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APPLICATIONS OF ION BEAMS TO MODIFY THE PROPERTIES OF MATERIALS
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APPLICATIONS OF ION BEAMS TO MODIFY  
THE PROPERTIES OF MATERIALS

by

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The increasing number of applications of ion beams to the modification of the properties of materials has led to several international conferences on this specialized subject. The most recent such conference, "The Application of Ion Beams to Materials" was held at the University of Warwick in England, 8-12 September 1975. The conference, sponsored by the Institute of Physics, was attended by 175 persons from 18 countries, including a delegation of nine scientists from the People's Republic of China. The 65 papers presented covered the applications of ion beams to semiconductors, insulators, and metals; and included studies of radiation damage.

Ion implantation involves (i) ionizing the desired species of atom, (ii) accelerating these ions to high speeds by an electric field, and (iii) then driving them into the desired substrate, for the purpose of modifying the physical or chemical properties of the host material. Ion speeds usually lie within the range  $10^{-2}$  to  $1$  of the speed of light; deposition depths are usually within the range  $10^2$  Å to  $10^4$  Å, and local relative concentrations of the implanted ion might range from trace amounts to values as high as perhaps 50%.

The modified properties might be electrical, optical, chemical, or mechanical. For example, ion implantation may be used to modify a material's charge-carrier concentration, its index of refraction, its corrosion resistance, or its surface hardness. The solid may be crystalline, polycrystalline, or amorphous. Because of the statistical nature of the collision process, as the ions slow down and stop in the material, the distribution of implanted ions in the host material has, to a first approximation, a relatively broad gaussian shape.

The first session was opened by K. A. Pickar (Bell Northern Research, Ottawa, Canada) who pointed out that ion implantation is now widely used commercially for producing many kinds of solid state electronic devices and that the main reasons for its commercial acceptance are the accurate control on the number of implanted impurity atoms and the adjustable and well-defined depth distribution profile which can be achieved. Three applications, discussed in some detail, were (i) the threshold adjustment of MOS (metal oxide semiconductor) transistors through accurate control of the number of implanted dopant atoms, (ii) the use of ion implantation for producing buried channel charge coupled devices (CCDs), and (iii) conductively connected CCDs. The

speaker speculated that although the past has been characterized by the application of ion implantation to devices difficult or impossible to fabricate in other ways, in the future, ion implantation will be increasingly substituted for diffusion processes and may provide possibilities for eliminating such wet chemistry steps as etching, cleaning, and photolithography. To make such applications practical he cautioned, however, that it will be necessary to understand more thoroughly the damage produced during implantation and its effects during subsequent annealing than we do at the present time.

Several of the papers dealt with the general topics of damage annealing and impurity depth profiles and migration mechanisms. Thus H. Ryssel, H. Kranz, and P. Eichinger (Institute of Solid State Physics, Munich, Germany) discussed the use of high current densities of hydrogen beams to obtain radiation enhanced diffusion of arsenic in silicon; they measured thereby a diffusion coefficient three orders of magnitude larger than normal. K. Yokota and co-workers (the Universities of Kansai, Osaka, and Kyoto, Japan) reported that the diffusion of arsenic implanted into boron-doped silicon depends on the boron concentration and that deeper arsenic diffusion depths correspond to higher boron concentrations. They proposed, as a possible explanation of their results, that arsenic-boron pairs are formed and that these pairs have a lower activation energy for migration than the arsenic atom alone. W. K. Hofker and his collaborators (Philips Research Laboratories, Eindhoven, Netherlands) reported that the lattice stress produced by an implantation is relieved if the implanted dose is sufficiently high and that thermal diffusion during annealing of implanted layers is influenced both by lattice strain and damage. To minimize redistribution in the case of double doping, they suggested that the first implantation be the one that produces the most damage.

The second session was opened by P. L. Hemment (University of Surrey, Guildford, England) who discussed ion implantation into compound semiconductors. Hemment concentrated on gallium arsenide since this is a compound which is currently being intensely studied. Examples given of successful fabrication applications of ion implantation were infrared detectors, light emitting diodes, lasers, field effect transistors (FET), and IMPATT diodes. Successful fabrication was reported also for a GUNN-effect diode which can operate at 35 GHz. Gallium arsenide is now starting to compete with silicon for FET fabrication. A particular advantage of ion implantation for compound semiconductors was stated to be that, by this means, doping can be achieved at low temperatures; the temperatures required for thermal diffusion, on the other hand, can decompose some of the compounds of interest. One interesting technique mentioned was that of implanting gallium and selenium simultaneously into gallium arsenide as a possible way of making up for the gallium that can be lost during processing. Dual implantation into gallium arsenide was discussed in greater detail and for other combinations of ions by

T. Ambridge and co-workers (Post Office Research Laboratories, London and the University of Surrey, Guildford, England).  $\text{GaAs}_{1-x}\text{P}_x$  light-emitting diodes with extremely high efficiency, produced by zinc implantations, were reported by Y. Shiraki and his associates (Central Research Laboratory, Hitachi Limited, Tokyo, Japan). The relative efficiency obtained by these investigators was approximately twice as large as has been obtained with thermal diffusion. The emitted light was produced over a much wider region of the p-layer than occurs in the usual diode.

In a session on ion implantation applications to insulators, T. J. Magee and M. Lehmann (Stanford Research Institute, Menlo Park, California--research supported by ONR) reported on the production of room temperature information storage centers in sodium fluoride crystals by high energy boron and lithium implantations. The authors stated that ion implantation can be used to produce very thin storage layers, a characteristic that is desirable for the storage of microimages and holograms. In a series of experiments to ascertain whether abrasion and corrosion resistant glass surfaces can be formed by ion implantation, G. W. Arnold and J. A. Borders (Sandia Laboratories, Albuquerque, New Mexico) implanted silver and gold ions into lithia-alumina-silica glass. The implanted gold was found, upon annealing, to form colloids 20-30 Å in diameter which were immobile and which produced nucleation and crystallization of the glass. Micro-hardness measurements then indicated that glass ceramic had been formed. The silver, on the other hand, diffused much more rapidly and was not effective in producing nucleation and crystallization.

W. A. Grant (University of Salford, Salford, England) in a paper entitled, "Surface Chemistry of Ion Implanted Solids," reviewed such topics as aqueous corrosion, anodic and thermal oxidation, chemical synthesis, and catalysis. With respect to aqueous corrosion, Grant reported on a number of metals and alloys which showed improved passivation as a result of ion implantation. A significant finding for the application of ion implantation to the passivation of metals is that, in general, an ion implanted alloy with a certain surface composition behaves like the bulk alloy with the same composition. In oxidation studies, it has been found that the relative effectiveness of an implanted atom for either inhibiting or enhancing oxidation correlates with electronegativity. In some cases, measurements have shown that the implanted atom species has a tendency to stay at the metal-metal oxide interface, thereby providing much longer protection than the shallow implantation depth would otherwise be expected to provide. Grant cautioned his audience that oxidation can occur during the implantation process itself because the supply of oxygen in most implantation vacuum systems is adequate to support such oxidation and that the reduced oxidation rate due to

the oxide already present may be confused with ion implantation passivation. In chemical synthesis, it was suggested that ion implantation should be capable of producing both conventional and unconventional compounds. An entirely new range of heteronuclear metal carbonyls may, for example, be produced in this way. As another example, electron diffraction measurements on implantations of carbon, nitrogen, phosphorous, and arsenic into aluminum showed that all the known binary compounds were formed with lattice parameters that agreed with the known values. For boron implantations, however, the diffraction pattern could not be identified with known borides, and it was proposed that an unknown boride,  $Al_xB_y$ , with  $y/x < 2$  was formed. In chemical synthesis applications, the sputtering that occurs during ion implantation will limit the amount of material that can be treated. In catalysis also, Grant was of the opinion that ion implantation has an important role to play. For solid catalysts particularly, since catalytic activity changes rapidly with composition, the ability to produce varying controlled surface compositions with ion implantation may be expected to be a significant advantage. Another interesting possibility is that scarce metals such as platinum can be conserved by implanting the surface instead of dispersing the metal throughout the host matrix. (The same comment applies to the use of chromium in steels to reduce oxidation.) The conditions under which ion implanted platinum can exhibit catalytic activity are not yet understood, but positive results have been obtained with implantations into pyrolytic carbon and into titanium.

Results from a continuing study of the influence of ion implantation on thermal oxidation of titanium were presented by J. D. Benjamin and G. Dearnaley (AERE, Harwell, England). In the latest experiments, an additional eleven elements were implanted into titanium to determine the effects of ion size and to test the previously found correlation with electronegativity. It was found that electronegativity does correlate with oxidation behavior, whereas valency does so only poorly. The experiments showed also that the dominant factor can be the interaction of implanted atoms and oxygen in such short circuit diffusion paths as grain boundaries; radiation damage can also provide short circuit diffusion paths. Thus it was postulated that the diffusion of the implanted atoms along grain boundaries blocks these paths to diffusion and thereby inhibits oxidation. Because grain boundary diffusion is generally much more rapid than bulk diffusion, an important consequence of these results is that it may be possible to protect titanium to a depth of as much as 100  $\mu\text{m}$  by following ion implantation with an appropriate heat treatment. In a related paper, S. Muhl and R. A. Collins (University of Lancaster, England) and G. Dearnaley (AERE, Harwell) pointed out that chemical effects, radiation damage, and stress are all major factors affecting oxidation behavior after ion implantation, with

chemical effects being relatively more important at low implantation doses and stress effects being more important at high doses. Studies of the surface chemistry of ion implanted tantalum, a metal used in hybrid circuits for making resistors and capacitor dielectrics, were reported by I. H. Wilson and co-workers (University of Surrey, Guildford, England). The study concluded that films of unique properties can be made by ion implantation but that the analysis of the electrical properties is complex because of the effects of sputtering and nonuniform doping. Diffraction studies of nitrogen implanted films showed the precipitation of hexagonal platelets of  $Ta_4N_5$ , a compound that has not been produced by ordinary chemical means.

B. Stritzker (Institute for Solid State Physics, Jülich, Germany) reviewed the applications of ion implantation to superconductors. He pointed out that it is known that the instability of an alloy and high critical temperature ( $T_c$ ) are correlated, so the search for metastable alloys can be very important. Ion implantation can be useful in this connection, both because it may be a way of producing metastable alloys at low temperatures and because it can simplify the preparation of alloys for a systematic investigation of a large number of alloys. Some of the results obtained to date by ion implantation are the formation of  $Nb_3Sn$ , the addition of carbon to  $NbC_{.39}$ , which gave a  $T_c$  of 12.5 K, and the formation, at liquid helium temperatures, of  $PdH$  with a  $T_c$  of 9 K. The latter is an example of an alloy which cannot be produced at room temperature; it was produced by implanting  $3 \times 10^{17}$  hydrogen atoms per square centimeter into  $PdH_{.74}$ , a compound which is not a superconductor. O. Meyer (Center for Nuclear Investigations, Karlsruhe) reported that implantations of nitrogen, carbon, sulfur, and phosphorous at liquid helium temperatures into thin films of molybdenum raised  $T_c$  from the value of  $\leq 1.2$  K for pure molybdenum to values of 9.5, 9.6, 9.8, and 9.6 K respectively. These values are several degrees higher than have been observed for similar systems produced by implantation at room temperature.  $T_c$  was found to increase with increasing implanted atom concentration up to a local value of about 15%. The explanation for the increase in  $T_c$  which was proposed was that the molybdenum electronic energy levels were being affected by the lattice stresses produced by the implantations. Further results on the effects of lattice distortions and micro-defects were presented by A. M. Lamoise and co-workers (University of Paris-South, Orsay, France) and J. M. Poate and co-workers (Bell Laboratories, Murray Hill, New Jersey). In the latter paper results obtained from bombardment of 2,000-Å thick  $Nb_3Ge$  films with 2-MeV helium ions showed that, as the film is damaged, the lattice parameter increases from 5.138 Å to about 5.19 Å and makes the thin film more like the bulk material; correspondingly,  $T_c$  decreases from the high value characteristic of thin films to the lower value characteristic of bulk  $Nb_3Ge$ .

S. T. Picraux (Sandia Laboratories, Albuquerque, New Mexico) spoke on "Implantation Metallurgy," summarizing the advantages of ion implantation for this application. He also listed the microscopic metallurgical parameters which need to be better understood so that this technique can be used to tailor metal alloys or to produce alloys which cannot be produced by normal metallurgical methods. The shallow penetration depth of implanted ions was cited, for example, as being particularly well suited for studying phenomena which are surface-controlled. In addition, the intimate mixture between the host metal and the implanted atoms was mentioned as leading to reduced reaction times and to the achievement of reactions at lower temperatures than would otherwise be possible. Also discussed were possibilities of bypassing some alloy phases and forming entirely new phases either through careful control of local concentration ratios or because of the athermal introduction of atoms and defects which is characteristic of ion implantation. The relevant microscopic parameters which were studied and discussed were the local environment, that is the lattice location and defect structure in which the implanted atom finds itself, and the mechanisms of diffusion, including radiation enhanced diffusion, and precipitation, nucleation and dissolution. A number of results were discussed which showed the complex ways in which these parameters can interact and affect each other. D. K. Sood and G. Dearnaley (AERE, Harwell, England) presented the results of a study of the implantation into copper and aluminum single crystals of ions which were either immiscible or had very small expected solid solubilities. In many cases the solid solubilities were measured to be much larger than the expected values. The Hume-Rothery rules for alloy formation were found to be violated by copper but obeyed well by aluminum. The importance of compressive stresses, produced by implantation, on the migration of vacancies and interstitials and on the formation of precipitates was emphasized. Thus, for a 200-keV implantation of tantalum into copper, backscattering and channeling measurements with helium ions showed that the disordered region extended to a depth of about 4,000 Å, a value which is twenty times the mean penetration range. This large disorder depth was ascribed to the action of the large compressive stress in the implanted region. J. A. Borders (Sandia Laboratories, Albuquerque, New Mexico) and A. G. Cullis and J. M. Poate (Bell Laboratories, Murray Hill, New Jersey) reported on the lattice locations of tungsten implanted into copper. These authors found that even though these two elements were expected to be immiscible, for concentrations of  $\leq 1$  at.% tungsten, it is possible to form stable substitutional solid solutions which, upon annealing, yield tungsten precipitates. For concentrations  $\geq 10$  at.%, the tungsten occupies random sites and again forms substantial numbers of metallic precipitates upon annealing.

N.E.W. Hartley (AERE, Harwell, England) introduced yet another new and rapidly developing application area for ion implantation; namely, its use for affecting the friction and wear properties of metal

surfaces. Improvements in wear and reductions in friction were found, in the studies discussed, to be dependent on the species of atom implanted. A phenomenological model was proposed in which ion size and solubility are the dominant factors influencing the plasticity or hardness of surface asperities. The asperities then affect the efficiency of the liquid lubricant used during wear measurements and, as a result, also the amount of wear which occurs. Surface stresses, chemical corrosion processes, and the effects of the implanted ion on local plasticity were all found to be factors which could affect friction and wear properties. One example given of the large effects that can be obtained in some cases was the reduction of wear by a factor of thirty which was produced by the implantation of 400-keV Mo into 440 C mild steel. Friction also has been reduced by ion implantation, in some cases by as much as a factor of two. In summary, ion implantation was presented as a powerful tool for tribological studies and as being potentially of major technological importance in friction and wear applications.

Because of collisions between an energetic incident ion and lattice atoms while the incident ion is slowing down, radiation damage is produced in the host material. This damage is qualitative, similar to that produced by fast reactor neutrons but is much more intense in terms of atoms displaced per unit volume per unit time. With a heavy ion irradiation it is possible therefore to simulate, in less than an hour, an amount of damage which would take a year or more in a reactor. Such irradiations therefore make it possible to survey the susceptibility of many different alloys to radiation damage. J. H. Rosolowski (General Electric Corporate Research and Development Center, Schenectady, New York) traced the history of research on voids and swelling in irradiated metals, from the discovery of these phenomena in stainless steel at the Dounreay fast reactor in 1966 and the recognition of swelling as a potentially critical problem for fast breeder reactors, through the development of heavy ion damage simulation for studying this problem, to the most recent results which show how swelling depends on alloy composition impurities and microstructure. The potential magnitude of the effect can be appreciated from a case, observed by the speaker, of a 120% swelling!

Although the composition range for stainless steel which will have low swelling is now known (high nickel and low chromium contents), a search for specific alloys which will have all the other required properties still must be made. D. J. Mazey (AERE, Harwell, England) discussed results obtained in aluminum and aluminum magnesium alloys after irradiation with 100- and 400-keV aluminum ions. In this work, it was found that voids could be produced quite readily in pure aluminum, with peak swelling occurring at 150 °C, but could not

be produced, even at very high levels of atomic displacement, in the aluminum magnesium alloy. B. Evans (Naval Research Laboratory, Washington, D.C.), in discussing his work with heavy ion damage produced in magnesium and aluminum oxides, pointed out that very little work has been done on neutron damage mechanisms in insulators. In magnesium oxide, optical absorption and electron spin resonance studies of defects showed that direct atomic displacement was the primary damage mechanism, with only one out of seven vacancies produced at room temperature surviving. The use of 4-MeV protons for studying irradiation induced creep in metals, also a serious problem area for fast breeder reactors, was reported by J. A. Hudson and R. S. Nelson (AERE, Harwell, England) and R. J. McElroy (University of Oxford, Oxford, England). Preliminary results were presented for the irradiation creep behavior of annealed nickel in the temperature range 400-600 °C under tensile stresses in the range 20-100 MPa. The creep exhibited a logarithmic dose dependence, and the creep rate was found to have two components: irradiation enhanced creep and irradiation hardening, both of which were dependent on dose, dose rate, and temperature. In these experiments the damage production rate is not greatly different from that which occurs in reactors, but the experimental parameters can be controlled and adjusted much better than can be done in reactor irradiations.

An ion moving along certain preferred directions within a single crystal experiences substantially reduced interactions with the lattice atoms. This effect, which is called channeling, has proven to be a powerful tool for studying defects in crystals. A number of papers dealt with damage studies based on channeling measurements as well as on the more common transmission electron microscopy. In a paper dealing with the implantation of group IB elements into silicon, L. T. Chadderton and co-workers (Oersted Institute, Copenhagen, Denmark) reported that the way in which damage anneals away is still not well understood. Even after a 1,000 °C anneal, for example, Rutherford backscattering measurements combined with the channeling effect showed six times as much residual damage in implanted regions as in unimplanted regions.

Limitations on the spatial uniformity and the accuracy of the implanted dose were discussed in a paper by J. K. Freeman (AERE, Harwell, England). For systems which use electrostatic scanning, the speaker pointed out, for example, that a 1% neutral beam component and a 10-to-1 scan ratio will lead to a 100% non-uniformity of the implanted dose. Two factors mentioned as affecting the accuracy with which the implanted dose can be determined were the sputtering away of the sample surface during implantation and the reflection of the incident beam by scattering. Thus, a 3% dose inaccuracy due to sputtering can occur for 50-keV phosphorus atoms implanted into silicon at a dose of  $10^{15}$  atoms per square centimeter. For boron implantations into silicon, reflection can produce a 5% effect.

The last two sessions of the conference dealt with ion trapping and agglomeration, with emphasis placed on gas bubble formation and blistering caused by high dose implantations of hydrogen and helium into metals. J. Roth (Max Planck Institute for Plasma Physics, Garching, Germany), in a review of this area, discussed such topics as the doses at which bubbles are formed and the effects on bubble size of the incident beam energy and incident angle. S. K. Das, M. Kaminsky, and G. Fenske (Argonne National Laboratory, Argonne, Illinois) reported on the correlation between blister skin thickness, the maximum in the deposited energy distribution, and the projected ranges of helium ions in aluminum, vanadium, and niobium. They found that for vanadium and niobium, skin thicknesses fell within 20% of calculations but that for aluminum, the measured thicknesses were 20% too low. Bubble formation and blister breaking were also found to behave differently at different temperatures. J. H. Evans and co-workers (AERE, Harwell, England), using transmission electron microscopy to study 25-60-keV helium ion bombardments of molybdenum, reported that the transition from high density small bubbles to a blister seems to be very rapid. They could detect bubbles as small as  $20 \text{ \AA}$  in diameter and observed bubble densities as high as  $1.5 \times 10^{19}$  per cubic centimeter.

Materials of interest for fusion reactor first wall applications were discussed in the final conference session. J. F. Ziegler and J. J. Cuomo (IBM Research, Yorktown Heights, New York) reported on sputtering and blistering studies of tungsten made with  $^4\text{He}$  ions in the range from 2 to 8 keV. The surfaces studied were highly polished tungsten surfaces and the same surfaces covered with tungsten whiskers of heights ranging from 5 to 80 microns. The sputtering of the nonplanar (dendritic) surface was the lowest for any metal surface observed to date and was about three to five times lower than for the planar surface. In addition, for  $^4\text{He}$  doses of  $2 \times 10^{19}$  atoms per square centimeter, no blistering or other microscopic material ejection was observed on the dendritic samples in contrast to the pitted/blistered surfaces of the polished samples. The gas release from low Z materials (which included the insulators silicon nitride, silica, and alumina) was reported on by S. K. Ehrents (Culham Laboratory, Abingdon, England), and results from studies of helium implantation effects in pyrolytic and bulk graphites and carbon composites were reported by W. Bauer and G. J. Thomas (Sandia Laboratories, Livermore, California).

The proceedings of the conference will be published by the Institute of Physics, 47 Belgrave Square, London SW1X 8QX.