Implantation of Gold Ions

ITS POTENTIAL FOR MODIFYING THE PROPERTIES OF SURFACES

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Implantation of gold ions in metals and alloys offers an exciting means of generating new types of surfaces. Data concerning such implantation and its effects are presented in this article.

Many materials are coated with gold, and a large number of processes is available for doing this. They include electroplating, evaporation, sputtering, and the recently developed technique of ion plating (1). Ion implantation is a newer and so far untried method for impregnating surfaces with gold. The technique of implantation differs fundamentally from all other methods in that ions are accelerated onto the target material and penetrate its surface, so that no boundary exists between the gold and the host material. Further, the gold ions as they penetrate the target collide with the atoms of this material and leave intense trails of radiation damage behind them. This damage gives properties to the surface quite different from those of an ordinary plated surface. The process is unavoidably accompanied by sputtering and both target material and newly implanted gold atoms are removed from the surface during ion implantation.

The removal of material by sputtering sets an upper limit to the surface concentration of gold and the maximum value obtainable can be shown to be approximately equal to 1/S, where S is the sputtering coefficient or number of target atoms sputtered per incident ion. The value of S depends upon the target material and the energy of the gold ions. Because it is a massive atom, gold has a high sputtering coefficient lying between about 3 and 50 in the energy range likely to be of most interest. Clearly, high concentrations of gold atoms cannot be expected to result from straight implantation but it is very likely that, in spite of this limitation, surfaces with very exciting new properties can be formed. Moreover, as will be discussed later, higher surface concentrations can be obtained by recoil implantation and this method may be particularly important for gold.

The list of surface characteristics that can be changed by ion implantation is a lengthy one. It includes:

hardness	corrosion resistance
wear resistance	catalytic activity
adhesive properties	electrical conductivity
tribological properties	superconductivity
fatigue resistance	appearance

There is no limit to the combinations of materials that can be generated because the process does not depend on solubility relationships or on the adhesion of one material to another. It is to be expected, therefore, that in some instances implanting gold will result in a surface possessing useful characteristics. For example, in almost all cases it would be surprising if implanted gold did not impart some of its chemical inertness to the surface of the substrate.

Although ion implantation can be carried out only in a vacuum chamber where the ions can move freely, this complication is offset by the fact that dimensional changes and bulk heating effects in the substrate are avoided.

There has been sufficient basic research work with many substances, and particularly with semiconductors where it has found its first major industrial applications, to show that exciting new materials can be created by ion implantation. There is, however, no longer any valid reason why the use of the technique should be limited to this area. Intense ion beams of many elements can now be generated on a reasonably cost-effective basis, and one of these elements is gold.

Range

Perhaps the most important parameter in ion implantation is the depth of penetration of the ions into the target. The ions do not all come to rest at the same depth. They straggle and the range is a statistical average of the individual penetrations. To a first approximation the range distribution of particles can be represented by a Gaussian function, for which the probability N(x) that an ion will be found at a given depth x is given by an expression of the form:

$$N(x) = N(\max)e^{-X^2/2}$$

where $X = (x - R_p)/\Delta R_p$, N(max) = surface concentration/$\sqrt{2}\,\pi\,\Delta R_p$ and ΔR_p = the root mean square fluctuation of the projected range R_p, measured parallel to the incident ion direction. (See, for example, Dearnaley (2), who in Appendix II gives a convenient set of tables for this function).

It would be useful to give some simple formula showing the range as a function of variables such as the incident ion mass M_1, nuclear charge Z_1 and energy E, and the target material atomic mass M_2 and nuclear charge Z_2. Unfortunately the more accurate range calculations as exemplified by those of Lindhard, Scharff and Schiott (3) are not amenable to simple analytic expression. Nielson (4) has given the following formula for the total range R_{tot} of a particle based on certain simplifying assumptions:

$$R_{tot} = 60(Z_1^{2/3} + Z_2^{2/3})^{1/2}(M_1 + M_2)M_2E/Z_1Z_2M_1\rho \qquad (2)$$

where R_{tot} is given in μm if E is measured in keV and the density ρ of the target material is expressed in g/cm³. R_{tot} is measured along the track of the particle and can be related to the more useful projected range R_p. Lindhard *et al.* have shown that:

$$\frac{R_{tot}}{R_p} = 1/4\left[\frac{(5+A)(1+A)}{2A}\cos^{-1}\frac{1-A}{1+A} - 1 - 3A\right] \qquad (3)$$

where $A = M_2/M_1$. Thus if $M_2/M_1 \ll 1$, for very heavy incident particles such as gold ions and light targets, the total and projected ranges are about the same. Equation *(2)* shows that the range of a heavy ion is proportional to its energy E and roughly inversely dependent on M_1.

Figure 1 gives the projected range of gold ions as calculated from the theory of Lindhard *et al.* (5) for three target materials. From a practical point of view it can be seen that this range is measured in tens of nm at 100 keV, even for light targets, so that even a very thin film of surface contamination will prevent implantation until it is sputtered off.

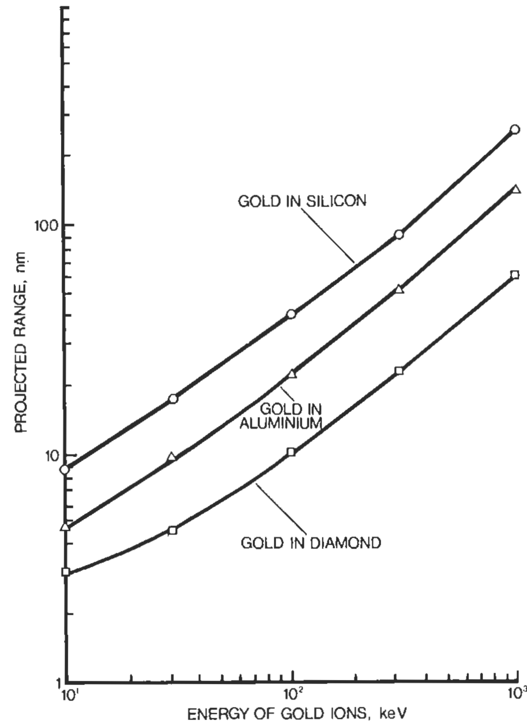

Fig. 1 Projected range (penetration depth) measured parallel to the incident beam) of accelerated gold ions in targets of silicon, aluminium and diamond, as calculated using the theory of Lindhart *et al.* (3)

Radiation Damage

Many effects are produced by the ions as they move through the target material until they finally come to a stop. Target atoms in the lattices of crystalline materials usually recoil from primary collisions with the incident ions with kinetic energies well in excess of their binding energy and form their own collision cascade, thereby increasing the spread of damage over a large volume.

The defects produced tend to form clusters in the collision cascade and whether these clusters build into stacking fault tetrahedra, voids and faulted or unfaulted dislocation loops depends on the internal energy of the system. The interstitials and vacancies in metallic targets either almost immediately recombine or migrate away from the damaged region. A large fraction of the migrating effects is also lost to the surface, at least until the bombarding dose is so heavy that entanglements of defect clusters are created which capture newly formed interstitials and vacancies. The range of these secondary particles and the damage they cause depend upon their direction of motion relative to the lattice. In metallic materials the ion-implanted region maintains its original crystalline structure to a surprising degree, even after each atom has been displaced several hundred times. However, semiconductors and insulating materials behave quite differently from true metals under bombardment. They have strong covalent bonding and rapidly become amorphous with complete destruction of the crystal lattice in the bombarded region.

Sputtering

According to Anderson (6) many of the basic features of sputtering are well understood but the design of a specific application requires a detailed knowledge of the dose effects in the system under consideration. For example, the energy dependence of the back sputtering by the heavy ion xenon from a

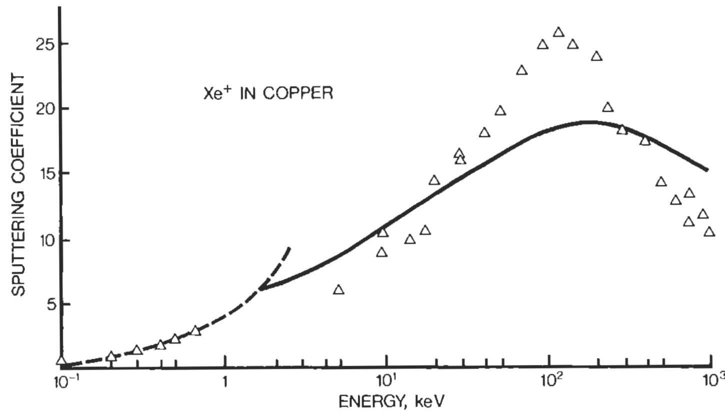

Fig. 2 Energy dependance of the sputtering coefficient (number of target atoms sputtered per incident ion) by xenon ions accelerated onto a copper target

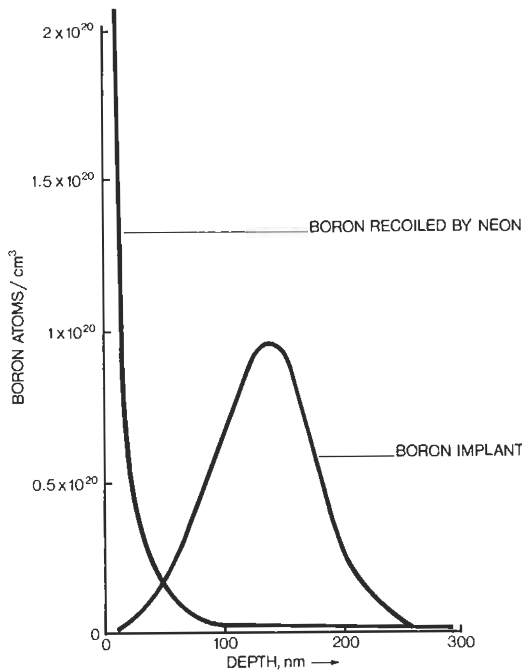

Fig. 3 Recoil range distribution of boron atoms recoiled into silicon by 5 x 10^{16} ions/cm^2, 100 keV neon ions. The distribution resulting from a 40 keV boron implant is shown for comparison. After Dearnaley (2), p. 225

copper target is shown in Figure 2. The sputtering yield peaks at about 120 keV and for gold ions which are heavier than xenon this peak will be at a somewhat higher energy and the sputtering yield will be greater, possibly as high as 40. Dose effects are also present which depend upon the increasing concentration of the implanted ion and the changes produced in the structure of the surface layers of the target. In metals such effects do not show saturation until very high doses have been implanted (above 10^{18} ions/cm^2). In semiconductors and insulators the strongest dose effects are caused by amorphization, and saturation occurs at lower implantation levels.

Almen and Bruce (7) have shown that the sputtering yield of different targets depends strongly on sublimation energies, with systematic variations of yield peaking at elements such as zinc, cadmium and gold, so it is most likely that when implanting with gold, a high sputtering yield will have to be taken into consideration. For example in any attempt to implant 10^{17} ions/cm^2 of 45 keV gold ions into copper, sputtering will clearly be a limiting process. The sputtering coefficient of gold on copper at this energy is 13, and as a result 150 nm of the surface is sputtered away while the range of 45 keV gold ions in copper is only just over 10 nm!

Recoil Implantation

A technique which would allow much higher concentrations is that of recoil implantation. In this method a layer (10 to 30 nm thick) of the material to be implanted is deposited on the target surface by sputtering or some equivalent technique. This surface is then bombarded with ions and many of the atoms in the thin layer are knocked into the target by the violent impacts of the incident particles. To minimize the total ion dose and maximize the transfer of momentum, a massive incident particle should be used, and in the case considered here, energetic gold ions would be especially useful, including for the recoil implantation of gold atoms. The distribution profile of particles implanted in this manner is quite different from that obtained by usual ion implantation (Figure 3).

Diffusion Effects

The above considerations imply that in many instances surface concentrations of implanted ions can be obtained above what is possible under conditions of thermal equilibrium. This factor, coupled with the

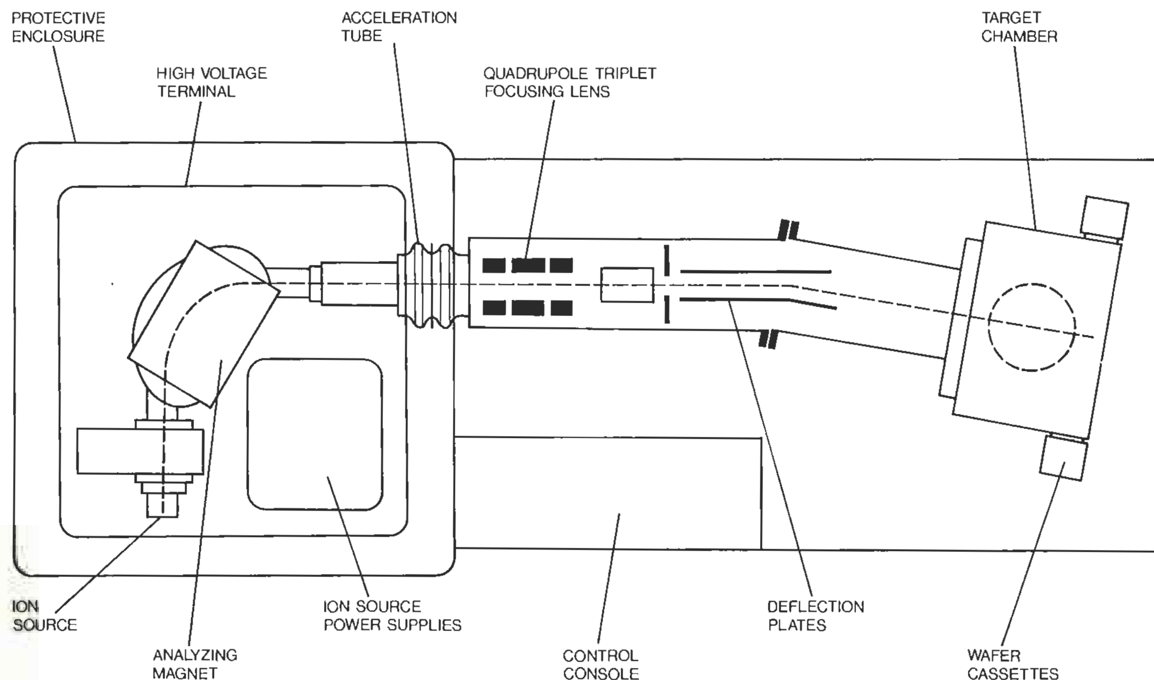

Fig. 4 Schematic diagram of an ion implanter used in the semiconductor industry

existence of complex dislocations produced by radiation damage, leads to expectations of unusual mobility of the implanted ions. This conclusion is supported by Fick's law which shows that the rate of diffusion depends directly upon the diffusion coefficient and concentration gradient of the implanted ions. Indeed, good experimental evidence has been obtained recently showing that under conditions of wear, a large fraction of the implanted ions can remain in the surface even when this has been worn away to much more than the implanted depth.

Apparatus

Ion implantation has been used extensively in the semiconductor industry for a number of years and production equipment is available from many commercial suppliers (8). The equipment is quite complicated because it must meet the stringent requirements of semiconductor processing. The beam must be pure and uncontaminated by other than the desired ion species, and the dose and uniformity of coverage over the target must be precisely controlled. A schematic drawing of equipment capable of meeting these requirements is shown in Figure 4.

In applications outside the semiconductor industry it should be possible to use much simpler apparatus. It is not difficult to generate gold ions from the liquid metal or from the vapour and it is most unlikely that analysis will be required. This removes the most complicating part of the implanter and makes it simple to obtain and use much higher beam currents. It is possible to predict with some confidence how industrial equipment will be developed. At first, slightly modified semiconductor type implanters will be used for research. This will be followed by a need for more rugged and simpler equipment capable of being used for industrial research (Figure 5 attempts to illustrate this equipment). Finally special and cost-effective apparatus will be built to meet specific process needs as they arise.

Ion Sources

It is worth devoting some extra attention to ion generation. There is a large literature on ion sources and this has recently been summarized by Valyi (9). Gold is an ion species which has seldom been accelerated because until recently it was considered too heavy to be of use as a primary particle in nuclear research. Being mono-isotopic it was also not a candidate for use in isotope separators except in cases where radioactive isotopes were being investigated. In the instances where gold ions have been used they have been obtained by sputtering in an ion source (10) or using the chloride in a vaporizer (11). Two techniques are clearly the best when high currents of gold for industrial applications are required. Gold ions can be generated directly from the metal in the form of vapour, in which case its temperature must be raised to nearly 1400°C in order to provide a vapour pressure sufficient for operation of the source (12).

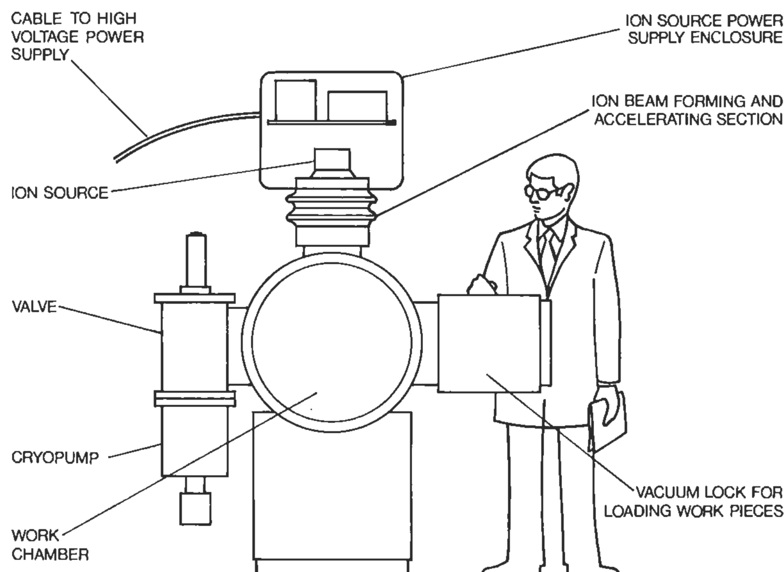

Fig. 5 Schematic diagram of an apparatus which would be suitable for testing on a laboratory scale the economic feasibility of gold ion implantation

This is not too difficult and sources exist and have been used to generate gold ions with relatively few problems because the metal is chemically inert and any alloying effects or reactive effects can be avoided by choosing appropriate materials. More recently, the liquid field emission sources of Clampitt (13) and Swanson (14) have also been used to generate gold ions. These are remarkably simple and can operate at a temperature just above the melting point of gold, say at 1100°C. Their advantages include long, stable lifetimes and almost no demand on the vacuum system because the liquid gold is at a temperature where the vapour pressure is negligible. In addition these sources use gold with almost 100 per cent efficiency, always a consideration with an expensive material.

Acknowledgements

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Electroplating of Stainless Steel with Gold

Firm bonding of electroplated gold to stainless steel has been possible to date only by prior application of a thin nickel coating in a nickel activation bath. This often leads, however, to high susceptibility to corrosion, by way of pores, of gold-plated parts such as stainless steel watch straps. Furthermore, the process cannot be used for dental and medical products, because of the possibility of allergic or other effects of the nickel.

The Electroplating Group of Degussa has developed for the direct and firm bonding of gold deposits to stainless steel a novel method that does not have these disadvantages. It employs a special highly stable gold complex and is suitable mainly for chrome-nickel steels, molybdenum-containing steels and nickel-based alloys. As the process has a strong activating effect, it can also be used for other passive materials that are difficult to electroplate with gold.

The bath for the new process has a pH value of 0.6 and is extremely stable and easy to maintain. The gold-coloured, bright coatings have a fine gold content of 99.5 per cent and a Vickers hardness of 165. As the deposition rate is low, Degussa recommends that it should be applied only in thicknesses of approximately 0.2 μm as a bonding layer and that a conventional bath with a high deposition rate should be used to build up this layer to the final thickness required.