areas up to one centimeter across were formed by depositing a thin layer of silver over the polycrystalline film and heating the substrate to a temperature between 500° and 600°C. Addiss proposed that the CdS-Ag alloy phase formed at high temperature has liquid-like properties which enables appreciable atomic mobility to occur. Measurements of the mechanical stress present in these films demonstrated that the presence of silver allows a film to anneal at a temperature somewhat lower than the critical temperature required for recrystallization. Recrystallization is observed to nucleate at corners and edges of the film, apparently because of surface-energy considerations, and to sweep across the area which has been coated with silver. Unfortunately, the large single crystals contain numerous small-angle grain boundaries which possibly arise from defects in the substrate or film.

The more common technique for growing single-crystal films is that of epitaxy, where the film material is deposited in the correct manner onto a single-crystal substrate. In general, a critical substrate temperature dependent on evaporation rate must be exceeded if epitaxial growth is to occur. It has been speculated that this temperature is also dependent on the vacuum in which the film is prepared. It was, therefore, interesting to hear from B. W. Sloope and C. O. Tiller (Virginia Institute for Scientific Research) that this critical temperature is essentially the same for films deposited at 7×10^{-9} torr or 7×10^{-6} torr. Moreover, the density of defects was not appreciably altered by pressure variations within this range.

The electrical characteristics of semiconducting films are, of course, structure dependent with the conductivity and mobility increasing with improved crystal structure. The mobility achieved in high-quality Ge films is approximately one-third that of pure single-crystal bulk material. Evaporated germanium films to date have always been strongly *p*-type. J. E. Davey and M. D. Montgomery (US Naval Research Laboratory) have shown that boron contamination originating from borosilicate glass may convert *n*-type material to *p*-type prior to evaporation. However, even after steps were taken to maintain the purity of the evaporant, thin films were found to be *p*-type, which suggests that defects in the film are the principal source of hole-type conduction.

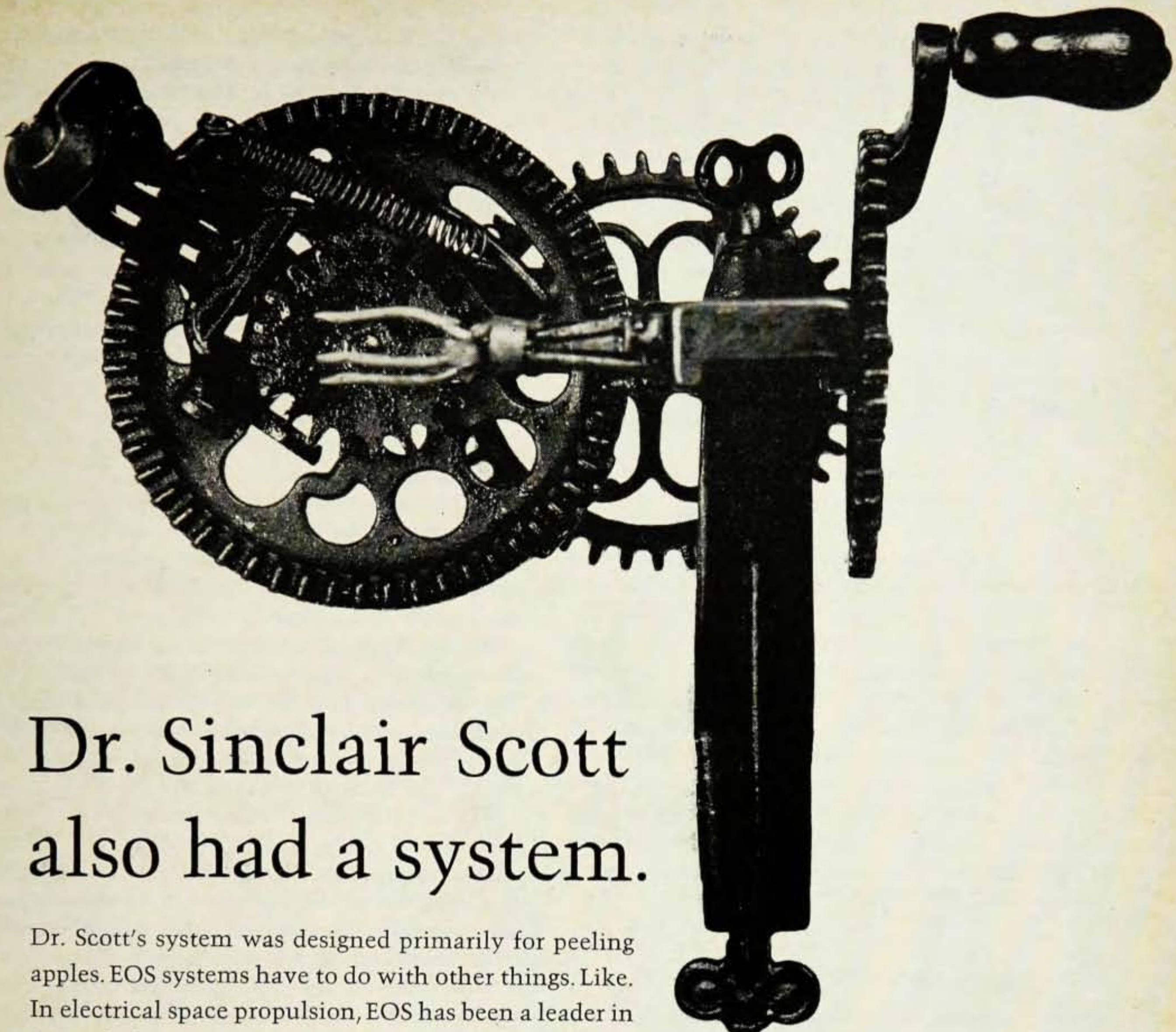
Many thin-film investigations have as their motivation various microelectronic applications. Rather elaborate apparatus is required to shift substrates, evaporation sources, and deposition masks in evaporators fabricating multilayer devices, and to control deposition parameters such as evaporation rate and film uniformity over the substrate. Several papers describing novel evaporation apparatus were presented at the symposium. The trend toward automation with elimination of human variation and error is strong, as evidenced by the avid attention given a commercial display of quartz-crystal rate-monitoring equipment which permits one to select an evaporation rate, choose a film thickness, and press a button to obtain the desired film. This is an important step in the thin-film field, since it is only through the use of automatic equipment that practical thin-film devices can be fabricated economically.

Friday afternoon saw the second session on thin film properties moderated by M. Francombe (Philco). M. Onchi (Kyoto University, Japan) discussed the adsorption of gases on cadmium films and showed that the resistance change is a linear relationship over a large range.

J. Dillon and R. Oman (Brown University), in this same session, utilized UHV for cleavage and bombardment studies and as a basic approach to work function and its dependence upon lattice defects. Interestingly, Dillon demonstrated how the work function, or photoelectric threshold, is strongly related to the surface-defect structure. He suggested that, by extension of this work, it may be possible to develop a better understanding of the lattice defects and the work function as it is influenced by the defects.

Also at this session, J. Nickerson and P. Goldberg (G T & E) discussed their preparation of thin electroluminescent films of ZnS:Cu by the evaporation of mixtures of ZnS:Cu, Cl-ZnS, which were deposited upon SnO_2. The substrates were rendered luminescent without breaking vacuum. They showed that the Cu is the critical variable and that it influences the crystallinity, conductivity, and luminescence of the substrate.

A paper on composition of thin films by H. Degenhart and I. Pratt (Army Electronics R & D Lab, Fort Monmouth) added some quantitative



data on vacuum-produced Ni-Cr thin films. They showed some new correlations between resistivity and thickness as well as with composition ratios. These authors postulated that the metal oxides were a factor in the change in resistivity.

P. della Porta and T. Giorgi (SAES, Italy) reported on their study of residual methane in sealed systems with Ba. Although della Porta agreed that Almer's postulate was admissible for the formation of hydrocarbons at low pressure (i.e., the reaction $BaC_2 + H_2O \rightarrow C_2H_2 + BaO$), he favored the theory of surface-reaction phenomena, represented by various hydrocarbon radicals chemisorbed on the Ba surface. He showed that variably saturated hydrocarbons with one, two, or three (and more) carbons are produced under his experimental conditions when Ba films encounter CO and are subjected to thermal treatments.

A. F. and E. E. Kaspaul (Erie Technological Products) presented a rather tantalizing extension of earlier work by others on the sensitization phenomena. Kaspaul showed some of the better known *prenucleation* techniques and then briefly introduced some intriguing extensions by demonstrating sensitization with water vapor on $BaSO_4$ and ZnO substrates and with ion beams. He brought out the powerful nature of the technique, as well as describing the reversal process reported earlier. Some of the propositions for this mechanism are interesting and caused the audience to call for a future detailed report on these surface condensation phenomena.

Friction and cleavage studies at UHV

A special session with three invited speakers was devoted to friction and surface-to-surface phenomena in UHV. The first invited presentation, by R. Parcel, F. Clauss, and C. O'Hara (Lockheed) was concerned with lubrication in space systems. The experimental pressures varied between 10^{-6} and 10^{-10} torr. The results of R. W. Parcel's work, designed for space operations, appears to be applicable to the laboratory as well. Best lubricant operation was observed for oils and greases. Dry-film lubricants and self-lubricants showed much shorter lifetimes and reproducibility. The greases were silicone oil base, and they were still operating after one year of testing at the above pressures. Significantly, very slight pressurization due to enclosure produced an increased lubrication period. An interesting aspect of this was the discovery of the beneficial effects of very small amounts of oil vapor in this system. Diffusion-pump oil backstreaming was clearly shown to decrease slip-ring friction, even though it appeared in very tenuous amounts. This finding, interestingly, was made simply by raising the nitrogen-trap temperatures.

Polytetrafluoroethylene compositions proved to be the best self-lubricating materials. Of the silicones, fluorosilicone oil and chlorophenyl methylpolysiloxane provided lubrication in vacuum for over 13 000 hours.

Sliding electrical contacts were studied at pressures of 10^{-8} torr. Significantly, it was found that partial pressures of silicone oil no greater than 10^{-8} torr produced significant improvements in lowered electrical noise levels. Solid lubricants (MoS_2) were studied, but low-vapor-pressure lubrication by oils (as above) outweighed the effect of surface and metal combinations in reduction of the friction coefficient.

A. J. Haltner (GE) also discussed friction determinations. He carried out a study of the coefficient of friction for various materials at pressures of 10^{-9} and 10^{-10} torr. The experimental mechanism was especially interesting in that he measured the angle of repose by a system in which the specimen under test rested on a tilted wire in the vacuum system. Haltner established that MoS_2 coefficients of friction were the same at 10^{-6} torr as at 10^{-10} torr, thus corroborating the work of Johnson and Vaughn in this area.

Haltner also showed that the substances under test released gas on sliding in this system. The gas release appears to be dependent upon the speed of sliding and at 10^{-9} torr was a serious source of gas evolution. Interestingly, this corroborates the related work done by Groskowski (Poland) and reported on at the 1961 International Vacuum Conference at Washington, D.C., in which he demonstrated this same phenomenon when a surface was abraded in vacuum.

P. Bryant (Midwest Research Institute) read a paper on cleavage of lamellar materials, which elicited a good deal of interest and discussion, both because of its fundamental approach and the possible extension to solid lubrication processes, as well as for the rather fascinating experimental design. Bryant used muscovite and some other related materials to study the interlamellar binding energies and stress-etch effects. Using UHV and various gas environments, his study has provided a basis for the general mechanism of lamellar solid lubrication, through the cleavage process. Bryant was able to show, in controlled stress-etch experiments, that water-vapor molecules are responsible for the reduction of binding energy between cleaved mica layers. He also calculated the surface energy of ionically bonded lamellar crystals and applied this to muscovite. These theoretical values were then applied to his experimental work to show the validity of the high-binding-energy measurements and of the stress-etch process.

High-dosage radiation effects on vacuum systems

J. C. Heindl and R. Belanger (Space Technology Labs) presented some new information on the use of MoS_2 and silver sintered mixtures for lubrication of bearing surfaces, under UHV conditions, a subject of some concern as the need grows to introduce complex motion into very-low-pressure systems. Excessive wear and cold welding, common at these pressures, appeared to be absent.

A systems paper by E. Kerlin, C. Morgan, and J. Warwick (General Dynamics), following the invited papers, was stimulating in that it demonstrated that a diffusion pump set-up, operating a bit below 10^{-6} torr, could be used in conjunction with the high radiation fields of a nuclear reactor (the GD/FW Ground Test Reactor). Significantly, Kerlin was able to show that predictions of radiation effects on the organics (oils, gaskets), extrapolated from the air radiation environment to the vacuum-radiation environments were not always valid. The vacuum-radiation effects *were* different.

Techniques

The final Friday afternoon session included papers on a variety of materials and techniques. J. H. Singleton (Westinghouse) described some results in Teflon-coated systems using flash-filament studies as a measure of the degree of adsorbed gas coverage on the walls. Both calculated and experimental results on a differentially pumped system of narrow slots were given by E. Donath (IBM). B. R. F. Kendall (Nuclide Corporation) reported means for simultaneously recording peak heights versus time for any peaks present in a mass spectrum. Examples were given for rapid changes in gas composition occurring during desorption. N. Milleron (Lawrence Radiation Lab) described a technique for leak detection using the change in light emitted from a Penning discharge upon introduction of a foreign gas.

H. Kobayashi (Nippon Electric, Japan) solved the problem of leak detection and pressure measurement in image orthicons by using their electron multipliers as ionization gauges. D. H. Holkeboer (Aero Vac) discussed measurement of the gas-flux density and distribution on a test piece, emphasizing that it may be different from the flux on the chamber wall.