Use of Accelerators in Material Research

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1. INTRODUCTION

Modern material research profits by energetic ion beams from various typs of accelerators. Thereby ion beams are used for modification of material surfaces as well as for material characterization. This is such a wide and rapidly extending field that a restriction with respect to the space limitation is necessary. Therefore this review will be focused only into the modification of materials by ion beams.

Ion beam techniques are very powerful tools in thin film technology due to their high flexibility and the possibility to control exactly technological important parameters like energy, fluence, beam size and position. According to the effect responsible for the change of surface properties the modification of materials by energetic ions may be classified in the following way:

Doping	Implantation of impurities at low doses (mainly in semiconductors)
Ion beam synthesis	Formation of buried layers or precipitates of new, also metastable compounds by implantation of doses exceeding the solubility limit
Ion beam mixing , Ion beam assisted deposition	Mixing of interfaces, layer systems or growing layers by implantation of inert or reactive ions
Use of radiation defects	Recrystallization, amorphization, sputtering, particle-track effects

Considering the energy of the ions and the mainly used accelerators material modification may be devided into three ranges:

- conventional ion implantation with energies up to 200 keV (in some cases also up to 500 keV, air-insulated implanters),
- irradiation with ions of one to several MeV (electrostatic accelerators, pressure vessel insulated)
- use of very high energies of several MeV/u (swift heavy ions, high-frequency accelerators).

Typical applications in these three ranges will be reviewed in the following sections having regard to different material classes like semiconductors, metals, insulators, ceramics and polymers.

2. CONVENTIONAL ION IMPLANTATION

For ion implantation with energies up to several hundred keV typical penetration depth are 0.1 to 0.5 μm. The maximum current of the used implanters ranges from μA to 100 mA. But in the most cases the current density has to be limited by beam scanning and/or rotating target stations to about 1μA/cm^2 for semiconductor technology (10 μA/cm^2 with special cooling) and to 5 - 10 μA/cm^2 for implantation in steels.

For the fabrication of semiconductor devices nearly all doping processes are realized at present by implantation. The fast progress of microelectronic technology demands a continuing improvement also of the implanters. The construction of high current implanters [e.g.1] enables the ion beam synthesis of buried insulating, semiconducting or metallic layers in silicon. This is now a major subject of the research work concerned with implantation into semiconductors. The formation of buried layers of SiO_2, Si_3N_4 or stacked arrangements of both by implantation of O^+ or N^+ into silicon (doses 10^{17}-10^{18} cm^{-2}) has been extensively studied [2,3,4]. Elevated implantation temperature (500 - 600°C) is necessary to avoid amorphization of the Si top layer. Expected advantages of the SOI technology (silicon on insulator) are an enhanced packing density of the devices, lower leakage current, higher switching speed and enhanced radiation hardness.

Buried silicide layers growing epitaxially within the Si crystal may be formed by high dose implantation of transition metals [5,6]. Here the mostly investigated compound is $CoSi_2$. Because of its low specific resistance and its thermal stability it is an ideal material for high density metallization schemes or for three-dimensional device structures. $FeSi_2$ is especially interesting because it exists in both a semiconducting low temperature phase (β-$FeSi_2$) with an orthorombic structure and a high temperature phase (α-$FeSi_2$) which is tetragonal. Fig.1 shows RBS spectra from our studies of ion beam synthesized iron silicide [7]. The buried silicide layer

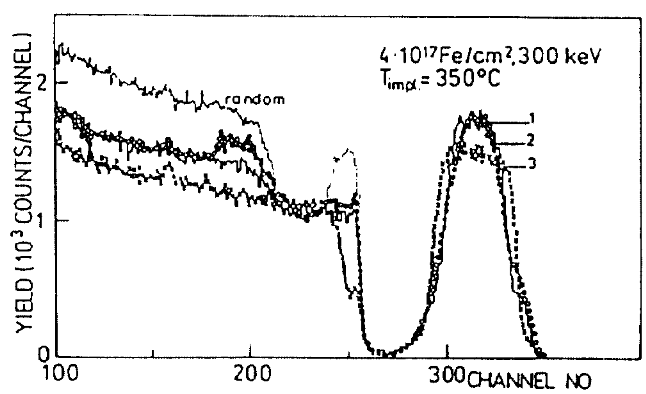

Fig. 1. RBS spectra of ion-beam synthesized $FeSi_2$ [7]
1- as-implanted; 2- annealed at 600°C + 850°C; 3- annealed at 600°C + 1050°C

is indicated by the dip in the silicon part of the random spectrum. The iron distribution of the sample annealed at 1050°C shows a lower maximum iron concentration as observed after annealing at 850°C. This indicates the transition from the semiconducting low temperature to the metallic high temperature phase which exists only with silicon excess due to vacancies within the iron sublattice.

Implantation into metals in order to improve tribological properties like wear and friction, surface hardness or the corrosion resistance is at the threshold of industrial use. First industrial applications are the surface treatment of artificial knee ore hip joints. The positive effect of nitrogen implantation in iron and steel is well established although the acting mechanisms are not completely understood. A comprehensive review of the state of the art is given in reference [8]. Improved wear resistance is obtained by implantation of high doses in the order of 10^{17} to 10^{18} N/cm^2 resulting in new phases, mainly nitrides. Hardness increase due to small precipitates which pin dislocations is one of the important factors for better tribological properties.

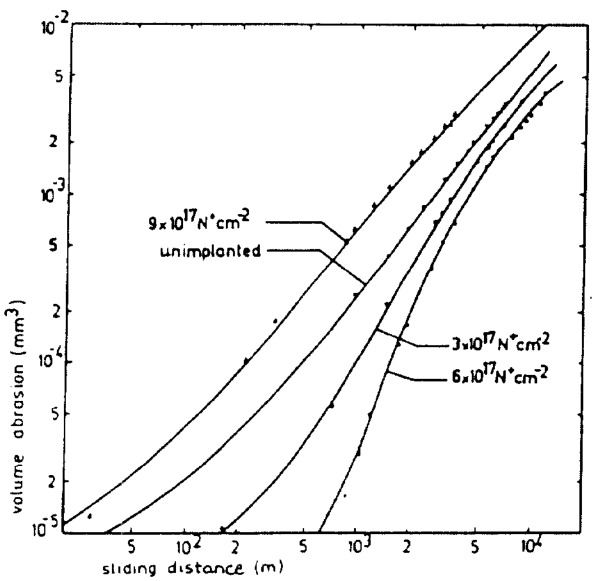

Fig. 2. Dependence of the volume abrasion on the sliding way (pin-on-disc arrangement) of a C100W1 steel after different nitrogen implantations (50 keV)

Figure 2 presents some results obtained in our institute [9]. The observed decrease of the wear rate with increasing dose up to $6x10^{17}$ cm^{-2} is explained by the formation of small nitride precipitates. Larger precipitates formed at higher doses have a opposite effect. Possible reasons are crack formation at internal interfaces and a reduced resistance for propagation of cracks.

3. MeV Implantation

Recently an increasing part of research activities concerned with ion beam techniques is devoted to MeV ions. The extended penetration depth of 1 to 5 μm achieved by these energies will enhance the flexibility of ion beam methods as demonstrated in the case of semiconductor technology; it will open new applications as for example the fabrication of electro-optical devices or it promises better results by the increased depth of influence like for the implantation into metals or ceramics. Modern electrostatic accelerators provide currents from several to > 100 μA. This enables also implantation of high doses. The current density is limited in most cases to 10 - 100 nA/cm^2 .

Semiconductor technology is also the front runner concerning already well established advantageous applications of MeV implantation. One of the most promising examples is the formation of n- and p-typ doped wells surrounding the devices. By MeV implantation a retrograde charge carrier concentration is obtained [e.g.10] which can not be achieved by diffusion. The carrier concentration in the near surface region is as low as necessary for the production of microelectronic devices. But its increase with increasing depth reduces the dangerous disturbance of neighbouring devices by space charge effects (latch-up effect). Further implantations are possible into this well profile in order to improve device parameters. Other applications under discussion for MeV implantation in semiconductor technology are programming of nonvolatile memories (ROM), the formation of buried conducting layers as collector contact of bipolar devices or as shielding grids and the creation of gettering centers for impurities near the devices (proximity gettering) for example by carbon implantation [11].

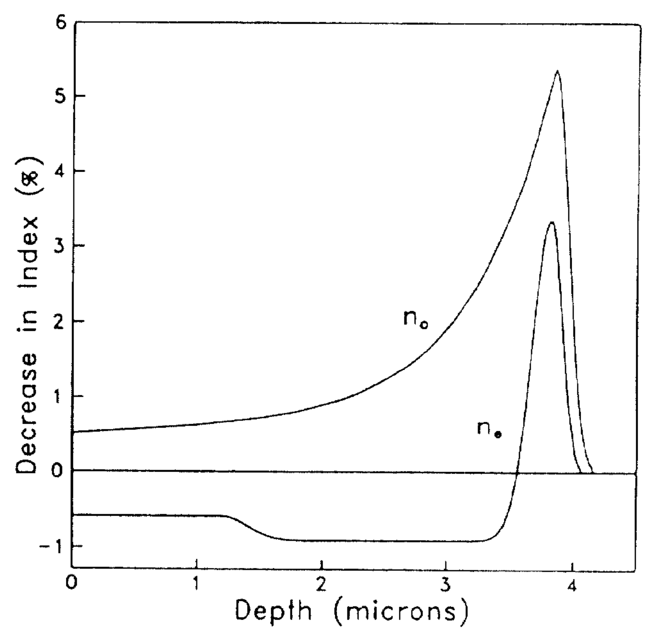

Fig. 3. Depth dependence of ordinary (n_O) and extraordinary (n_e) refractive index of $LiNbO_3$ after MeV He implantation [12]

For the production of electro-optical devices ion implantation can be only applied if energies in the MeV range are available, because the influenced material depth has to be comparable with the wavelength. Low loss waveguides are a basic structure of all integrated electro-optical devices. One possible way to produce waveguides by implantation is the creation of radiation damage beyond the waveguide region. By this way the refractive index of the damaged layer is lowered and an optical barrier is formed at which total reflection occurs. Examples are the irradiation of electo-optical crystals like $LiNbO_3$, $Bi_4Ge_3O_{12}$ or quartz by MeV helium ions [12]. Figure 3 shows corresponding depth profiles of ordinary and extraordinary refractive index of $LiNbO_3$ after He implantation. The observed decrease of the extraordinary index in the end of range region of the He ions and its increase in the waveguide region results in a very sharp optical barrier. Another approach to fabricate waveguides is the enhancement of the refractive index by implantation of impurities in the waveguide region, e.g. implantation of Ti into $LiNbO_3$ [12]. These applications of ion implantation are especially advantageous for the production of integrated optical structures or in cases where the conventional modification of the refractive index by diffusion or ion exchange does not work like for $KNbO_3$ which is used for second harmonic generation [13].

An attractive field for high energy implantation will be the improvement of the mechanical properties of materials as metals or ceramics. The aim is to enhance the depth of the influenced surface layer in order to get for example an increased stability against more severe wear stress.
Successful application of MeV implantation into metals needs still extensive basic research. First positive effects have been observed. In reference [14] for Ti and Fe implanted by 1 MeV N^+ ions an improvement of the load- carrying ability at hardness measurements is reported compared to low energy implantation.

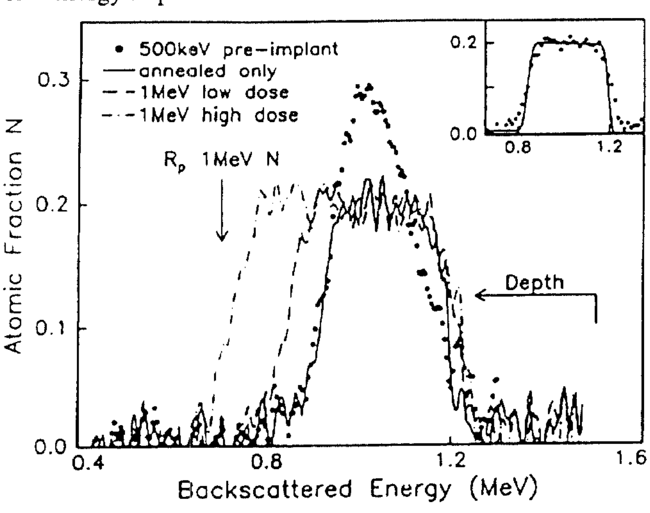

Fig. 4. RBS spectra showing the depth distribution of nitrogen in iron obtained by a two step implantation [15]

A two step process as proposed in reference [15] may be a very useful concept in order to optimize deep implants in metals. In this experiment a shallow buried layer of ε-Fe_2N_{1-x} is formed by a first implantation of nitrogen in iron at 500 keV. By the second nitrogen implantation at enhanced temperature (300°C) with 1 MeV beyond this layer a broader sheet of γ'-FeN_4 is formed by diffusion of iron to the already existing nitride layer. It grows into the depth with increasing dose up to the projected range of the 1 MeV nitrogen ions. Fig. 4 [15] shows the corresponding depth distributions of nitrogen as determined by RBS. In this way closed buried nitride layers of tailored depth and thickness can be prepared.

Another promising technique in order to improve the surface properties of metals, alloys and other materials is ion beam mixing of sheet structures. Also for ion beam mixing high energy irradiation is characteristic. In many experiments MeV implantation of noble gases is used in order to exclude chemical effects of the impurities and to deposit the mixing ions far below the mixed layer; although for further applications also the implantation of reactive ions may be of interest. One preferred goal of ion beam mixing is till now an improved adhesion of cover layers like hard coatings on metals or metallic films on ceramics or plastics. MoS_2 is the most common solid lubricating material. An improved sliding-life time of one order of magnitude in tribological tests of MoS_2 deposited on sapphire is reported after implantation of 2 MeV Ag^+ ions [16].

A second important application of ion beam mixing is the formation of metastable compounds. With this respect at present the main part of investigations is devoted to formation and stability of amorphous alloys. Amorphous surface layers are obtained by ion beam mixing of convenient sheet structures already by an implanted dose which is about one order of magnitude lower compared to amorphization by direct implantation of impurities.

The improvement of mechanical properties of ceramics has been studied mainly by implantation in the energy range of several hundred keV. But the observed positive effects suffer from the fact that the test results reflect both the properties of the thin implanted layer and the unchanged substrate. Therefore the future use of MeV implantation is very important in order to obtain reliable quantitative results.

These are necessary for systematic studies as well as to get more severe improvements of the material properties like strength and ductility. A comprehensive review of implantation in ceramics is given in reference [17]. One main aim is to enhance the fracture stability. Ceramic materials are very sensitive against fracture by tensile stress. Therefore it is aimed to create compressive stress in the near-surface region which has to be overcome by the externally applied tensile stress. The precipitation of new phases with a demand of larger volume or the creation of heavy radiation damage are possible ways to introduce residual compressive stress.

The most important fracture mechanism of ceramics is the propagation of flaws already existing in the surface layer. Therefore an increased resistance to crack propagation or a reduced number of pre-existing flaws will improve the mechanical properties. Amorphization reduces almost the hardness of ceramics. But it results in many cases in compressive stress and it may also reduce the number of pre-existing flaws or their severity. The so called fracture toughness indicates the resistance to propagation of a crack under the influence of stress. Fig. 5 shows the increase of fracture toughness obtained by Ni implantation in Al_2O_3 according to reference [18]. A remarkably stronger increase of fracture toughness with increasing Ni dose is observed

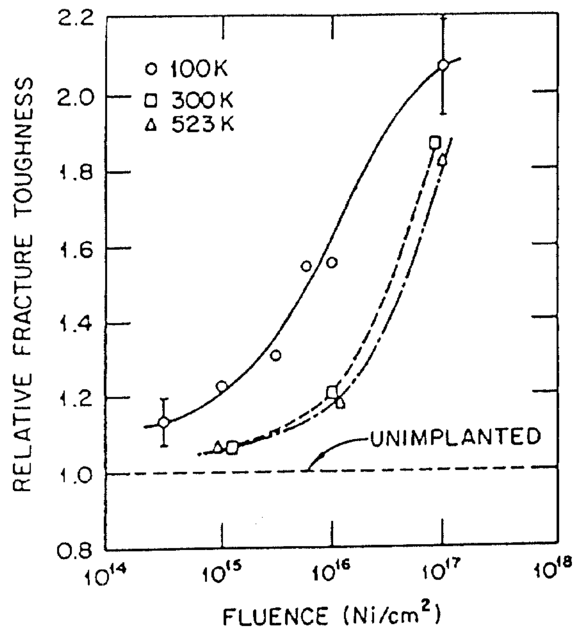

Fig.5. Dependence of the fracture toughness on the dose of implanted Ni (300 keV) and on the implantation temperature [18]

for the low temperature implantation which results in an amorphized surface layer. Also the flexure strength is enhanced for about 30% by this implantation. Compressive stress caused by the implantation is discussed as the main reason for this improved mechanical properties.

4. Swift Heavy Ions and Ion-Track Techniques

Ions with energies of several MeV per mass unit are available only at a few very large accelerators. Therefore their use in material research is still at the very beginning. An increasing number of experiments is aimed to clear the effects due to the very high energy density deposited in electronic excitations. Thereby it is one aim to explore new applications of ion beam techniques. The electronic energy loss of ions with energies of several hundred MeV up to several GeV is nearly constant over a large depth range. This in connection with ion ranges of several ten to several hundred μm enables a nearly homogeneous treatment of thin films without deposition of the impurity ions within the film. But a better knowledge about the effects due to electronic energy loss are also very important for the successful application of MeV implantation.

New kinds of defects due to the electronic energy loss are observed if a material dependent threshold is exceeded. In a first stage a relaxation or a transformation to more complex defect structures is observed considering the primary defects caused by nuclear collisions. Examples are the semiconductors Ge and GaAs up to very high values of the electronic stopping power [19] and some metals and alloys like Fe, Ni, NiFe and Ni_3Fe for values of the electronic energy loss in the range between 1 and 4 keV/Å [20,21]. In a second stage at higher electronic stopping power, in 3d metals for example above 6 keV/Å, new defects arise which can be explained by electronic excitations only. The shape of these defects changes with increasing electronic energy deposition from small circular defect regions along the particle track up to continious columns.

In amorphous materials macroscopic distortions have been observed. Obviously the relatively large free volume in these substances easily enables structural rearrangements as consequence of the mutual Coulomb repulsion of a large number of ionized atoms. In metallic glasses (e.g. $Fe_{40}Ni_{40}B_{20}$ or $Fe_{40}Zr_{60}$) very pronounced anisotropic dimensional changes after irradiation by 360 MeV Xe ions [22] have been measured. The area perpendicular to the beam increases, but the thickness decreases so that the resulting change in density is neglegible.

Swift heavy ions are already in use for the production of particle-track membranes by irradiation of polymer foils and subsequent etching of the latent tracks. If only ions with medium mass and energies of several ten MeV are available an additional sensibilization of the material is necessary before etching [23]. The high electronic stopping power of ions in the mass range from 100 to 200 with energies of 5 to 20 MeV/u is desired in order to avoid sensibilization and to allow the treatment of more stable polymers. The particle track technique enables the fabrication of really cylindrical pores with defined size in a broad range (0.03 to 5 μm).The density of pores is exactly controllable from single pores for application in medicine [24,25] to high track densities for filtration with high flux and high dirt loading capacity.

Another interesting application for swift heavy ions seems to be the enhancement of the critical current density of high T_c superconductors. In materials, where the critical current density is determined by core pinning and flux creep, an enhancement of the critical current under applied magnetic field is possible by the formation of additional flux pinning centers. No j_c enhancement has been observed in polycrystalline material where the current transport is governed by weak links between the grains. An enhanced critical current has been obtained in epitaxial single crystalline films of $YBa_2Cu_3O_7$ after irradiation with 137 MeV Xe ions [26] or by 580 MeV Sn ions [27]. The additional flux pinning centers formed by the irradiation are especially effective at high magnetic fields, for the field direction parallel to the ion tracks and at temperatures not so far from the transition point.

A promising candidate for future applications of swift heavy ions are also magnetic oxides. Non-magnetic latent tracks in a magnetically ordered surrounding or a magnetic anisotropy due to the stress caused by the tracks have been observed [28]. In this way the domain structure of magneto-optical materials can be influenced [29].

5. Demands of Material Research on New Ion Beam Equipment

The employment of ion beams for material modification is characterized by an increasing number of applications which need ion energies in the range of several MeV and high doses in the range of 10^{16} cm^{-2} to 10^{18} cm^{-2}. The transfer of research results into practical use will be dependent to a high degree on the successful development of powerful compact accelerators designed for a special field of applications. Promising candidates with this respect are high frequency linear accelerators, especially the RFQ type [30]. But a necessary condition is a variable energy at least in a certain range. In order to decrease the length of the accelerator the use of multiply charged ions is of great interest. The development of a corresponding MeV accelerator is part of the japanese AMMTRA project [31].

Improved ion sources are of great importance for many branches of ion beam techniques. High current sources of negative ions for a broad spectrum of ion species are of special interest with respect to the increasing use of tandem accelerators for material modification. A crucial task of the effort to design a 100 mA metal implanter within the AMMTRA project is the development of a corresponding ion source.

To promote the application of ion beam techniques for material research research centers are a very effective way. They should offer a wide spectrum of ion beams of different energy in a surrounding where all modern methods of surface analysis and material preparation, especially sheet deposition methods, are available [31]. In centers, where different accelerators are in use, it is possible to irradiate simultaneously with two or three ion beams (e.g. ORNL [32], TIARA) . Such experiments are of interest for development and testing of materials for fusion and fission reactors. Also the in-situ diagnostics of ion beam modifications using ion beam methods or electron microscopy [33] is very important for a fast progress of this research branch.

6. References

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