PREPARATION OF THIN COATINGS OF TITANIUM COMPOUNDS WITH ION IMPLANTATION

M. Mozetič[1], A. Zalar[1], J. Jagielski[2,6], G. A. Evangelakis[3], M. Drobnič[4] and V. Chab[5],
[1]Institute of Surface Engineering and Optoelectronics, Ljubljana, Slovenia
[2]Institute of Electronic Materials Technology, Warszawa, Poland
[3]University of Ioannina, Ioannina, Greece
[4]IBM Slovenija, Ljubljana, Slovenia
[5]Institute of Physics, Czeh Academy of Sciences, Praha, Czech Republic
[6]A. Soltan Institute of Nuclear Studie,Swierk/Otwock, Poland

Keywords: microelectronics, ion implantation, surface technologies, surface engineering, surface coatings, thin coatings, semiconductor compounds, computer simulations, SRIM IBM software, Stopping and Range of Ions in Matter, Ti compoounds, titanium compounds, Ti oxides, titanium oxides, Ti nitrides, titanium nitrides, ion beams, irradiation damages, thin films, AES, Auger Electron Spectroscopy, AES depth profiling

Abstract: The growth of thin coatings of titanium oxide and nitride during ion implantation of respective ions into titanium substrate was studied theoretically and experimentally. The IBM SRIM software was used to determine the concentration profiles of implanted ions, the sputtering rate, probability of back – scattering and ion energy loss mechanisms. Theoretical results were compared with experiments. Samples of pure titanium plates were carefully polished and exposed to a flux of oxygen and nitrogen ions with the kinetic energy of 100 keV per molecule (50 keV per atom). The ion doses were $5x10^{16}$, $1x10^{17}$, $2.5x10^{17}$, $5x10^{17}$, $7.5x10^{17}$, $1x10^{18}$ atoms/cm^2. Depth profiles of the samples were determined by the AES method. Both the theory and experiment showed that the ion range at the low dose was about 90 nm for the case of nitrogen, and 80 nm for the case of oxygen, with depth distribution typical for ion implantation. Experimental results showed that a layer of titanium compound with a constant composition was formed at the ion dose above 7.5 x 10^{17} atoms/cm^2.

Priprava tankih prevlek titanovih spojin z ionsko implantacijo

Ključne besede: mikroelektronika, implantacija ionov, tehnologije površin, inženiring površin, prevleke površinske, prevleke tanke, snovi polprevodniške, simulacije računalniške, SRIM oprema programska IBM, Ti snovi titanove, Ti oksidi titanovi, Ti nitridi titanovi, curki ionski, poškodbe vsled obsevanja, plasti tanke, AES Auger spektroskopija elektronska, AES prifiliranje globinsko

Povzetek: Prikazujemo rezultate teoretične in eksperimentalne preiskave rasti tankih plasti titanovega oksida in nitrida med ionsko implantacijo z ustreznimi ioni. Z uporabo programske opreme IBM SRIM smo določili koncentracijske profile implantiranih ionov, razprševanje titanovih atomov, verjetnost za odboj vpadnega iona od površine in mehanizme izgube kinetične energije ionov. Teoretične rezultate smo primerjali z eksperimentalnimi. Vzorce ploščic iz čistega titana smo gladko polirali in izpostavili toku kisikovih in dušikovih ionov s kinetično energijo 100 keV na molekulo (50 keV na atom). Doza ionov je bila $5x10^{16}$, $1x10^{17}$, $2.5x10^{17}$, $5x10^{17}$, $7.5x10^{17}$ in $1x10^{18}$ atomov/cm^2. Globinske profile vzorcev smo določili z metodo AES. Tako teoretični kot eksperimentalni rezultati so pokazali, da je doseg ionov približno 90 nm za dušik in 80 nm za kisik. Globinska porazdelitev elementov je bila značilna za tehniko ionske implantacije. Eksperimentalni rezultati so pokazali, da se formira tanka plast titanove spojine s konstantno sestavo pri dozi, ki je večja od 7.5 x 10^{17} atomov/cm^2.

1. INTRODUCTION

The performance of technical products is considerably influenced by surfaces. A coating with proper characteristics can significantly increase the resistance against physical and chemical attack by the medium in environmental, tribological, electrical or electrochemical contact with the surface. In the past few decades, numerous techniques for changing of surface and/or deposition of protective coatings have been developed. Many of them are based on different chemical vapour deposition (CVD) processes and physical vapour deposition (PVD) processes /1/. Operating pressure, the temperature of both the substrate and the surrounding gas, vapour phase composition and particle energy are the main parameters, which distinguish between the two deposition processes. The CVD processes are based on the interaction of gaseous chemical compounds in the immediate vicinity of the substrate surface and the subsequent deposition of the reaction products. In the PVD processes, on the other hand, the material vapour source primarily emits atomic particles, which hit the substrate surface and remain bonded. The kinetic energy of incidence particles in PVD processes is of the order of 0.1 eV for the case of evaporation, 1-10 eV for sputtering and 100 – 1000 eV for ion plating. An even higher kinetic energy of incidence particles is in the process of ion implantation, where the energy may be of the order of keV or even MeV /2,3/. In the present paper, we describe experimental and theoretical study on ion implantation of oxygen and nitrogen ions into titanium substrates.

2. COMPUTER SIMULATION

Theoretical study of the formation of thin ceramic films on titanium substrates was performed by the use of the IBM SRIM software package /4,5/. A typical output of

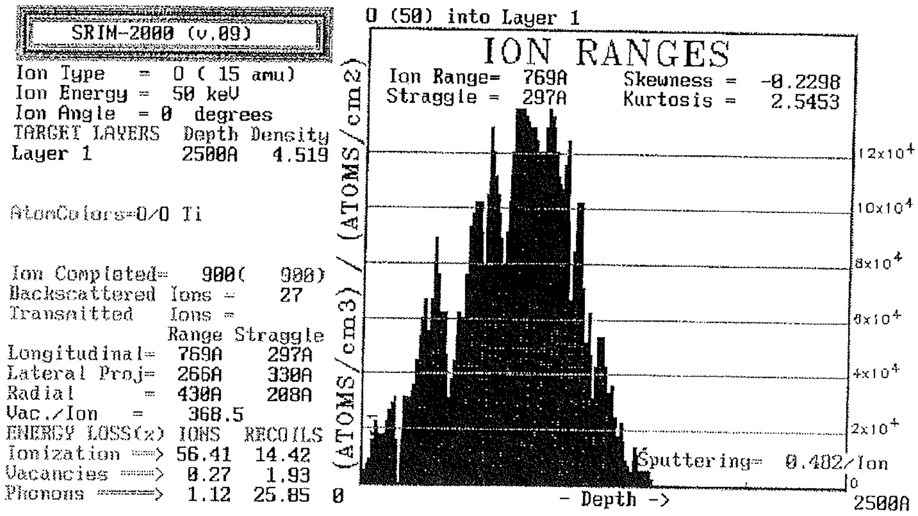

Fig. 1. A typical output of SRIM simulation of 50 keV O^+ implantation into titanium substrate.

the computer simulation is plotted in Figure 1. In this case, we simulated implantation of 50 keV O^+ ions into perfectly flat titanium substrate. The calculated distribution of oxygen atoms show that the ion range is 76.9 nm. Damage in the surface layer of the sample is caused both by the original ions and the recoils. The major part of the kinetic energy of incident ions is lost by ionization of titanium atoms in the bulk. The ions hardly cause any formation of vacancies or phonons. The recoils, on the other hand, lose most of their kinetic energy by formation of phonons. The great difference of the channels of the energy lost between the ions and the recoils is due to a great difference of their kinetic energy. As long as the kinetic energy is high, the far most probable way of lose of the energy is ionization. As the energy decreases, the ionization becomes less probable on the expense of phonons and vacancies. Since the kinetic energy of recoils is much lower than the original kinetic energy of ions, there is a great difference in the way of losing their energy. At the kinetic energy of oxygen ions of 50 keV and the normal incidence angle the calculated rate of sputtering is 0.482 titanium atoms per ion. The probability of back - scattering at that kinetic energy and angle of incidence is low. The computer simulation calculated only 3 out of 100 ions are back – scattered.

Similar results were obtained also at simulation of 50 keV nitrogen ions into titanium substrate. The calculated data for oxygen and nitrogen implantation are summarized in table 1.

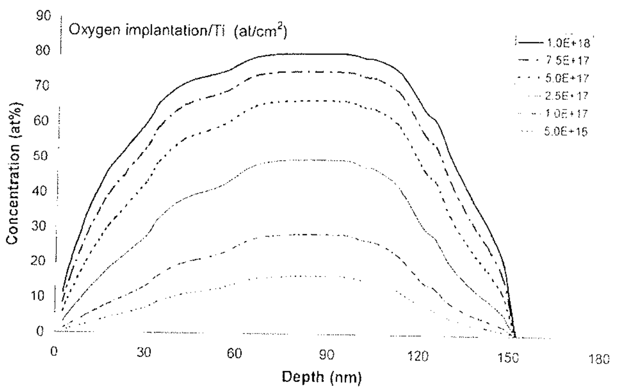

Fig. 2. Calculated oxygen concentration profiles in titanium samples treated with 50 keV oxygen ions at different doses, obtained with a SRIM simulation.

Table 1. Comparison of different mechanisms of energy loss for oxygen and nitrogen

Type of ion	O^+ 50 keV	N^+ 50 keV
Ion range	76.9 nm	84.7 nm
Sputtering rate	0.482 atoms/ion	0.341 atoms/ion
Ions energy loss (ionization)	56.41 %	60.22 %
Ions energy loss (vacancies)	0.27 %	0.27 %
Ions energy loss (phonons)	1.12 %	1.75 %
Recoils energy loss (ionization)	14.42 %	12.94 %
Recoils energy loss (vacancies)	1.93 %	1.75 %
Recoils energy loss (phonons)	25.85 %	23.68 %

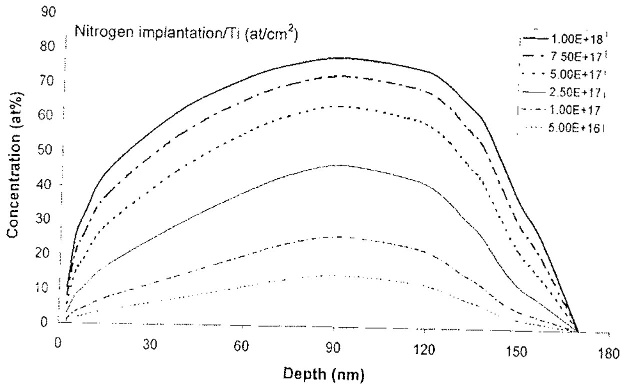

Fig. 3. Calculated nitrogen concentration profiles in titanium samples treated with 50 keV nitrogen ions at different doses, obtained with a SRIM simulation.

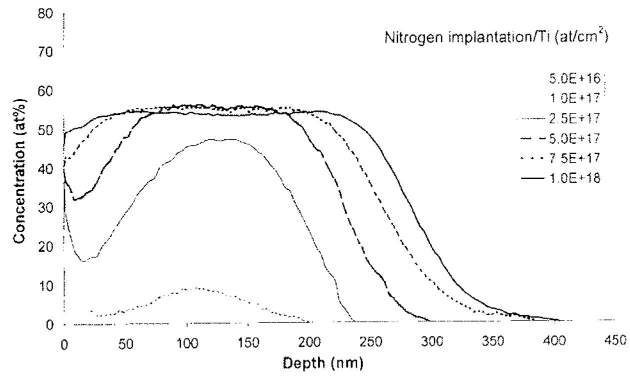

Fig. 5. AES nitrogen depth profiles in titanium samples treated with 50 keV nitrogen ions at different doses.

In order to calculate depth profiles of thin ceramic films on titanium substrate the doses of O^+ and N^+ ions was varied between 5 x 10^{16} and 1 x 10^{18} ions/cm^2. The calculated distribution of O and N atoms in the target is shown in Figure 2 and 3, respectively.

3. EXPERIMENTAL

Samples of pure titanium plates were carefully polished and exposed to a flux of oxygen and nitrogen ions with the kinetic energy of 100 keV per molecule (50 keV per atom). The ion doses were 5x10^{16}, 1x10^{17}, 2.5x10^{17}, 5x10^{17}, 7.5x10^{17} and 1x10^{18} atoms/cm^2. The composition of the surface layer on the samples was determined by the AES depth profiling. The samples were analyzed with a scanning Auger microprobe (Physical Electronics Ind. SAM 545 A). A static primary electron beam with 3keV energy, 0.5 μA beam current and about 40 μm diameter was used. The electron incidence angle with respect to the normal to the average surface plain was 30°. The samples were ion sputtered with two symmetrically inclined beams of 3 keV Ar^+ ions, rastered on a surface area larger than 5 x 5 mm at an incidence angle of 47°. A sputter rate of about 2,5 nm/min was determined on a reference multilayer Cr/Ni thin film structure.

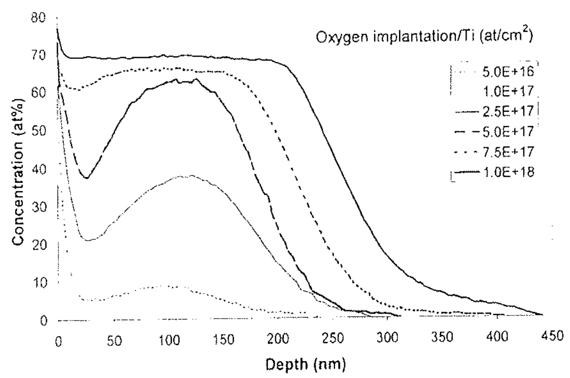

Fig. 4. AES oxygen depth profiles in titanium samples treated with 50 keV oxygen ions at different doses

The depth profiles of the samples for the case of oxygen and nitrogen implantation are shown in Figure 4 and 5, respectively.

4. DISCUSSION AND CONCLUSION

Formation of a thin ceramic layer on titanium substrate was studied theoretically and experimentally. For theoretical study we performed computer simulation using the IBM SRIM software package. The simulation allowed for estimation of the energy loss during implantation of oxygen and nitrogen ions with the kinetic energy of 50 keV. At the normal incidence angle the most probable loss of kinetic energy of ions was via ionization of bulk titanium atoms. The ionization efficiency was somewhat higher for nitrogen ions. In both cases, the recoils lost most of their energy via interaction with crystal lattice. For this mechanism the energy loss was about 10% higher for recoils displaced during oxygen implantation. The ion range in the target was 76.9 nm for oxygen and 84.7 nm for nitrogen. The sputtering rate was 0.482 atoms/ion for the case of oxygen implantation and 0.341 atoms/ion for the case of nitrogen implantation. The difference in both the ion

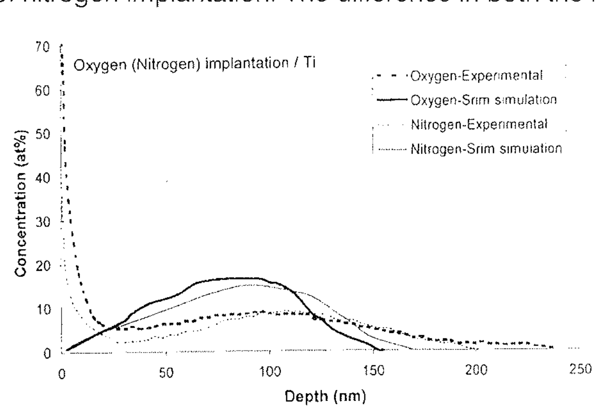

Fig. 6. Theoretical and experimental distribution of oxygen and nitrogen atoms in titanium substrate after implantation with respective ions at the dose of 5 x 10^{16} atoms/cm^2.

range and sputtering rate is due to a different mass of the ions.

Results of computer simulation are reasonably sound with the experimental observations at low doses (Figure 6). The discrepancy between the computer simulation and experimental results increases with increasing ion dose. At high doses (in our case above 5 x 10^{17} ions/cm^2) the computer simulation give much different results than the experiment. This is due to at least two reasons: i) the software package does not take into account the chemical interaction of implanted ions with solid material, and ii) the package does not take into account the change of the surface line position due to extensive sputtering of the surface atoms.

Acknowledgement

This work has been funded by the Ministry of Science end Technology of the Republic of Slovenia. M. Mozetič gratefully acknowledges a grant from NATO Science Fellowship Programme.

5. REFERENCES

/1/ H. Freller, Vapour – phase coating processes for hard coatings, Vacuum 45 (1994), 997-1000.

/2/ J. Jagielski, G. Gawlik, A. Zalar and M. Mozetič, "Ion implantation; a modern tool for surface engineering", Inf. Midem 29, 2, (1999), 61-67.

/3/ A. Vesel, M. Mozetič, J. Kovač, Izračun koeficienta razprševanja, Vakuumist 18 (1998),14-18.

/4/ J.F. Zeigler, SRIM-The Stopimg and Range of Ions in Matter, IBM-Research, YorkTown, (1998).

/5/ J.F. Ziegler, J.P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids, Pergamon Press, New York, (1985).

M. Mozetič, A. Zalar,
Institute of Surface Engineering and Optoelectronics,
Teslova 30, 1000 Ljubljana, Slovenia,
miran.mozetic@ guest.arnes.si,
anton.zalar@ guest.arnes.si

J. Jagielski,
Institute of Electronic Materials Technology,
Wolczynska 133, 01-919 Warszawa, Poland,
jagiel_j@sp.itme.edu.pl
A. Soltan Institute of Nuclear Studies,
05-400 Swierk/Otwock, Poland

G.A. Evangelakis,
University of Ioannina
P.O.Box 1186, 45110 Ioannina, Greece,
gevagel@ cc.uoi.gr

M. Drobnič,
IBM Slovenija,
Trg republike 3, 1000 Ljubljana, Slovenia,
matija_drobnic@si.ibm.com

V. Chab,
Institute of Physics,
Czech Academy of Sciences,
Cukrovarnicka 10, 16253 Praha, Czech Republic,
CHAB@FZU.CZ

Prispelo (Arrived): 05.09.99 *Sprejeto (Accepted): 15.09.99*