ION IMPLANTATION; A MODERN TOOL OF SURFACE ENGINEERING

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Abstract: Ion implantation is a doping technique which uses energetic ion beams as vector of mass transport. The atoms to be implanted (often called impurity atoms) are thus ionized, accelerated, selected and directed towards the target. Due to the high kinetic energy (typically tens to hundreds of keV) the accelerated ions penetrate the target up to the depths from tens to thousands of nanometers. This method allows one to dope virtually all solids with any kind of atoms with high uniformity and up to very high concentrations. The basic principles, advantages and drawbacks as well as possible fields of applications of ion implantation technique are briefly presented.

Ionska implantacija, sodobna metoda za obdelavo površin

Povzetek: Ionska implantacija je tehnika dopiranja, ki za prenos mase uporablja curke energetskih ionov. Atome, ki jih želimo implantirati, najprej ioniziramo, pospešimo, preberemo in usmerimo proti tarči. Zaradi njihove visoke energije (značilno desetine ali stotine keV) ioni prodrejo v tarčo do globine od nekaj deset do nekaj tisoč nanometrov. Metoda omogoča dopiranje praktično katerekoli trdne snovi s katerimikoli atomi do zelo visoke vsebnosti. Temeljne zakonitosti, prednosti in pomanjkljivosti, pa tudi možna področja uporabe te tehnike na kratko opisujemo v tem članku

1. Introduction; the history of ion implantation.

The beginnings of ion implantation are related to the Manhattan Project. Searching for the efficient method of fission isotopes production the scientists tested also the technique of mass separation of accelerated ions in magnetic field. This method was found less efficient than the diffusional and centrifugal isotope enrichment, however, the interest was attracted by the modification of the properties of target on which ions were collected. The observation that accelerated atoms are not deposited on the target surface but penetrate into its crystalline structure becamed a basis of ion implantation.

The rapid development of ion implantation in late sixties is mainly due to the emerging semiconductor industry. From technological point of view main characteristics of implantation such as: high uniformity, precision, repetability and low processing temperature resulted in the wide use of implantation for silicon doping. Till now this technique remains the basic doping method in silicon technology.

In early seventeens the development in the construction of industrial ion implanters required for efficient doping of bipolar devices resulted in high current implanters delivering ion beams in milliampers range. This made possible high dose implantations what opened new areas of applications, namely the modification of composition of metals. Quite soon the research projects devoted to study the effects of ion implantation into metals allowed to determine the beneficial role of nitrogen implanted into ferritic steels. This in turn resulted in the construction of dedicated implanters without mass separation but equipped with specialized target chambers containing manipulators permitting the homogenous treatment of details of complicated shapes. The huge market for the improvement of mechanical properties of tools leaded to a rapid development of this particular application, however, till now ion implantation into metals is used only in niche domains, mainly biomedical or highly precise cutting and forming tools.

Despite two main fields of applications, semiconductors and metals, ion implantation is also used for several specific purposes. Among them the fabrication of micrometer size membranes, optoelectronic and catalytic devices fabrication seems to be of particular interest. Recently, a new promising field of applications was identified, namely ion implantation into polymers. Low irradiation doses required and strong effects observed after implantation into polymers made this idea very promising.

The above description deals with classical ion implantation, i.e. the line-of-sight processes carried out at energy range of tens to hundreds of keV. Recently numerous new techniques have emerged from ion implantation such as: ion beam mixing, plasma source ion implantation or high energy ion irradiation. These methods will be shortly presented later on.

2. Description of the method.

2.1 Interaction of energetic ions with solids

Energetic ions when penetrate the solid target loose their energy in elastic collisions with target nuclei (so called nuclear stopping, S_n) and in inelastic collisions with the electrons (electronic stopping, S_e) /1/. The stopping is defined as:

$$S = dE/dx$$

where E is ion energy and x the length measured along the ion path in solid (total range) or along the beam direction (projected range). The dependence of stopping versus ion velocity is presented in Fig. 1. The important feature of these dependencies is that for high velocity the ion losses its energy mainly in collisons with target electrons, whereas at the end of the path, when the ion energy decreases the collisions with target
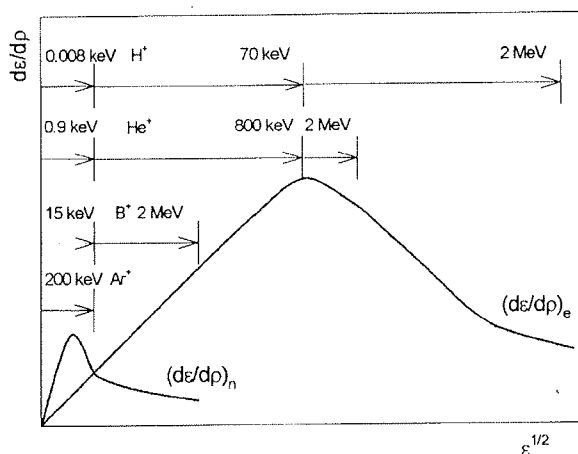

Fig. 1. *Variations of nuclear stopping (Sn) and electronic stopping (Se) with the ion velocity. Please note that both, stopping and energy, are expressed in normalized values (defined in the LSS theory /2 LSS/).*

nuclei dominate. The statistical character of the stopping process results in Gaussian-like distribution of implanted atoms, the determination of profile parameters was the first objective of the research on ion implantation. The first approach allowing the determination of stopping of ions in solid (hence the depth profile of implanted atoms) was developed by Lindhard, Scharff and Schiott /2/. The model, called from the authors names LSS theory, introduces normalized values of energy, range and standard deviation of atomic distribution. According to the LSS theory the depth distribution of implanted atoms can be described as:

$$N(x) = C_{max}\, e^{\left(-\frac{(x-Rp)^2}{2\Delta Rp^2}\right)}$$

Where C_{max} is maximum concentration of implanted atoms, R_p is a projected range of implanted ions, and ΔR_p is a standard deviation of atomic distribution. Maximum concentration of implanted atoms, C_{max}, can be calculated from the formula:

$$C_{max} = \frac{D}{\sqrt{2\pi}\Delta R_p}$$

Where D is implantation dose (i.e. the number of ions implanted in surface unit of the target).

The results of calculations were tabulated and can be used for the determination of the depth distribution parameters /3,4/. The development of Monte-Carlo numerical computer codes allowing the simulation of the processes occurring during the slowing down of the ions within the target made from them the generally used tool for the prediction of the effects of ion implantation. The best known and most widely used code is TRIM by Biersack and Ziegler /5/.

The energy lost in inelastic collisions with electrons leads to the creation of ionized states which, in most cases, recombine rapidly with target electrons. Consequently, these collisions lead only to slowing down the ions but do not induce structural changes to the target. The only exceptions can be observed in weakly bonded insulators or in processes using extremely heavy and energetic ions (with energies exceeding hundreds of MeV /6/). On the other hand the energy transferred from the ion to the target nuclei in elastic collision may reach tens or even hundreds of keV what exceeds the binding energy of atom in crystalline structure by orders of magnitude. The elastic collisions lead thus to the displacement of target atoms from their initial positions, hence to the radiation damage creation /1, 2, 4/. The radiation damage is an intrinsic and very important characteristic of ion implantation as each ion may displace even thousands of atoms from their lattice sites /7/. When the hit atom (often denoted as PKA from Primary Knock-on Atom) received sufficiently high energy it may collide with other atoms creating so-called displacement cascade, i.e. local volume characterized by a high concentration of radiation defects. The example of TRIM calculation showing the cascade formed by 100 keV argon ion implanted into iron is presented in Fig. 2. The radiation defect depth distribution can also be extracted from TRIM simulations together with the distribution of the implanted atoms. An example presenting the results obtained for 50 keV nitrogen ions implanted into iron up to a dose of 1×10^{17} atoms/cm^2 is shown in Fig. 3.

In order to understand better the specific character of ion implantation it is crucial to discuss in detail the processes occurring during the cascade evolution. The fast ion penetrating the target collides with few target atoms and is stopped after about 10^{-12} second. Therefore most of radiation damage is created by displaced target atoms, not by incoming ion itself. The typical defect created by atomic collision is a simple Frenkel pair. The separation between displaced atom and its vacancy is usually small therefore most of the created defects recombine during the cascade evolution. Molecular dynamic simulations /8/ allowed to get a deeper insight into damage process. The concentration of defects during cascade evolution extracted from molecular dynamic simulation is presented in Fig. 4. Three stages can be noticed. The first one is collisional phase
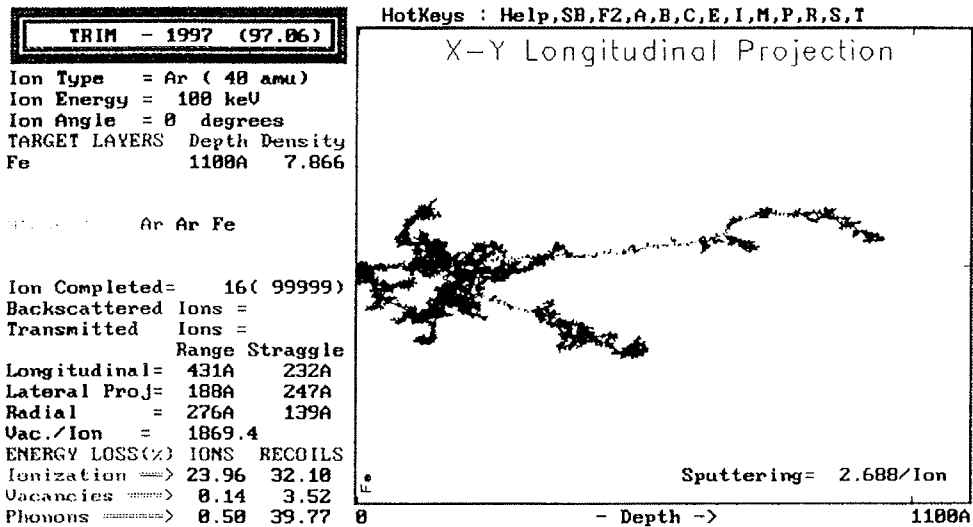
Fig. 2. Results of TRIM calculations showing the formation of displacement cascade in Ar implanted Fe. The ion path is shown as a solid line, the points correspond to displaced target atoms. One can note the formation of isolated cascades in the vicinity of primary knock-on atoms.
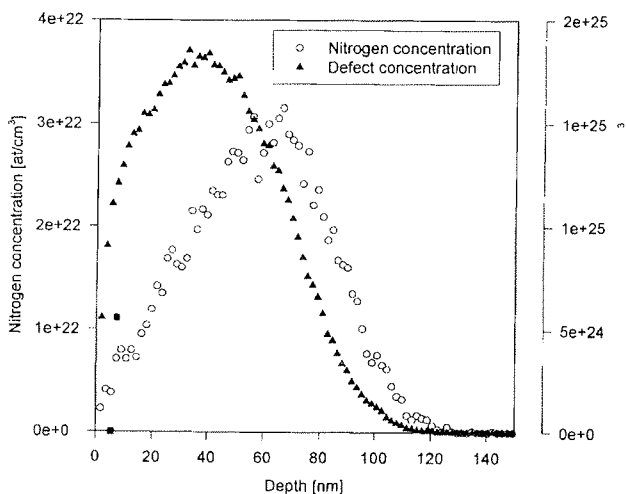

Fig. 3. Depth distribution of implanted atoms and of the defects created by 50 keV nitrogen implantation into iron. The left vertical scale corresponds to the defect concentration and the right scale to the implanted atom concentration.

(I) when ion collides with target nuclei. This stage takes about 10^{-12} sec and is characterized by rapidly increasing concentration of defects. This is followed by a displacement phase (II) when the ion is already stopped and collisions are created only by displaced target atoms. During this stage the recombination of close Frenkel pairs took place leading to a rapid decrease of defect concentration. This stage lasts about 10^{-11} sec. The last stage of cascade evolution is called cooling phase (III). All close Frenkel pairs disappeared already and the defect anihilation requires long range diffusion

mechanisms. The average energy of displaced atoms drops below 1 eV, i.e. is in thermal energy range.

The spatial evolution of defects in cascade is of great importance for the phase formation in implanted systems. The structures of vacancy clusters formed in tungsten irradiated with various ions are presented in Fig. 5 /9/. One can note the density of the vacancy cluster strongly increases with the mass of the incoming ion. The vacancy cluster is surrounded by the interstitial-rich zone. It is believed /10/ that the phases formed in ion implantation mainly depend on processes in central, vacancy rich region of cascade during its cooling phase.
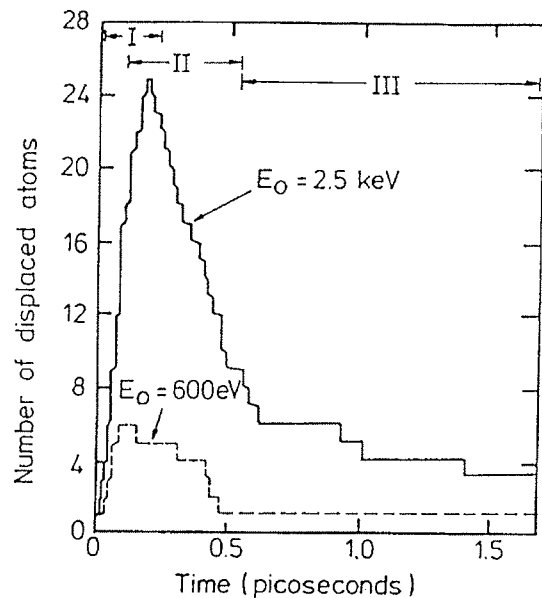

Fig. 4. Evolution of radiation defect concentration upon time for cascade created by 2.5 keV and 0.6 keV W atoms in tungsten.
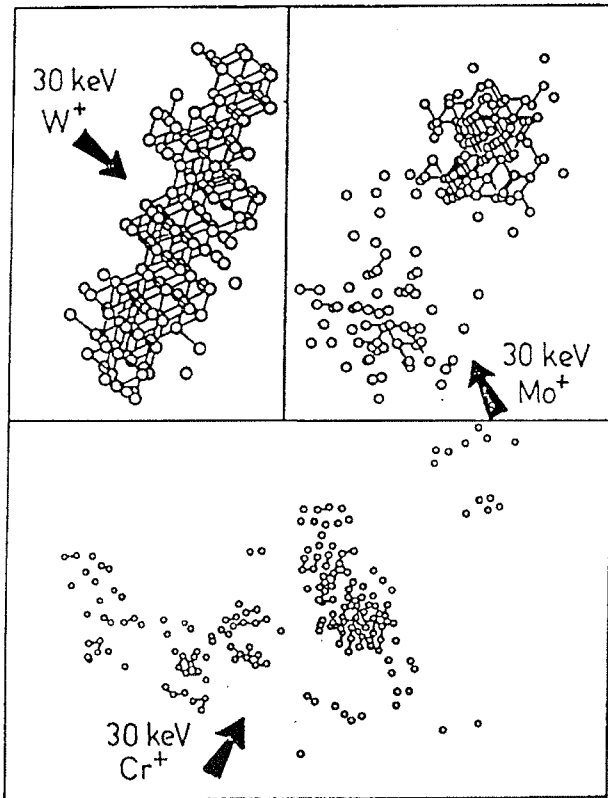
Fig. 5. *Spatial distribution of vacancies in cascades formed by various ions in tungsten (picture taken from Ref. 9).*
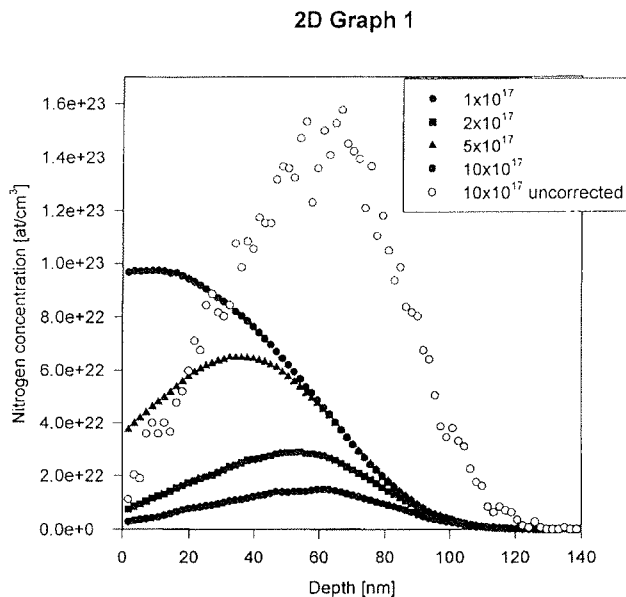
2D Graph 1

Fig. 6. *Depth distribution profiles of 50 keV nitrogen ions implanted into iron up to doses of 1, 2, 5 and $10x10^{17}/cm^2$ corrected for the sputtering coefficient $S = 0.8$ (dashed lines) and profile for the highest dose of $10x10^{17}/cm^2$ directly extracted from TRIM simulation (solid line).*

In the case when the displacement cascade touch the surface of the target some atoms may be ejected from the surface. This process is termed sputtering and is a main reason limiting the maximum concentration of the implanted atoms /11/. The parameter describing the sputtering is sputtering coefficient, S defined as number of target atoms ejected by one incoming ion. The S value vary from almost zero for light energetic ions to tens for heavy ions of low energy. As a general rule one can assume that the maximum concentration of implanted atoms is roughly proportional to 1/S /11/. The TRIM code do not take account of the target composition changes due to the implantation and sputtering, hence it can be used reliably only for the simulation of low dose implantations. For higher doses more advanced versions like TRIMDYN should be used or TRIM results should be corrected for sputtering effects. The importance of this correction is clearly visible on Fig. 6 showing the nitrogen profiles after high dose implantations into iron. Several profiles corrected for sputtering are presented together with the one without correction. The uncorrected calculations may lead to unrealistic nitrogen concentration exceeding the target atomic concentration.

2.2 Ion implanters

The layout of BALZERS MPB 202RP ion implanter is presented in Fig. 7. The device is composed of several main parts, such as:

Ion source. The role of ion source is to ionize the impurity atoms to make possible their acceleration in an electrostatic accelerator. In case of non-gaseous impurities these elements should first be vaporized, thus the ion sources are also equipped with high temperature oven.

Extraction optics. The ions formed in an ion source should be extracted from it and an ion beam should be formed. Taking into account that one of the main problems in implanters design is to maximize ion beam current the ion optics composed from extraction and focusing electrodes should ensure that as much as possible of extracted ions will be directed towards the target.

Accelerator. The role of an electrostatic accelerator is to create uniform electric field accelerating the ions to final energy. Once again the ion beam dispersion should be kept as low as possible to avoid the decrease of ion beam current.

Analyzing magnet. The ion beam extracted from the source may contain not only the impurity ions but also unwanted elements like noble gas atoms used to sustain the stable operation of ion source or chlorine atoms (in many cases the elements are introduced into an ion source in form of chlorides). Therefore these unwanted elements should be separated from the impurity atoms in magnetic analyzer. The typical analyzing magnets have the mass resolution reaching 500/M allowing the isotopic separation for all elements.

Scanning electrodes. The ion beam current density in beam footprint is usually non-uniform and the beam diameter is often too low (few cm^2). Therefore it is crucial to swap the beam over a large area what makes
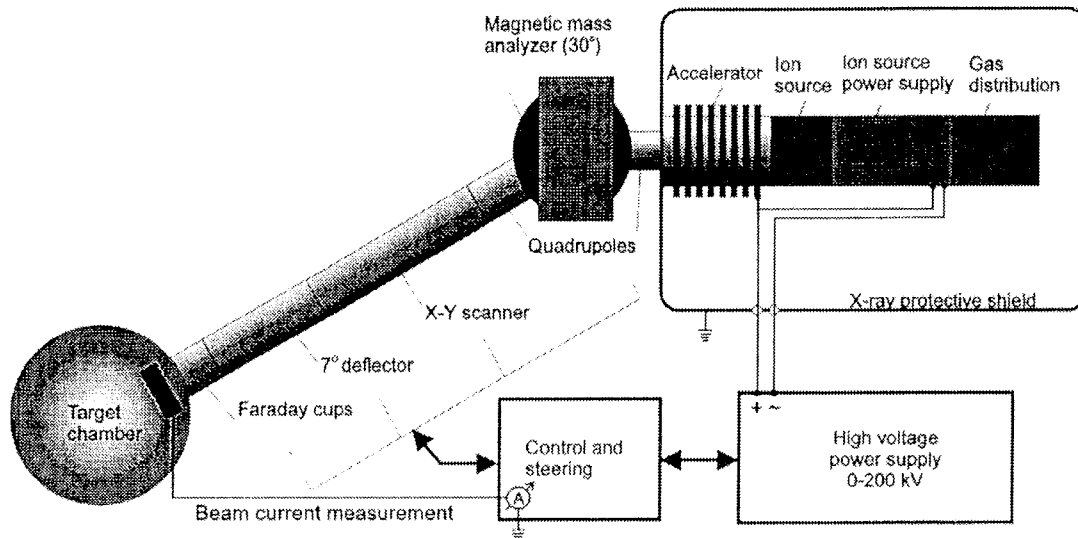
Fig. 7. Layout of the BALZERS MPB 202 RP ion implanter.

possible implantation of surfaces reaching one square meter and ensures uniform doping over the implanted area. The uniformity obtained in commercial implanters used in semiconductor technology reaches 2 % over wafer area and from batch to batch.

Target chamber. The vacuum chamber containing the samples to be implanted. The target chamber is fitted with the sample holder in which the samples are fixed. One of the major problems in the construction of target chambers and sample holders is evacuation of heat due to the incoming energetic ion beam. The total ion beam power may reach few hundreds of watts, almost completely transformed into heat. The temperature rise may thus be of the order of few hundreds of Kelvins. Such high temperature may be detrimental for the samples treated. In the case of nitrogen implantation into tools the complicated shapes of treated objects together with the tight temperature limits makes the target chamber and sample manipulator the most expensive parts of ion implanter.

2.3 Related techniques

During the development of ion implantation several derivative methods have emerged from this technology. The most widely used are briefly described below.

2.3.1 Ion beam mixing

Ion beam mixing (IM) /12,13/ is a two step process in which thin layer of material is deposited first on the surface of treated sample. This layer is then bombarded with inert gas ions. The incoming ions collide with the layer atoms transferring to them part of their kinetic energy. This permit the layer atom to penetrate the target. In IM process the ion beam serve thus only the purpose of energy carrier, the doping mass transport occurs from the deposited layer. In some cases the superstructure composed of numerous layers of different materials is also used. After ion bombardment this

superstructure can be transformed into a homo-genous layer having the concentration depending on the initial sublayers thicknesses. The main advantages of IM with respect to classical ion implantation are no concentration limits due to the sputtering and much lower irradiation fluences required. From economical point of view the IM process is about one order of magnitude less expensive than ion implantation of metallic ions.

2.3.2 Plasma source ion implantation

One of the major disadvantages of ion implantation used for tool treatment is line-of-sight character of this process. It was the main reason to develop the plasma source ion implantation (PSII) process /14/ in which the treated object is confined in plasma and is polarized with high voltage negative pulses. The strong electric field first swap the electrons from the vicinity of the object creating an accelerating gap in which ions from plasma are accelerated towards the treated object. In PSII process all sides of the detail are treated simultaneously greatly improving the process efficiency.

2.3.3 High energy irradiation

The main interest of basic research in nuclear physics continuously move towards higher energies leaving many accelerators more available for the materials studies. Consequently more and more tandem accelerators and cyclotrones become available for solid state physics. This allows one to extend the materials studies towards the energies reaching few gigaelectronvolts. Very low beam currents available in such machines limit the research to studies of defect creation in solids. Very high energy deposition density reaching some keV/angstroem allowed the discovery of numerous spectacular effects such as giant plastic deformation /6/ or amorphization induced by inelastic collisions. The high energy irradiation remain, however, almost exclusively a research tool, the practical applications are not expected soon.

3. Main fields of application

3.1 Semiconductors

Ion implantation is a standard doping process in semiconductor technology used for MOS and bipolar devices fabrication /15/. Except of junction formation it is used also to diminish the contact resistance by doping of semiconductors in contact area or by using ion beam mixing of contact material with the semiconductor substrate. In many cases, especially in several compound semiconductors, ion implantation is the only used technique of type conversion. Since several years the high current implanters allowed the heavy doping of materials, thus the synthesis of compounds. One of the examples of this possibility is the fabrication of SIMOX devices in which high dose oxygen implantation into silicon leads to the formation of buried silicone oxide layer. These devices are characterized by a thin crystalline silicon layer on insulating SiO_2 substrate. Consequently the electrical insulation of elements formed within this layer do not require any polarized junction. High dose of germanium implantation into silicon leads to the synthesis of SiGe material characterized by much higher carrier mobility when compared with pure silicon. Complete reviews of current status of ion implantation in semiconductor technology can be found e.g. in recent papers of Pearton /15/.

3.2 Metals

The main field of applications of ion implantation for metal modification is the improvement of mechanical properties of steels and titanium alloys. Nitrogen implantation into tool and high speed steel may increase the lifetime of precise tools and details by a factor of four /16,17/. Taking into account that typical processing costs are less than one USD per cm^2 and the price of precise tools often exceeds thousands of dollars the use of implantation may lead to significant cost savings /18/ in many industrial applications. The unique features of ion implantation when compared with other surface modification methods are: no dimensional or surface finishing changes and no risk of layer delamination. The fact that implantation is used only in several niche applications in machine industry seems to be due mainly to the low thickness of the treated layer.

The rapidly growing market for ion implantation was identified in biomedical applications. The best known example is probably the implantation into hip joint prosthesis. Some data report the increase of their lifetime by a factor of 20 /19/. Less known is information concerning lower patient discomfort observed when using implanted dental drills from tungsten carbide.

3.3 Others

It is not possible to enumerate all applications of ion implantation. Some well established examples are: nanoporous filter fabrication via high energy irradiation of polymers, modification of optical properties of materials used for waveguide processing, changes in surface energy properties of plastics and polymers, modification of electron work function (allowing lifetime increase of lightning protectors) or increase of adhesion between layers and substrates. In general the use of ion

implantation and related ion beam techniques may be expected in all fields requiring precise doping of thin surface layers.

4. Advantages and drawbacks

The kinetic character of doping in ion implantation results in the absence of any thermodynamical limitations, consequently any solid target can be doped with virtually all elements. Numerous impurities can be introduced into same target leading to the formation of multielemental phases. The radiation damage favorize the formation of metastable structures such as, e.g. amorphous phases. Another advantage comes from the fact that all process parameters can be controlled independently. This last feature is especially important when wide process temperature range is required. Ion implantation allows one to perform the same process in temperatures ranging from liquid helium to more than one thousand degrees centigrade. Very good precision, uniformity and repeatability (the differences in doping uniformity are usually lower than few atomic percent) are also of interest. In mechanical applications the absence of any dimensional or surface finishing changes as well as no risk of layer delamination are main advantages of ion implantation. Finally, the ion beam techniques are clean vacuum processes which do not produce any hazardous wastes requiring special treatment.

Main disadvantage of the method is low thickness of modified layer which rarely exceed few hundreds of nanometers. Most of ion beam techniques are also line-of-sight processes, therefore the treatment of the objects of complicated shapes require special manipulators and often part of the object surface is hidden against the ion beam. It is often claimed that ion implantation is a very costly treatment. Whereas the initial investment costs may be in fact heavy (modern ion implanter used in semiconductor industry costs even few millions of dollars) the processing costs are acceptable in most of applications. For example, the nitrogen implantation into steels costs about =0.5 USD/cm^2 and it should be noted that only the working part of the tool is treated. As a rule of thumb one can thus expect that the treatment costs do not exceed 20-30 % of tool costs whereas the lifetime increase may reach four times. Moreover main semiconductors companies exchange their equipment roughly every three years, hence on the second hand market three or four years old and fully operational implanters are available at surprisingly low cost (even few tens of thousands of USD).

5. Concluding remarks

The "gold rule" of technology claims that there are no good or bad methods, there are only correctly and improperly used techniques. Ion implantation is not, of course, a miraculous method able to replace all other doping techniques. It seems however, that this technique reached its maturity stage and proved to be one modern technologies very useful in many applications and necessary in modern material engineering. The experience gathered till now in many countries suggests that the most efficient way to implement this technique is the creation of specialized service center

equipped with modern universal ion implanter. Such a center should be preferentially located at the material research laboratory ensuring both; research studies and commercial services.

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