UDK 620.179.11
Pregledni znanstveni članek

ISSN 1580-2949
MTAEC9, 39(1–2)9(2005)

APPLICATIONS OF BEAM-INDUCED SURFACE MODIFICATION

UPORABNOST SPREMEMB POVRŠINE ZARADI OBSEVANJA S CURKOM ENERGIJSKIH DELCEV

Tomislav M. Nenadović
Institute of Nuclear Sciences Vinca, P.O.B. 522, 11001 Belgrade, Serbia

Prejem rokopisa – received: 2004-10-26; sprejem za objavo – accepted for publication: 2005-04-06

The interaction of any energetic beam with a solid leads to a variety of physical and chemical phenomena. The changes induced in a solid depend on the characteristics of the beam and the properties of the target.

The formalism of the particle-solid interaction provides a quantitative guide for energy loss, penetration depth, defect concentration and sputtering values. If the target is a multi-component material, the controlling factors are not so well defined. Besides the general dependence on beam and target properties, the behavior of multi-component systems is associated with preferential sputtering, compositional changes, enhanced diffusion in local regions and many other effects.

Energetic beam bombardment forms the basis of a wide range of engineering processes. The beam-induced modification of a material will make a substantial contribution for tailoring the performance of the bulk material and the surface, to the development and understanding of metastable materials and nanostructures and will be widely applicable in modifying the structure and properties of polymers.

Key words: Energy beam, interaction with solid, surface microcharacterisation, engineering application

Interakcija vsakega curka energijskih delcev s trdno snovjo povzroči vrsto fizikalnih in kemijskih pojavov. Spremembe v trdni snovi so odvisne od karakteristik curka in od lastnosti tarče. Narava interakcije delec-trdna snov daje kvantitativno sliko o izgubi energije, o globini vdora delcev, o koncentraciji napak in o deležu razprševanja. Če je tarča večkomponentni material, kontrolni dejavniki niso tako dobro definirani. Poleg odvisnosti od lastnosti curka in snovi je vedenje večkomponentnih sistemov povezano s prednostnim razprševanjem, spremembami v sestavi, povečano difuzijo na lokalnem nivoju in številnimi drugimi efekti.

Bombardiranje s curkom energijskih delcev je temelj za veliko inženirskih procesov. Spremembe inducirane s takim curkom, v materialu omogočajo, da krojimo lastnosti površine in materialov kot celote, da se razvijejo in razumejo metastabilni materiali in nanostrukture in bodo zelo uporabljene pri modifikaciji strukture in lastnosti polimerov.

Ključne besede: Energijski curek delcev, interakcija s trdno snovjo, mikrokarakterizacija površine, inženirska uporaba

1 INTRODUCTION

The interaction of any energetic beam with a solid leads to a variety of physical and chemical phenomena. Changes induced in solids depend on the beam's characteristics and the properties of the target. Any type of incident beam can be used to study these interaction phenomena. The most commonly used are charged particle beams (protons, ions and electrons) and uncharged particle beams (neutrons, γ-ray, laser beam and sand blasting)[1].

It is quite impossible to make a review of all the possible combinations of beam interactions with solids, energy interaction mechanisms (elastic or inelastic collisions) and modifications of material properties [2]. Generally, along the path of the radiation in solids the electron beam induces undesirable effects, radiation damage and alters mechanical properties. Primary-ion collisions can lead to a redistribution of the elements on the surface and within the target, sputtering of the target atoms, radiation-enhanced diffusion, chemical reactivity and radioactivity (MeV energy ion). Apart from collision sputtering in which atomic or electronic collisions are necessary, photo-deposition sputtering (by the incident laser beam) and mechanical sputtering (with macroscopic particles) have also been investigated [3,4]. Such an interaction results in modifications to the material properties, mainly to melting and evaporation from the interaction zone (laser sputtering), or to mechanical, thermal and chemical phenomena in the bombarded area (mechanical sputtering).

The basic physics governing particle-solid interactions provides quantitative data on energy losses during collision, the number of collisions, the range of the incident radiation, the distribution of induced defects and the sputtering coefficients. Most of these developments have been in the area of atomic physics and material science. The physical phenomena of interactions include the following: radiation damage effects in crystals (production of vacancies, interstitials and their clusters), structural changes in the range of an atomic collision cascade (amorphization and recrystallization), compositional changes (multicomponent target) and topographical changes (due to erosion and redeposition). In material-science studies ions, electrons, γ-rays and mechanical particles have been utilized in surface treatments for different applications. With a low-energy beam the surface properties can be altered, while the bulk properties remain unchanged. The problem during the bombardment of multi-component materials is the controlling factors, which are not so well defined.

In addition to the scientific and application problems, new techniques for material characterization using incident energetic beams are also very important. Since the development of ultra-high-vacuum techniques in the sixties the rapid development of characterization techniques has been continuous. Well-focused techniques are used to introduce a local disturbance in the bombarded zone[5]. In the resulting relaxation, characteristic signals are emitted and registered by a suitable analyzer. By analyzing the emitted signal, structural and compositional information from the sample can be obtained[6]. Since many of the beam techniques are complementary, it is recommended to use more than one technique in the characterization of the sample.

2 BASIC CONCEPT OF THE BEAM-TARGET INTERACTION

The irradiation of solids with an energy-carrying beam leads inevitably to changes in the atomic arrangement of the target atoms. For all crystallographic structures the crystal is built of an infinite, regular array of atoms, arranged on a space lattice of perfect periodicity[7]. As all the interactions with the target take place through its surface, then if the surface is modified the analyzed body of the sample must be modified too.

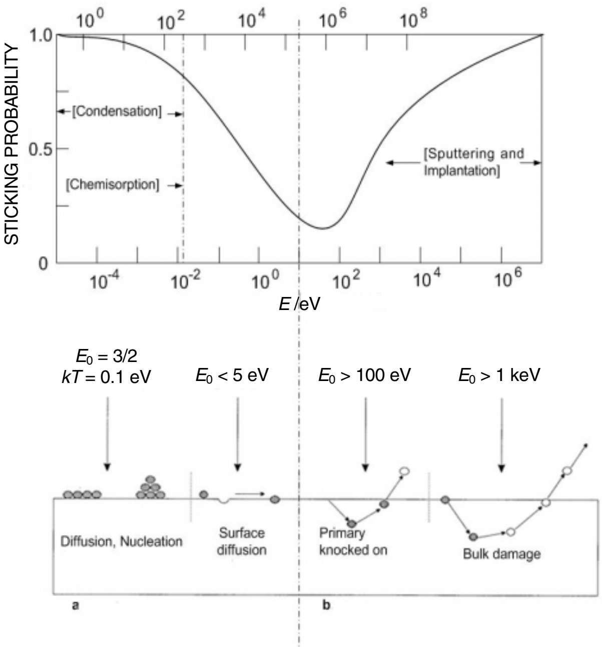

Figure 1: Illustration of the interaction processes as a function of ion-beam energy: a) low-energy ions and b) collision cascade.

Slika 1: Shema procesov interakcije v odvisnosti od energije curka: a) ioni z majhno energijo in b) slap trkov

For a low-energy beam (< 100 eV), the projectile energy is transferred in elastic collisions that are close to the surface. The resulting rearrangements are as follows: accommodation of the incoming beam particle and a small number of displaced target atoms. The bombardment leads to the formation of interesting surface compound layers formed by adsorption and chemisorption (**Figure 1**). During the bombardment with a higher-energy beam (≥ 1 keV) incident-beam particles scatter several times on target atoms, creating primary recoil atoms, which in turn collide on other regular arrays of atoms, and so a collision cascade develops [8]. In the ion-beam experiments, the beam parameters, such as mass (M), energy (E), dose (D) and incident angle (θ), are well controlled, so a lot of information on interaction mechanisms can be obtained.

a. Physical sputtering. When an atom leaves the surface, as a result of receiving momentum from the collision cascade induced by an incident particle, the process is denoted as physical sputtering. The quantities that are of greatest interest for the interaction analysis of the elemental targets are[9,10]:

1. Sputtering is a collision effect; the number of collisions (N_s) between the incident radiation and the target atoms is

$$N_s\ (\mathrm{cm^3/s}) = n\ v\ N\ \delta$$

where n is the density of the incident particles, v is the velocity, N is the atomic density of the solids and δ is the cross-section of the particular event.

2. The total sputtering yield is defined by the number of ejected target atoms per incident ion. The total sputtering yield is proportional to the energy deposited in the surface layer:

$$S(E) = 4\pi a_{1,2} Z_1 Z_2 e^2 (M_1/M_1+M_2) s_n$$

where Z is the corresponding atomic numbers, e is the electronic charge, $a_{1,2}$ is the screening radius and s_n is a universal function. When the number of ejected target atoms per incident ion is known, S_{exp} can be easily calculated:

$$S_{\mathrm{exp}} = M_i/N_I = 96.400\ \Delta g/A\ I^+\ t$$

where A is the atomic weight of the target, Δg is the weight loss of the bombarded sample, I^+ is the positive ion current to the target and t is the bombardment time.

3. The sputtering yield at various angles of incidence (θ) is roughly proportional to $1/\cos\theta$, until a maximum at an angle of about 70°, and then it falls until the grazing angle is reached. For heavy-ion bombardment in the keV region

$$S(\theta)/S(0) = 1/\cos^f\theta$$

where f is a function of the mass ratio M_2/M_1.

4. The distance traveled in the target (R, range of radiation, penetration depth) before coming to rest

$$R = 0{,}6\,\frac{Z_1^{2/3} + Z_2^{2/3}}{Z_1 \cdot Z_2} \cdot \frac{(M_1 + M_2)M_2}{M_1} \cdot E$$

(index 1 for incident beam and index 2 for target)

The probability of a lattice atom leaving the lattice site depends on the specific parameters of the crystal, i.e., the structure, the chemical composition, the defect concentration and the temperature. The minimum energy to displace an atom from its lattice site (the threshold energy E_d) is of the order of 25 eV. While the range of a medium-energy incident beam in a solid is rather short, the deposition of energy tends to be accumulated at the surface layer. The thickness of the altered layer agrees roughly with the penetration depth of the incident ions.

The sharp threshold model is widely used in calculations of atomic displacement in crystalline solids, but it is not quite realistic. If the target is a multi-component material, the controlling factors are not so well defined. In addition to the general dependence on beam and target properties, the behavior of multi-component systems is associated with preferential sputtering (until the equilibrium composition is reached) compositional changes, enhanced diffusion in the local region and some other effects[11,12]. Advanced material science requires one-component materials with exquisite properties, strong alloys that resist heat and corrosion, hyperfine surface structure as the basis of intelligent systems and radiation treatment for altering surface properties[13]. The beam-induced modification of materials will make a substantial contribution to tailoring the performance of bulk material and surfaces, to the development and understanding of metastable materials and nanostructures and be widely applicable in modifying the structure and properties of polymers.

b. Microanalysis by beam bombardment. Since materials science became the basis for new applications and engineering it also required new characterization methods for analysis. Controlled, medium- or low-energy incident beams exist for the structural and compositional analysis of surfaces and deposited material on substrates. The incident beam interacts with the solid sample and gives rise to scattered beams, which can be in the form of electrons, photons or charged particles. By analyzing the emitted characteristic signals, structural and compositional information of the samples can be obtained[14]. The equipment for a microanalysis-by-beam-bombardment technique basically consists of a mono-energetic beam source, a target chamber, a suitable analyzer and detection electronics. The basic principle of the beam technique for material characterization is presented in **Figure 2**.

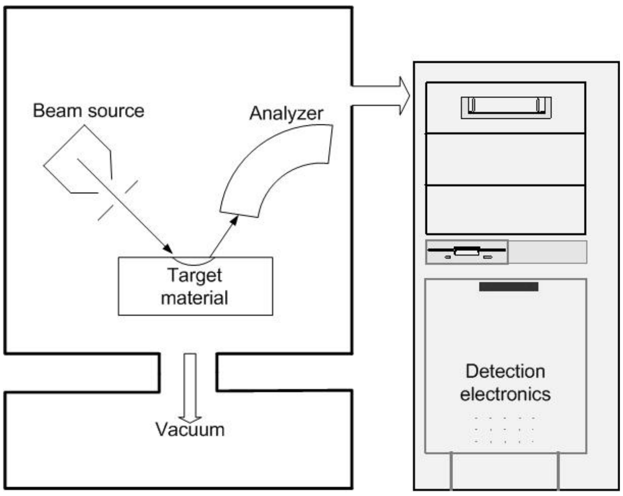

Figure 2: Schematic illustration of the beam technique for structural and compositional analyses.

Slika 2: Shema metod za strukturne in sestavne analize na osnovi energijskega curka

To obtain the surface structure of a material it is necessary to make a series of grinding and polishing operations. The purpose of this step is to remove the damaged surface that is formed during cutting, oxidation, mechanical polishing or other processes. To provide the details the surface must be etched by a chemical reagent or a low-energy beam.

As a consequence of the beam-target interaction, previous preparation of the sample and the surface structure, different surface features, such as topography, roughness and morphology, can be observed. In a lot of published papers these terms are not correctly used.

Topography is defined as the depth of view. It is about as large as the field of view and depends on the resolution of the instrument for analysis. Topography is a macroscopic parameter and can be observed using an optical microscope. With new techniques topography is moving into the analysis of a very small area of material, or micro-topography.

The roughness of a material is due to irregularities on the surface, including height (from 0.1 nm to 100 μm), width (nm to a few mm) and direction. Surface roughness is an important quantitative variable that must be measured during material testing (an indicator of fracture mechanisms, the activity of catalysts). The two most suitable techniques for the measurement of surface roughness are stylus profiling and light scattering. Microscope techniques – optical, electron and scanning – are mostly used in research studies.

Surface morphology is a crucial characteristic for material properties. The morphology is part of the structural characteristics of real crystals, which depend on the nature and the state of the surface. An atomically flat surface does not exist with real crystals. Crystal structure is defined as the arrangement of atoms in the interior of a crystal. Crystal defects, imperfections and the grain boundaries must be considered as a crystalline deformation where the atoms have been removed from their lattice sides. These structural features do change the surface morphology and can degrade the surface characteristics. Powerful tools for the examination of surface structural features include the scanning electron microscope (SEM), the scanning-tunneling microscope (STM) and the atomic force microscope (AFM).

In the past decade material characterization has moved in the direction of analyzing the structure and composition of very small volumes of material. One basic requirement of microanalysis is to have a high lateral resolution, of the order of an atomic dimension. This is not available with most characterization techniques; their lateral resolution is sacrificed to gain depth resolution. To improve the lateral resolution in scattering-based techniques the size of the primary beam must be reduced. And to image a large area, the beam must be scanned on the sample.

3 ENERGY-BEAM MODIFICATION OF MATERIALS

Any beam processing of solids leads to changes in the atomic arrangement of the surface and subsurface atoms. Modification of the material properties involves complex processes due to the created defects, the interaction of impurities, diffusion, and for some material systems, a break in the chemical bond or new molecule formation. Due to accommodation or collision the structural, electrical, chemical and mechanical properties of the bombarded material may be modified.

Since 1950 applications of various ion-beam-bombardment processes have become important. Initially, ion bombardment was used to produce an atomically clean surface, to etch the surface before structural analysis, to deposit thin films of various materials and, in the semiconductor industry, to introduce controlled amounts of impurities below the surface to act as donors or acceptors. Later, it was found that the ion bombardment of solids can produce a passive surface or accelerate chemical reactions on the surface due to the presence of sorbent ions from the beam.

a. Low-energy ion-beam nitriding. It was well known that thermal and mechanical treatments can change a material's mechanical properties. However, it was difficult to explain the significant changes frequently observed when ions were implanted into metals. In the earliest studies it was found that the implantation of nitrogen in steel improves the mechanical-wear properties of the material. Based on

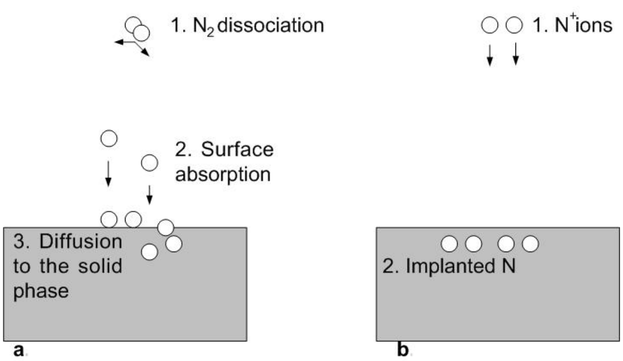

Figure 3: The kinetic path for a) thermally activated and b) ion-beam activated nitriding.
Slika 3: Kinetična pot za: a) termično aktivirano in b) ionsko aktivirano nitriranje

this it was concluded that the mechanical properties that can be affected by implantation are those that are mainly influenced by surface conditions[15]. The comparison between thermal and ion-beam nitriding is illustrated in **Figure 3**.

During nitriding with low-energy nitrogen molecules, the growth of nitride thin films is a thermally driven processes. The adsorbed particles migrate over the surface and aggregate. The agglomeration of the deposited atoms increases with increasing surface mobility. The deposited material will reach continuity at a higher thickness and will have a larger grain size and a smaller number of structural defects. Depending on the surface properties and the deposition parameters, different types of growth can occur.

A new technique that involves increasing the kinetic energy of the deposited atoms or ions by a glow discharge was introduced to further improve the adhesion[16]. The excellent adhesion is attributed to the high energy of the deposition.

b. Beam modification of metals. The main goal of modifying the material properties is to improve the physical, chemical or mechanical properties through the control of changes in the microstructure or chemical composition and to tailor materials to achieve specific properties. The processing methods for producing new metal alloys, ceramics, composites or polymers, very often yield more efficient and cost-effective products.

It is interesting that those mechanical properties that can be affected by ion implantation are those mainly influenced by the surface condition, i.e., erosion, fatigue, friction and wear[17]. All the mechanical properties of crystalline materials are sensitive to near-surface dislocation behavior. When these dislocations are formed the materials become stronger. Erosion is the destruction of material surfaces by the action of working fluids or solid particles. Fatigue failure generally occurs during cyclic loading at some stress lower than the fracture stress. It was found when using low-carbon steel that nitrogen implantation and low-temperature annealing improve the fatigue resistance[18]. Friction and wear are complex phenomena involving surface and near-surface properties, and they can also be modified by ion implantation. Changes in the friction associated with alloy steel can be increased or decreased by ion implantation[19]. High-dose implantation of steel with Pb increases the friction by 40 %, while the implantation of Mo shows a decrease in friction by 20 % for the same dose.

In real devices (steam/gaseous turbine blades) the different mechanisms of surface degradation can play a role. However, a quantitative statement about the contribution of each individual mechanism is not possible because the contribution of each mechanism is different to the sum of the individual effects.

In our previous work a series of sputtering-erosion experiments was carried out with pure iron, an

Table 1: Chemical composition of the used target
Tabela 1: Kemična sestava uporabljene tarče

Material / Comp.[wt%]	C	Cr	Ni	Mn	Si	other
Fe (99.999)						
Martensitic stainless / Steel (ASTM 420)	0.15 min.	12-14	–	1 max.	2 max.	P, S
Austentic stainless / Steel (AISI 304)	0.08 max.	18-20	8-12	2 max.	2 max.	P, S

iron-based alloy and stainless steel for a fusion device's vacuum vessel [4,11]. Here, using martensitic and austenitic stainless steel, the experiments are performed on samples with implanted nitrogen. The chemical composition of the target material is given in **Table 1**. The samples were bombarded with different types of incident beam: ions, laser beam and fast oxide particles (silica in a blast cleaning machine). The sputtering yields were determined using weight loss, the depth erosion measurements using a profilometer, and the beam-induced modification of the target was followed using an optical and a scanning electron microscope.

Our results of the total-sputtering-yield measurements as a function of beam energy are presented in **Figure 4**. The results show that the total sputtering yield rises linearly with the energy transferred from the incident particles. Besides the general dependence on beam and target properties, the sputtering behavior of multi-component systems is associated with preferential sputtering, compositional changes and enhanced diffusion in a localized region. For ion-implanted samples the sputtering yield also rises with the energy transferred from the incident beam. During steady-state conditions (dose of ions 10^{17}–10^{19} 1/cm^2) the obtained values are always lower than those for a non-implanted target.

The second characteristic parameter is the behavior of the sputtering yield as a function of the angle of incidence. Our results for $S(\theta)/S(O)$ performed on martensitic and austenitic stainless steels are presented in **Figure 5**. The results show that there is a good agreement between the angular dependence of ion-beam sputtering and mechanical sputtering using a silica beam.

Interesting results were obtained with a beam of fast metal-oxide particles and laser beams[4,12]. Using mechanical sputtering/erosion, with the beam of fast oxide particles, a similar energy and the same angular dependence of the sputtering yield is obtained as when an ion beam is used. For an implanted target, under steady-state conditions, the sputtering yields are lower than for the non-implanted target. However, the results were not so convincing and the disagreements between the results were high. For photon beams the sputtering/erosion of the bombarded surface proceeds in two steps: the formation of damage by some fraction of the energy as heat on the surface and the expansion of the material outside these regions as a result of the heat flow. Photodeposition sputtering is governed by three different mechanisms, depending on the laser-beam parameters and the target properties. At the beginning of the process the sputtering yield and the sputtering rates increase with the increased power density. After reaching a maximum they begin to fall, due to plasma screening of the target. Exfoliation sputtering appears when thin films are bombarded with low beam densities. Hydrodynamic and thermal sputtering becomes dominant when coatings or the crystal are bombarded with a powerful laser.

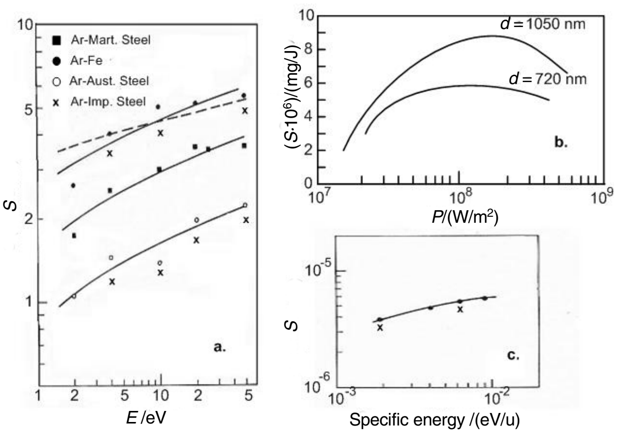

Figure 4: Experimental sputtering yields data vs. incident energy of the: a) Ar$^+$-ion beam, b) laser beam and c) mechanical-particles beam
Slika 4: Eksperimentalni izkoristki razprševanja v odvisnosti od curka: a) Ar$^+$ ionski curek, b) laserski curek in c) curek mehanskih delcev

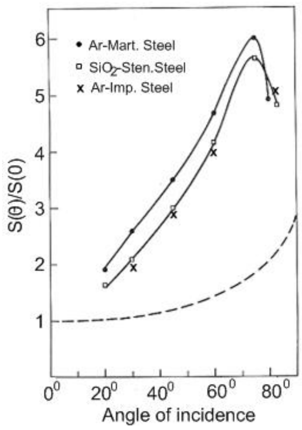

Figure 5: Variation of sputtering yield of stainless steel as a function of the angle of incidence: Ar$^+$ on martensitic steel (•), silica on austenitic steel (□) Ar$^+$ on implanted steel (×); the dashed line indicates the theoretical prediction.
Slika 5: Sprememba izkoristka razprševanja nerjavnega jekla v odvisnosti od incidenčnega curka: Ar$^+$ na martenzoitno jeklo (•), silicijev dioksid na avstenitno jeklo (□), Ar$^+$ na implantirano jeklo (×); črtkana linija je teoretična napoved

The morphological changes of the bombarded surfaces, observed by means of scanning electron microscopy, show that the lateral inhomogeneity arises from different sputtering rates of the individual crystals, different erosion rates in small, local regions, and surface imperfections (**Figure 6**). A study of the surface topography of Ar^+-bombarded chromium-iron alloys showed a variation in the bombarded morphology in agreement with our previous experiments and with the theoretical predictions. When ion-implanted stainless steels are bombarded with a clean silica beam a complex form of beam-induced roughness (not the morphology) is obtained: the beam path within the target is short and the damage due to individual impacts is clearly visible. The shape and the magnitude of the silica particles are changed during the interaction as a result of a large number of collisions. An investigation of the topographical changes induced by a laser beam shows their dependence on the applied laser beam's power densities and the properties of the target (crystallinity). A

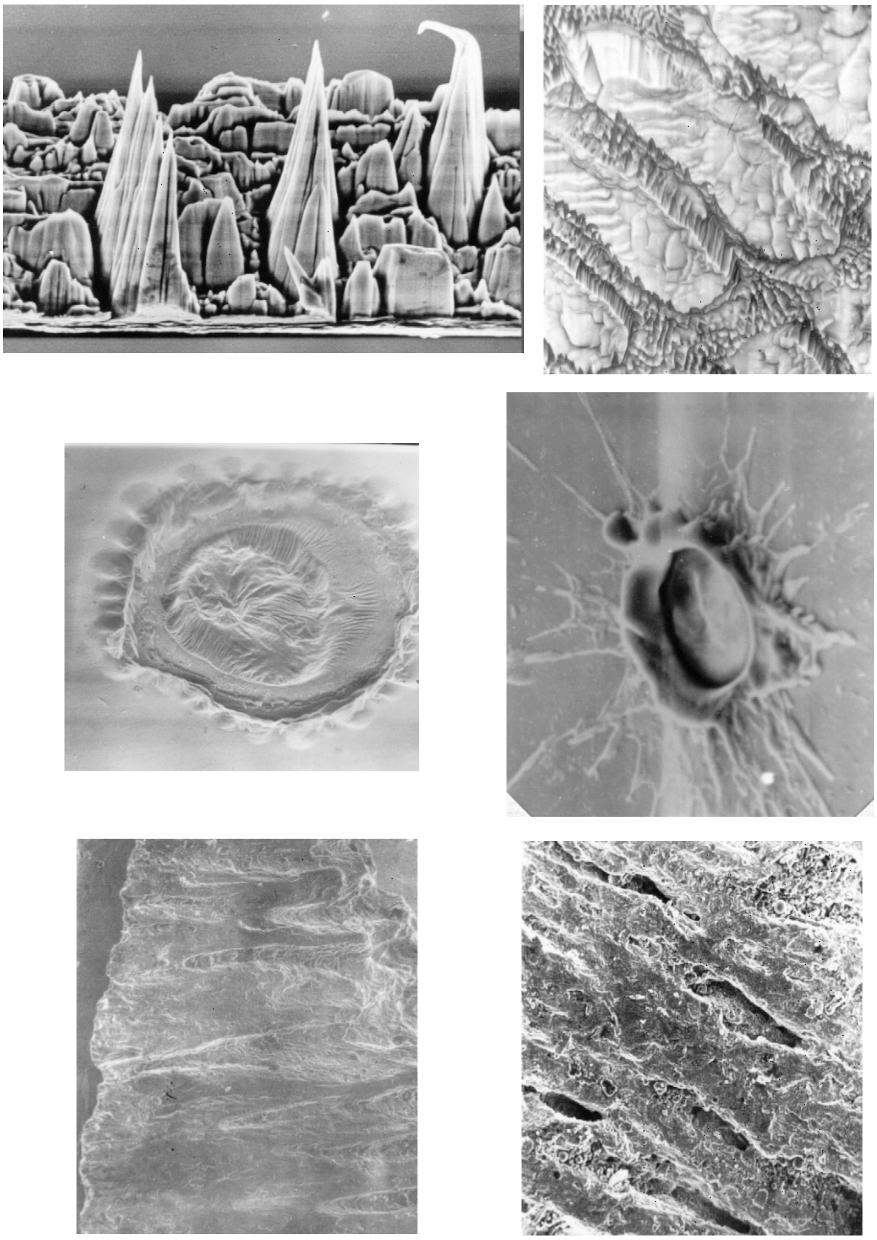

Figure 6: Surface features (SEM analysis) of samples bombarded with an energetic beam: a) ion-beam induced morphology on Au wire (a1) and (a2) Cu-Ag alloy (50 keV, 10^{19} /cm^2); b) laser-beam damage/topography on Zr-alloy 2, coated with W_2C (b1, d = 100 nm, $E = 2{,}9\cdot10^4$ W/m^2) and on stainless steel coated with TiN (b2, d = 200 nm, $E = 5{,}2\cdot10^8$ W/m^2); c) mechanical-particles induced roughness on austenitic steel at the glancing angle (c1) and by individual impact (c2).

Slika 6: Značilnosti površine (SEM-mikroskop) vzorcev, obsevanih z energijskim curkom: a) ionsko inducirana površina na Au-žici (a1) in (a2) na Cu-Ag zlitini (50 keV, 10^{19} /cm^2); topografija površine Zr zlitine pokrite z W_2C, poškodovane z laserskim curkom (b1, d = 100 nm, $E = 2{,}9\cdot10^4$ W/m^2); c) hrapavost na avstenitnem jeklu, inducirana pri zdrsnem kotu snopa mehanskih delcev (c1) in pri posamičnem trku (c2).

Table 2: Quantitative values of some changes in TiN film after Ar^+ ion bombardment at different dose
Tabela 2: Kvantitativne vrednosti nekaterih sprememb v tanki plasti TiN po kombardiranju z različno dozo ionov Ar^+

Ion dose /cm^{-2}	Ar concentration in TiN film (intensity ratio)	Erosion depth /nm	Mean roughness /nm	Microhardness (MN m^{-2})
As deposited	1	–	38	9557
$5\cdot10^{17}$	1.8	6	49	9252
$5\cdot10^{18}$	2.2	60	70	9223
$5\cdot10^{19}$	2.5	360	141	5654

characteristic crater-like form of damage with a rim of molten material was formed as a result of melting and evaporation from the beam's interaction zone.

We believe that with these effects, new technologically important surface-modification processes – with gas cluster ion bombardment – have been developed. Cluster beam interactions with surfaces cause topographical changes, surface smoothing and crater formation. In spite of some similarity in the surface features there is a fundamental difference in the cluster-beam energy deposition on the surface. When a cluster with 1000 atoms has an energy of 10 keV each constituent atom has only 10 eV. In cluster ion bombardment 60 % of the incident energy is deposited on the surface without defect formation[20,21].

c. Ion implantation in semiconductors. Interest in ion implantation has been stimulated by the possibilities of fabricating semiconductor devices. In contrast to conventional methods of introducing atoms into solids, ion-implanted atoms in solids are introduced by accelerating them to kinetic energies in the keV region. The advantage of this method is that the concentration and the depth profile of the implanted ions can be varied independently[22]. The implanted profile is affected by the energy of the incident ion, the bombardment dose, the type of incident ion and the crystal characteristics (orientation). The potential disadvantages of ion implantation are surface and radiation damage of the bombarded materials.

Much of the effort has been focused on the behavior of dopants in semiconductors. The impressive progress in microelectronic is based on silicon technology using metal-oxide semiconductors (MOS and C/MOS), transistors and electro-optic devices. Three adjacent regions on the chip – source, channel and drain – make it possible to obtain the desired electrical properties by doping with impurity atoms. Silicon technology involves the formation of active device areas in the Si substrate by doping (B, P), the fabrication of dielectric layers and the deposition of a metal layer. All the regions and layers require patterning by photolithography and etching.

d. Implantation of insulators. Ion implantation is a conventional method for altering the near-surface properties of insulators, like polymers, oxides, ceramics and glasses, which are characterized by a low electrical conductivity and transparency in the visible-light region. Two common radiation types for industrial applications are γ-radiation from Co^{60} for the radiation sterilization of medical items (elimination of toxic residues) and e-beam accelerators for processing polymers for specific products. Ion-beam processing has been extensively investigated for altering the surface properties of

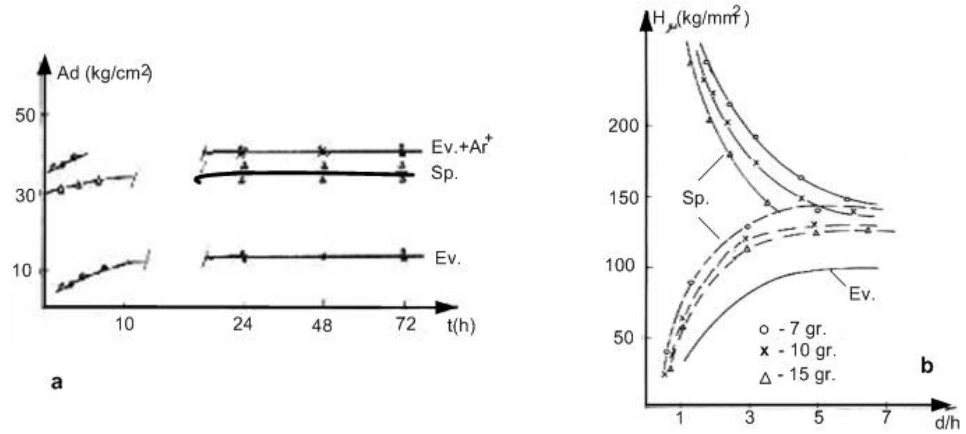

Figure 7: Adhesion and microhardness of dental gold thin films on acrylate substrate: a) adhesion vs. aging time of evaporated (•), sputtered (Δ), and evaporated and then Ar^+ bombarded (x) thin gold films; b) microhardness vs. d/h for different loads on glass (solid lines) and on acrylate (broken lines).

Slika 7: Adhezija in mikrotrdota tankih plasti dentalnega zlata na akrilatni podlagi: a) adhezija v odvisnosti od časa staranja naparjenih (•), napršenih (Δ) in naparjenih nato pa bombardiranih z Ar^+ (x) tankih plasteh zlata; b) mikrotrdota v odvisnosti od *d/h* za različno obremenitev na steklu (cele črte) in na akrilatu (črtkano) polymeric surfaces and thin films, because of their limited penetration depth. The ion-doping processes in polymers are different from those observed in metals and alloys, and the fundamental beam-insulator interactions are not well understood. The charge state of implanted ions, the microstructural evolution, the reaction with the host atoms and the phase evolution during annealing cannot be predicted accurately.

In recent years numerous papers have been published on the subject of the surface treatment of insulators by keV-ions, γ-rays, and electrons in order to modify the surface morphology, the adhesion between polymers and metal (in the microelectronics packaging industry), biocompatibility, or enhanced surface stability and durability. The results suggest that irradiation has a positive effect on the adhesion due to the electronic excitation effect in a high-energy region [23]. In our study, commercial polytetrafluoroethylene and acrylate with a deposited dental gold thin film (d = 50–150 nm) were bombarded with Ar^+ ions (E = (5–20) keV). The surface topography of the samples was investigated with a scanning electron microscope, while the adhesion was determined with a pull test. The samples were cemented to the holders and the tensile force to break the thin-film substrate bond was measured.

Our experimental results have shown that the adhesion of deposited thin films on polytetrafluoroethylene is poor due to the chemical inertness of the polymer. After the bombardment the surface topography and the adhesion were examined as a function of Ar^+ ion dose. The change of color was dependent on the implanted dose. For a dose of ions $3\cdot10^{12}$ 1/cm^2 only poor color changes have been observed, while for ions $2\cdot10^{16}$ 1/cm^2, as a result of polymer destruction mainly through carbonization, the surface was almost black The influence of ion dose on adhesion is positive, but not very significant. The increases of ion dose in these intervals improve the adhesion by about 5 %.

The results of deposited thin films on acrylate were different [24]. Surface treatment with Ar^+ ions resulted in an improvement in adhesion as a result of the alteration of surface topography (increased surface roughness) and enhanced surface diffusion. Adhesion tests have shown that with a high ion energy, the adhesion of evaporated thin films is about 10 % higher than the adhesion of sputtered deposits. In comparison with evaporated thin films, the adhesion is seven times higher when ion bombardment is employed. As the dental gold contains about 14 % of other metals (Ag, Cu, Pd, Pt and Zn) it is possible that oxidation also contributes to the increase in adhesion. From a stomatologist's point of view, the results are satisfactory too (**Figure 7**).

One of the most exiting developments in the ion bombardment of thin polymer films is the formation of microporous and nanoporous membranes (ion track membranes). By bombarding polyethyleneterephalate with MeV heavy ions (Au, Xe and U) uniform cylindrical pores through the sample can be obtained. The materials are used for filtration applications.

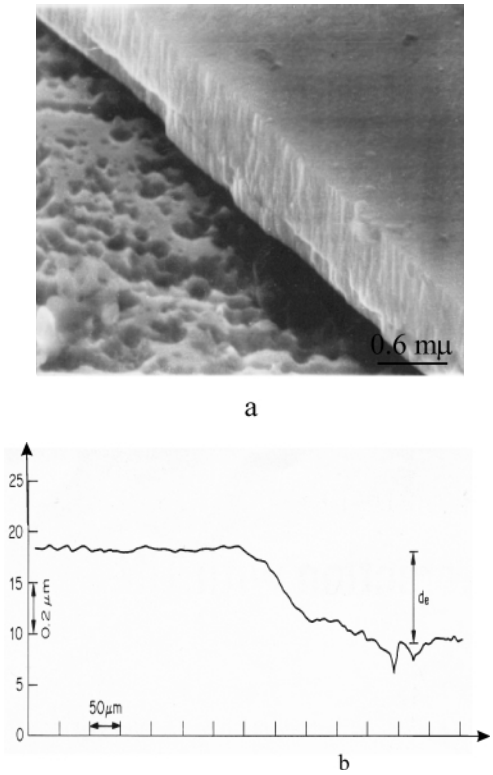

Figure 8: Erosion depth of the TiN coating determined by profilometer (Ar^+ dose $3\cdot10^{19}$ ions/cm^2).

Slika 8: Globina erozije TiN-plasti, določena s profilmetrom (Ar^+ doza ionov $3\cdot10^{19}$ 1/cm^2)

e. Beam modification of ceramics. Ion bombardment is a promising method for modifying the surface properties of ceramics[25]. The problems for the broad application of engineering ceramics are sensitivity to fracture, unsatisfactory friction and surface finishing. The deposition technique and the ion-beam technique have been developed to achieve appropriate properties of ceramic materials. Our results have shown that the ion-beam surface modification of TiN ceramics (E_o = 3keV) induces microstructural changes, which should be distinguished from those of deposition techniques. The erosion stability of coatings is relatively good (**Figure 8**). The Ar concentration in TiN coatings, the erosion depth and the roughness increase with bombarded doses, while the microhardness decreases (**Table 2**).

4 CONCLUSIONS

The beam-induced modification of materials will make a substantial contribution to tailoring the performance of bulk materials and surfaces, to the development of advanced materials and to understanding metastable structures and nanostructures. A central goal of modifying the material properties is to improve the physical, chemical or mechanical properties through the control of changes in microstructures or chemical composition. The processing methods for producing advanced metal alloys, ceramics, composites or polymers very often yield specific, more efficient and cost-effective products.

For the process to be important in the modification of materials properties we must attempt to understand and to explain what is going on during the complex problems of interaction and accommodation in a crystal. In other words, it is not enough only to use new experimental techniques and more precise measurements, but we must move from a technique-driven discipline to a science-driven discipline.

REFERENCES

[1] A. Bishay, Ed. Interaction of radiation with solids, Plenum Press, New York, 1967

[2] B. Navinsek, Ed. *Proc. 8th SPIG, Partizanska knjiga,* Ljubljana, 1976

[3] T. M. Nenadovic, T. P. Mihac, Z. L. Rakocevic, *Thin Solid Films* 218 (**1992**), 247

[4] T. Nenadovic, N. Popovic, J. Fine, *J. Mat. Science* 24 (**1989**), 3699

[5] G. A. Somorjai, *Surf. Interface Anal.* 19 (**1992**), 493

[6] M. J. Bennett, *Surf. Interface Anal.* 22 (**1994**), 421

[7] J. Friedel, Ann. Phys., No.6 (**1976**), 257

[8] J.W. Rabalais, D. Morton, *Nucl. Instr. and Meth.* B67 (**1992**), 287

[9] P. Sigmund, *Phys. Rev.* 184 (**1969**), 383

[10] H. H. Andersen, H. L. Bay, *J. Appl. Phys.* 46 (**1975**), 1919

[11] T. Nenadovic, R. Simovic, T. Jokic, *Nucl. Instr. and Meth.* B67 (**1992**), 560

[12] M. Trtica, B. Gakovic, T. Nenadovic, M. Mitrovic, *Appl. Surf. Sci.* 177 (**2001**), 48

[13] E. W. Plummer at all. *Progress in Surface Science,* 67 (**2001**), 17

[14] D. Brune at all. *Surface Characterization,* Wiley, New York, 1997

[15] G. Dearnaley, Practical Application of Ion Implantation, *Proc. Mat. Res. Soc. Ann. Meeting*, Cambridge, 1979

[16] D. Mattox, *J.Appl. Phys*. 34 (**1963**), 2439

[17] G. Dearnaley*, Mater. Eng. Appl.* 1 (**1978**), 28

[18] M. Fine, *Metall. Trans. A,* 11A (**1980**), 365

[19] N. Hartley, W. Swindlehurst, G. Dearnaley, J. Turner, *J. Mat. Sciences* 8 (**1973**), 900

[20] J. Matsuo, T. Seki, T. Aoki, I. Amada, *Nucl. Instr. Methods* B 206 (**2003**), 838

[21] R. Birtcher, J. Matsuo, I. Yamada, *Nucl. Instr. and Methods* B 175 (**2001**), 36

[22] H. Ryssel, H. Glawisching, *Ion Implantation Technique,* Springer, Heidelberg, 1982

[23] S. Sugden, C. Sofield, M. Murrell, *Nucl. Instr. and Methods,* B 67 (**1992**), 452

[24] T. Nenadovic, N. Bibic, N. Kraljevic and M. Adamov, *Thin Solid Films,* 34 (**1976**), 211

[25] W. Bolse, S. Peteves, *Nucl. Instr. and Methods*, B 68 (**1992**), 331

[26] T. Nenadovic, B. Gakovic, Z. Rakocevic, *Science of Sintering,* 31 (**1999**), 23