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# Review

# Ion sputtering and its application to biomaterials

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The main purpose of this article is to review the mechanisms of surface morphology and chemistry changes induced by ion sputtering of solids, and in so doing, discuss the influence of ion processing on surface morphology and chemical composition of biological implant materials. The influence of the ion bombardment induced morphological and chemical changes of biomaterials on mechanical properties and tissue response is also presented in the article.

## 1. Introduction

In recent years there has been a growing interest in the study of ion sputtering of solid surfaces largely because of the practical applications of this process. Numerous experiments have been performed to investigate the development of the surface topographical features on ion-bombarded amorphous and crystalline targets and the surface compositional changes of multicomponent materials induced by ion irradiation. These experiments enable one to explain and/or predict the development of some topographical features and to clear up some problems of modification of chemical composition resulting from ion bombardment of solids. In the last seven years the ion sputtering technique has become widely used in attempts to modify the surface morphology (topography) and chemistry of biological implant materials. It appears that this technique has a unique capability to vary the surface morphology of these biomaterials. The microscopically rough surface texture produced by ion processing may result in improvements in biological response and/or performance of implanted devices, and also in the modification of mechanical characteristics of implant materials. As yet, it is difficult to say anything definite about the influence of compositional changes induced by ion processing on the mechanical properties of biological implant materials and/or tissue response in the tissue surrounding the sputtered implant. Ion bombardment of solids causes both chemical and morphological changes and therefore it is not easy to attribute alterations in mechanical properties and tissue response data to one or the other cause. It seems that additional studies are necessary to answer these difficult questions. For example, the use of transfer cast biomaterials peeled from ion beam textured surfaces may allow morphological changes to be fabricated with minimal surface chemical alteration.

It is the purpose of the present paper to review the mechanisms of surface morphology and surface chemistry changes induced by ion sputtering of solids, and in doing so, discuss the influence of ion sputtering on surface morphology and chemical composition of biological implant materials. The influence of the ion bombardment induced morphological and chemical changes of biomaterials on mechanical characteristics and tissue response is also presented in the article.

## 2. Sputter texturing processes

Sputter texturing is the microroughening of the solid surface resulting from the ion bombardment of this surface. There are three major methods of ion texturing usually used to alter the surface morphology of biological implant materials, i.e. natural texturing, seed texturing, and pattern texturing.

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## 2.1. Natural texturing

Natural texturing (NTex) is the microroughening of the ion bombarded surface of the sample that occurs if there are spatial variations in the sputtering yield of the target surface. Different kinds of materials, such as multicomponent materials, chemically pure materials, heterogeneous and homogeneous materials, can develop natural texture in consequence of ion bombardment. Ion sputtered targets composed of two or more materials or forms of materials that are present in a spatially segregated heterogeneous mixture throughout the target develop this kind of texture. A chemically pure material composed of randomly oriented crystallites with each having a different sputtering yield (which is dependent upon their orientation) reveal a patchy texture surface showing enhanced visibility of these crystallites as a result of ion irradiation. Pure materials may also develop a microrough natural texture if there are small voids distributed throughout the bulk that are exposed by the ion beam. Variations in sputtering yield with the angle of ion incidence and the presence of voids can result in a pitted surface [1]. Heterogeneous materials with microscopic sites of compositional segregation will produce a natural textured surface if there are adequate differences in the sputtering yields of the various sites. Homogeneous materials may also develop this kind of texture if the target is sufficiently hot to provide surface atom migration to result in sites of nucleation of segregated elements. Nucleation sites of more sputter-resistant elements covering in a patch like manner less sputter-resistant bulk material would then become the tops or sides of standing surface topography features that we left.

## 2.2. Seed texturing

Sputtering with a sputter-resistant material, seed material, supplying the target surface during ion irradiation is normally referred to as seed texturing (STex). A low sputtering yield seed material is located in the proximity of the target and usually at a 30 to 45° angle with respect to the ion beam axis. The ion beam simultaneously sputters both, the target and the seed material. Some of the seed material is deposited on the target surface. It has been generally understood that the obtained surface texture results from clusters of seed atoms protecting the underlying substrate while the surrounding substrate material is sputtered away. Kaufman and Robinson [2] and Robinson [3] have made analytical models of the dynamics of seed texturing. Seed atoms are assumed to move from adsorption site to adsorption site on the target surface by a random walk process. Only those seed atoms that acquire an energy greater than the activation energy $E_d$ (i.e. the potential barrier between adjacent sites) are mobile. Activation energy is a function of the seed–substrate material combination together with a small temperature effect and ranges from about 0.5 to 2 eV for metallic materials of interest for seeding. The radius $r_d$ over which surface diffusion can be expected to take place is $r_d = 2 \times 10^{-4} \exp(-E_d/2kT)$. This radius is a function primarily of the activation energy $E_d$ and the substrate temperature $T$. Other factors such as seed atom mass, ion flux, and the adsorption site spacing are considerably less important. Having found the radius from which diffusion will supply a seed cluster, it is appropriate to consider the stability of that cluster. There is a critical size for a seed cluster below which steady growth is not possible. Whether or not a seed cluster is stable will depend on the diffusion rate to the cluster being sufficient, or insufficient, to supply the sputtering loss from a cluster of critical radius. The required diffusion radius $r_d$ to sustain a seed cluster of critical radius $r_c$ is $r_d = r_c/F_s^{1/2}$, where $F_s$ is the ratio of incident seed atoms to incident ions. A seed texturing theory [2, 3] based on the surface diffusion accurately predicts both a minimum temperature for texturing to take place and the variation of cone density with temperature. The minimum substrate temperature that will give the required diffusion, i.e. the minimum critical temperature for texturing is $T = 587 E_d$, ($E_d$ in eV). It was predicted from the theory, and also verified experimentally, that a high sputter yield material could serve as a seed for coning of a lower sputter yield material if the seed were sufficiently mobile on the target surface. The existence of a minimum temperature for coning is also important for the production of smooth surfaces, in that a sufficient reduction in surface temperature should reduce the mobility of any seed material enough to avoid coning. The seed material sputtering yield does not always have to be lower than the target material in order that texturing occurs. It seems that the seed material must simply have a higher melting temperature than the target material to be

TABLE I Sputtering yields and melting points of various elements

| Symbol | Elements | Sputtering yield, at/ion | Melting point (° C) |
|---|---|---|---|
| Ag | Silver | 3.12 | 960.8 |
| Al | Aluminium | 1.05 | 660.0 |
| Au | Gold | 2.40 | 1063.0 |
| B | Boron | – | 2030.0 |
| Be | Berylium | 0.51 | – |
| Bi | Bismuth | – | 271.3 |
| C | Carbon | 0.12 | 3727.0 |
| Cd | Cadmium | – | 320.9 |
| Co | Cobalt | 1.22 | 1495.0 |
| Cr | Chromium | 1.18 | 1875.0 |
| Cu | Copper | 2.35 | 1083.0 |
| Dy | Dysprosium | 0.88 | – |
| Er | Erbium | 0.77 | – |
| Fe | Iron | 1.10 | 1536.0 |
| Ga | Gallium | – | 29.8 |
| Gd | Gadolinium | 0.83 | – |
| Ge | Germanium | 1.1 | 937.4 |
| Hf | Hafnium | 0.70 | 2222.0 |
| In | Indium | – | 156.2 |
| Ir | Iridium | 1.01 | 2454.0 |
| Mn | Manganese | – | 1245.0 |
| Mo | Molybdenum | 0.80 | 2610.0 |
| Nb | Niobium | 0.60 | 2468.0 |
| Ni | Nickel | 1.45 | 1453.0 |
| Os | Osmium | 0.87 | 3000.0 |
| Pb | Lead | 2.7 | 327.4 |
| Pd | Palladium | 2.08 | 1552.0 |
| Pt | Platinum | 1.40 | 1769.0 |
| Rb | Rubidium | 1.15 | – |
| Re | Rhenium | 0.87 | 3180.0 |
| Rh | Rhodium | 1.30 | 1966.0 |
| Ru | Ruthenium | – | 2500.0 |
| Sb | Antimony | – | 630.5 |
| Si | Silicon | 0.50 | 1410.0 |
| Sm | Samarium | 0.80 | – |
| Sn | Tin | – | 231.9 |
| Ta | Tantalum | 0.57 | 2996.0 |
| Th | Thorium | 0.62 | – |
| Ti | Titanium | 0.51 | 1668.0 |
| U | Uranium | 0.85 | – |
| V | Vanadium | 0.65 | 1900.0 |
| W | Tungsten | 0.57 | 3410.0 |
| Y | Yttrium | 0.68 | – |
| Zn | Zinc | – | 419.5 |
| Zr | Zirconium | 0.65 | 1852.0 |

– No data.

Sputtering yield values, for 500 eV argon ions bombardment, are from B. A. Banks [4].

Melting points are from Ron Iscoff, Semiconductor International, October 1982, 57.

textured [4]. Sputtering yields and melting points of various elements are listed in Table I.

Textured surfaces are considered for applications such as low-reflectance solar cells, high emissivity heat radiators and medical implants.

## 2.3. Pattern texturing

The third way of sputter texturing a solid surface is ion sputtering through a screen mesh mask imposed on the material during ion irradiation. The screen prevents the erosion of the target material directly beneath it, resulting in the surface with an array of pores of constant dimension, for example square hole pattern etched in the surface. The technique could be termed "pattern texturing" (PTex).

Associated with both, the screen mesh mask and seeding techniques to alter the surface morphology, there is some contamination of the target material with the mesh or seed material. This can be partially removed by further sputtering. Clean-up sputter etching and aqua regia acid bathing appears to eliminate much of the mesh or seed atoms but a small fraction usually remains entrapped.

# 3. Surface morphological and chemical modification induced by ion beam processing

It is well known that ion bombardment of solids can modify the surface morphology of these materials. In addition to these modifications the changes of the chemical composition may also be observed (in the case of multicomponent materials). Some major problems concerning the morphological and compositional changes induced by ion irradiation of solids (especially biomaterials) are discussed below.

## 3.1. Surface morphological changes

The changes in surface morphology (topography) which occur as a consequence of ion sputtering have been studied for many years. The majority of the theoretical work has been concerned with amorphous (or random) solids.

In the subsequent discussion we will distinguish between studies with:

(a) random media where point and extended defects have little or no meaning, and the dominant effects will be a result of the macroscopic variations of sputtering yield as a function of the incidence angle, and microscopic yield variations near the point of ion impact due to spatial variations of energy deposition distribution, and

(b) crystalline media where such effects may be additional to that due to microscopic scale variation in yield as a result of defect production and interaction with the surface.

Each of these effects may contribute in some way to the development of surface morphology, but other processes of atomic scale morphological change may also operate, especially surface and volume diffusion [5], particle flux variation [6] and local sputtering yield variation [7]. Some significant deviations of the ion sputtered morphology from theoretical predictions can be expected as a result of these processes. There are several rather less important problems which also must be considered, i.e. the redeposition of sputtered material on the closely adjacent planes, the ion reflection at grazing incidence, dechannelling at dislocation lines, the surface binding energy modifications arising from variations in crystallographic orientation or elastic stress, sample temperature changes resulting from irradiation, etc.

The first analysis of the topography change of the amorphous solids was made by Steward and Thompson [8] who investigated the motion of surface elements composed of intersecting semi-infinite planes. They, assuming that the dependence of the sputtering yield on the angle of ion incidence could possibly be responsible for the observed microscopic surface features, were the first to give the equation of motion of intersection of two planes during ion erosion. These results, applied to the step erosion, show the dominant role played by the planes inclined at an angle $\theta_m$ corresponding to the angle where the sputtering yield is a maximum ($\theta$ is the angle between the beam incidence and surface normal). Barber *et al.* [9] adapted a theory of chemical dissolution to ion induced erosion and developed a geometric construction method. Using the same basic assumptions as Steward and Thompson [8], Carter *et al.* [5] developed a theory for the sputtering of amorphous solids by an ion beam and the changes in the surface topography to which this sputtering leads. These authors proposed [10] a generalized approach to sputter erosion, which was shown to incorporate their own earlier work [11, 12], where they studied the motion of individual points on a general two-dimensional surface, the planar motion investigated by Steward and Thompson [8], and the Barber *et al.* method. This model shows that a steady state is reached when the surface topography consists of planes aligned either parallel or perpendicular to the direction of the ion beam and inclined at $\pm\theta_m$. It should be noted, that similar results have also been obtained by Ducommun *et al.* [13, 14] who treated a general surface contour as an envelope of linear segments and investigated the time dependent behaviour of this envelope during erosion.

An analytical approach to the development of surface morphology allows prediction of trends in the surface development and prediction of the final steady-state contours. However, a complete analytical solution is generally unobtainable except for the simplest of contours. What the analytical approach does give is a set of equations describing the instantaneous change of a surface contour over a short time interval.

It is well known, that during the ion bombardment of solid surfaces, well-defined surface topographical features are developed. In crystalline solids these can usually be associated with the generation of defects below but very close to the surface and the interaction of the complex defect forms which are produced with the surface. Even with amorphous solids, however, in which such interactions should not be present, regular features (undulations) are generated and it is generally believed that their development results from the fact that the sputtering yield is a non-monotonic dependence of the angle of ion incidence to each point of the surface. Experimental observations of ion sputtered crystalline surfaces indicate the development of regular features (undulations) associated with the symmetry of the crystal, rather than irregular features associated with local perturbational effects such as impurities and inclusions, which appear on amorphous solids.

Hermanne and Art [15] suggested that if a regular array of dislocations was formed by a defect agglomeration below ion bombarded crystalline surface, then ion channelling would be interrupted by these dislocations, the ion energy loss rate would increase locally near the surface and a spatially periodic variation of sputtering yield would occur at the surface, giving rise to the regular features. Hermanne [16] has made a first attempt at defining the conditions for such dislocation growth and stability to occur. The necessary condition for the possible initiation of a surface structure of the type for which the origin is related to the radiation damage is satisfied if the averaged migration speed of all the defects participating in the elaboration of the extensive defects

TABLE II Topographical features observed at the ion sputtered surfaces of solids

| Name of the feature | Kind of material sputtered | References |
|---|---|---|
| blister | metals | [16, 25–27] |
| bump | semiconductors | [18] |
| column | semiconductors | [18] |
| cone | metals, semiconductors, metal alloys, glass, resin | [7, 8, 11, 18–23] |
| crater | metals | [7, 15, 24] |
| furrow | metals | [7, 15] |
| groove | metals | [7, 15] |
| hummock or hillock | glass, metals | [7, 11, 15, 24] |
| pit | metals, semiconductors glass | [11, 18, 15, 20, 23] |
| ridge | metals | [7, 8, 22] |
| roof | metals | [15] |
| step | metals, semiconductors | [8, 11, 15] |
| whisker | semiconductors, resin | [18, 19] |

is larger than the minimum required speed. If, however, sputtering is more rapid, dislocations do not have time to form before the required defect population is removed. Nelson and Mazey [17] observed that a regular dislocation array located beneath a surface may lead to a periodic variation of the surface stress, thus leading to a periodic variation of the surface binding energy and thus of the sputtering yield and allowing surface undulations to form. They also indicated that if the array intersected the surface then again the binding energy would be disturbed locally in the vicinity of the dislocations and undulations would occur.

Concluding, we can say that there are several mechanisms by which regular structures can be initiated on solid surfaces during ion irradiation. However, whether any of these are themselves sufficient to account for the observed topographies which develop after continued sputtering, is not clear.

It was stated earlier that ion sputtering can modify the surface topography (morphology) of solids. Many topographical features have been observed at the surfaces after ion bombardment but generally two types [16] or classes [18] of surface topography should be distinguished, according to their origin. One type consists of features of different aspects appearing on amorphous, polycrystalline and single-crystal surfaces, whose origin is related to impurities or irregularities present in or under the surface before the beginning of ion irradiation. These features, most often observed at the sputtered surfaces, are listed in Table II.

Table III presents, as an example, topographic features usually observed at the ion bombarded surfaces of glasses. It is important that the origin of this first class of topography is independent of the radiation damage created by the incoming ions. The second type is more or less a regular pattern of arrays or any of the previous features appearing on single-crystal surfaces or on the surface of only some grains of polycrystalline samples. Their origin is related to radiation damage, i.e. the defects created and the impurities implanted during the bombardment, and is dependent on the irradiation parameters, i.e. ion type, dose, energy and incidence direction, target type, crystal orientation of the sample, target temperature, etc. A model for the mechanism of formation of this

TABLE III Ion etching of glass – conditions and results (observed topographic features) [28]

| Beam characteristic | Target material | Incident angle | Observed topographic features |
|---|---|---|---|
| air, 4 kV | Natrium–calcium glass | $\theta = 0^\circ$<br>$20^\circ < \theta < 60^\circ$ | Hummocks<br>Parallel grooves perpendicular to the beam |
| Ar$^+$, 50 kV 10 mA cm$^{-2}$ | Fused silica | $\theta > 75^\circ$<br>$\theta = 0^\circ$<br>$\theta = 85^\circ$ | Parallel grooves along the beam<br>Pitted surface<br>Striated surface |
| N$^+$, 20 kV 10 $\mu$A cm$^{-2}$ | Corning 7059 | $\theta = 50^\circ$ | Cones |
| Ar$^+$, 20 kV 30 $\mu$A cm$^{-2}$ | Silica glass | $\theta = 0^\circ$ | Depressions, steps, terraces |
| Ar$^+$, 6–8 kV 500 $\mu$A cm$^{-2}$ | Soda-glass | $\theta = 27^\circ$ | Parallel grooves along the beam |
| Ar$^+$, Ne$^+$ 50 kV | Glass | $\theta = 0^\circ$ | Blisters |

class of surface topography is based on the migration of point defects in clusters. These clusters become bigger (by absorption of more point defects) and grow out to one of the configurations of so-called extensive defects, for example dislocations. If the surface which is regressing due to ion sputtering approaches one of these defects, these cause a local decrease of ion penetration into the target, and as a consequence a local increase in the sputtering yield. The regularity or randomness of the second type of surface topography depends on the configuration of the extensive defects, when the surface reaches their level. There is evidence that some of the microscopic effects are closely related to the type of bulk damage produced within the solid, whilst more macroscopic effects are related to initial surface morphology, impurity inclusions at the surface and variations in the sputtering yield as a function of the angle of ion incidence to the surface.

The ion sputtering of materials may result in a biomedical application of ion beam technology. Ion beam sputtering of various polymers, metals and alloys used as biological materials can produce a controlled microscopic roughening of the surfaces of these materials. This controlled roughening has the potential to improve the performance of prosthetic materials, i.e. synthetic materials used to replace natural tissue or organs. There are several ways (mentioned in Section 2) to enhance the formation of the ion sputtered surface topography: natural sputtering, seed texturing, and pattern texturing. A natural, seed or pattern texture can be generated in most of the biological implant materials [4, 29, 30]. The surface microstructures obtained after natural or seed texturing are typically a few microns high or smaller. It is evident that the topographical features usually observed at the ion sputtered surfaces of solids (see Table II) can also be seen at the surfaces of biomaterials. The main problems which concern the influence of surface morphology of biological implant materials on the biological response are presented in Section 5.

## 3.2. Surface chemical modification

In addition to surface morphology changes the ion sputtering process can also modify the surface or subsurface chemical composition of solids (multicomponent materials), mainly as a result of preferential (non stoichiometric) sputtering of one of the components. This is indicated in the work of several investigators [31–40]. In the absence of surface roughening the degree of preferential sputtering should decrease with time because of the increasing impoverishment in the surface (subsurface) region of the easy-to-sputter component. At some level of depletion non stoichiometric sputtering ceases. Finally after steady-state conditions are reached, the target will be sputtered stoichiometrically. However, in general the surface will have another composition to that of the bulk [39].

Ion bombardment leads generally to the surface enrichment of the component having a lower sputtering yield. Conceptually, if one of the elements (components) has a significantly different sputtering yield than the other, the element with the higher yield will be preferentially depleted from the target surface leaving the other (others) element enriched. It is worth noticing that the term "sputtering yield" is used in the literature to mean two separate things. One definition is the number of atoms of the element in question sputtered, divided by the total number of ions which are incident on the target. A second definition sometimes used is the number of atoms of the element sputtered, divided by the number of ions striking atoms in the element. If we denote the first as $S$ and the second as $Y$, then the two definitions are related by the relationships: $S = NY$, where $N$ is the atom fraction of the element in question at the surface or near surface of the sample. One important question in sputtering studies is the correlation of the sputtering yield in multicomponent materials with those of the pure elements [39]. The preferential sputtering behaviour of these materials cannot be predicted according to the sputtering yields of individual elements. Also total sputtering yields of multicomponent systems have been found to be quite different from a superposition of the yields of the components (elements). It was found that the component sputtering yield ratios in the alloys are in general larger than for the pure elements, independent if the lighter or heavier component is the enriched one.

Although the sputtering yield studies are very important they do not contribute to understanding the mechanism of the preferential sputtering in multicomponent materials. The main reason is that the sputtering yield is the phenomenological coefficient [41] and it depends on many factors

[42, 43], particularly on the ion energy, its angle of incidence, the target atomic mass to ion mass ratio and the target surface binding energy. For multicomponent materials the effects of the component mass difference and binding energy seem to be of fundamental importance for understanding the nature of the preferential sputtering mechanism. Kelly [40] has presented the relevant theory, with mass effects being shown to be associated most explicitly with recoil sputtering and bonding effects being shown to be associated with all three of cascade sputtering, thermal sputtering and surface segregation. Recoil sputtering was treated as a "second generation" problem in which the emphasis was placed on the target atoms struck directly by incident ions (it contains a significant mass dependence). Cascade sputtering, in view of the proportionality: $S_c \propto 1/U \propto 1/\Delta H^a$, where $U$ is the surface binding energy and $\Delta H^a$ is the heat of atomization, is governed more by chemical bonding than by mass. Thermal sputtering and surface segregation also involve bonding because of the proportionality (for surface segregation a relation is very similar in form to that for thermal sputtering):

$$S_{\text{th}} \propto M^{-1/2}\, \hat{T}^{3/2}\, (\Delta H^a)^{-2} \exp(-\Delta H^a/k\hat{T}),$$

where $M$ is atomic weight and $\hat{T}$ is the "thermal spike" temperature. Kelly has also shown [40] that most experimental observations can be understood rather well in terms of bonding, whereas mass correlations are found to be quite unsuccessful. The basic problem is that the cascade component of sputtering, normally judged to be predominant, should give significantly less compositional change than is observed (real systems show much greater changes). Thermal sputtering [44] would lead to more significant modification, because even a small thermal contribution in the overall sputtering process could be important, but the absolute yields are probably rather small. A combination of surface segregation with sputtering would also lead to more significant changes, but it is unclear whether segregation is rapid enough to be important in room-temperature bombardments. These changes can be very large, provided only that the temperature is not too low for the necessary mass transport to occur (such an alteration normally requires a relatively high temperature).

Except for the sputter-induced surface roughness (texture) and the compositional changes, the ions used for sputtering can "mix" atoms over depths comparable to the ion range. The mixed-layer thickness is nearly proportional to the ion energy [45]. Schwarz and Helms [46] have developed an ion knock-on mixing model based on an analogy to thermal diffusion theory, but it should be noted that the basic phenomena of ion beam mixing is not yet well understood. Often more than one mechanism appears to be contributing to the large effects observed in which 1 to 50 atoms are mixed per incident ion. Two primary mechanisms have been proposed for ion beam mixing [47]. The first is collisional mixing, involving both direct large-energy recoil events and small displacements in the collision cascade. The second mechanism is diffusional mixing and involves enhanced diffusion within the cascade owing to the defects created.

Another interesting problem is the influence of diffusion on the compositional changes of multicomponent materials. Koshikawa *et al.* [37] have evaluated the surface composition of binary alloys sputtered by $Ar^+$ ions. The surface analysis (AES) was made at room temperature and also at low (− 150° C) temperature at which the thermal diffusion of the constituent elements to the surface could be ignored. The small difference in the surface concentration at each temperature has indicated that the diffusion enhancement is rather small in the ion bombardment induced compositional changes of multicomponent materials at room temperature.

Summarizing the discussion presented above we can say that ion bombardment of a multicomponent material usually modifies the chemical composition near the surface of this target. Data obtained from surface analyses, however, do not seem to allow one to distinguish between compositional changes caused by sputtering or by the rearrangement of material within the target [35]. Some bulk processes tend to generate spatial variations in composition under ion bombardment, others tend to randomize the target. To the first category belong: segregation, which may produce different phases both at the target surface and in the deeper layers and recoil implantation, which tends to transport the lighter species deeper into the target. Cascade mixing and diffusion both randomize existing composition variations. The relative significance of recoil implantation, recoil and cascade sputtering, thermal sputtering, mixing, diffusion and segregation for observed compositional changes in various materials has not been clarified yet.

It is worth mentioning that this is not always the most important problem. For instance in medicine, especially in the field of implantology, the most important problem is not the mechanism of chemical composition changes of biomaterials but the practical effects of this process, i.e. for example, the question of whether compositional changes are significant or not, do they or do they not influence the mechanical properties of biological implant materials and/or tissue response for the biomaterial after implantation. In the last seven years some experiments were performed to investigate the influence of the ion sputtering of implants on the surface chemical composition of implant materials [4, 48–52]. For example, McIntyre *et al.* [51] have stated that argon ion bombardment of iron–nickel–chromium alloys and binary iron–nickel alloys does not result in the significant alteration (about 10%) of the surface composition of either alloy. Also energy dispersion spectrometry (EDS) results obtained by Weigand *et al.* [48] indicated very little change in the surface composition of a cobalt–chromium–tungsten surgical implant alloy (ASTM designation F90-68, Co–20 Cr–15 W alloy) as a result of ion beam sputtering. Except for biomedical alloys, the near-surface chemical changes of biomedical polymers resulting from ion beam irradiation were also investigated [49, 50]. These materials included: bioelectric polyurethane, cross-linked polyurethane (Tecoflex) and segmented polyurethane (Biomer), ultrahigh molecular weight (UHMW) polyethylene, UHMW polyethylene with carbon fibres, polyoxymethylene (Delrin), 32% carbon-impregnated polyolefin, silicon rubber (Silastic) and polytetrafluoroethylene – PTFE (Teflon). All ion sputtered samples, except 32% carbon-impregnated polyolefin and PTFE, showed detectable amounts of argon in the surface (probably either implanted or surface adsorbed). ESCA surface chemistry characterization of the control and ion sputtered biopolymers in question is presented in Table IV (only the main elements are listed, i.e. elements which are common to each of the polymers presented in the table). For the two polyethylenes, silicon rubber and PTFE the ion bombardment caused a reduction in the amount of carbon relative to oxygen. Ion processing increased the C/O ratio for the three polyurethanes, polyoxymethylene, and 32% carbon-impregnated polyolefin. Picha [52] investigating tissue response to peritoneal implants (polytetrafluoroethylene, polyetherurethane, and 2 hydroxyethylmethacrylate) has stated that the influence of ion sputtering upon chemical composition is minimal based on ESCA (electron spectroscopy for chemical analysis) and ISS (ion scattering spectroscopy). Both analyses suggest a slight increase in fluorene concentration (for PTFE).

In general it can be concluded that the surface chemical changes of biomaterials resulting from sputter-etching are rather minimal in spite of the often significant changes in the surface morphology.

## 4. Influence of ion sputtering on mechanical properties of biomaterials

Information about the influence of ion beam sputtering on the mechanical properties of biomaterials is rather sparse. There are only several articles concerning this problem. In order to show the importance of the question some experimental results, as examples, are presented below.

Weigand *et al.* [48] have evaluated the influence of ion texturing of biomaterials on such mechanical properties as ultimate strength, strength of the bond between two different materials, hardness and ductility. They have stated that an ion sputtered surface microstructure on samples of cobalt–chromium–tungsten alloy (Haynes 25) and stainless steel did not reduce the ultimate strength or hardness. The strength of the bond between polymethyl methacrylate and titanium–aluminium–vanadium alloy (Ti-6,4) was not significantly increased as a result of ion processing. The total elongations of the ion-treated samples of Haynes 25 and stainless steel did not change from the control sample values, which indicates that ion sputtering does not modify the ductility of these materials.

Standard diameter tensile samples of Haynes 25 and stainless steel, and standard fatigue samples of Ti-6,4 alloy and stainless steel were also sputtered to study the influence of ion processing on mechanical properties [49]. Examination of the effects of ion textured surface on the ultimate strength, yield strength and fatigue strength revealed very little degradation of the properties. The results of tensile tests of nine biomedical polymers, obtained by Weigand and Cenkus [50], indicated a per cent reduction in ultimate tensile strength resulting from ion bombardment ranging from 1 to 19%. Because of the large range of variations of some of the results the authors have concluded that the

TABLE IV ESCA surface chemistry characterization of control and ion sputtered biopolymers [50]. Surface elemental composition expressed as atom per cent for the detected elements

| Element | Sample | Material | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Polyurethanes | | | Polyethylenes | | Polyoxymethylene | 32% carbon – impregnated polyolefin | Silicone rubber | PTFE |
| | | bioelectric | cross-linked | segmented | UHMW | UHMW with carbon fibres | | | | |
| C | control | 74 | 75 | 72 | 81 | 87 | 57 | 85 | 50 | 34 |
| | sputtered | 79 | 84 | 85 | 73 | 86 | 85 | 95 | 51 | 39 |
| O | control | 20 | 19 | 19 | 12 | 7.6 | 37 | 8.2 | 23 | 0.7 |
| | sputtered | 15 | 13 | 11 | 17 | 12 | 14 | 2.8 | 25 | 1.0 |
| Si | control | 4.7 | 3.8 | 5.5 | 5.4 | 3.7 | 3.2 | 4.5 | – | 0.5 |
| | sputtered | 4.2 | 2.0 | 1.2 | 5.5 | 0.5 | 0.2 | – | 23 | 0.2 |
| N | control | 1.4 | 1.5 | 2.1 | 0.2 | 0.4 | 1.5 | 0.4 | – | – |
| | sputtered | 0.5 | 0.7 | 1.8 | 0.7 | 0.4 | – | – | – | – |
| C/O ratio | control | 3.7 | 3.9 | 3.8 | 6.7 | 11.4 | 1.5 | 10.4 | 2.2 | 48.6 |
| | sputtered | 5.3 | 6.5 | 7.7 | 4.3 | 7.2 | 6.1 | 33.9 | 2.0 | 39.0 |

– no observation of a signal.

reduction of tensile strength after ion irradiation is not a significant change. The general shape of the stress–strain curves for both untreated and ion sputtered samples was the same.

Very interesting fatigue tests were made by Wintucky *et al.* [53]. These tests were conducted at room temperature with test sections of cobalt–chronium–molybdenum alloy (MP35N), as the fatigue specimens, immersed in an artificial physiological solution formulated to simulate the corrosive environment of the human body. Both types of ion beam sputtered surface structure, i.e. natural texture and square hole pattern texture, were found to reduce the fatigue strength below that of a smooth surface (unsputtered).

Concluding this short section, it could be stated that the examination of the effects of an ion textured surface on the mechanical properties of representative biological implant materials revealed rather small changes in these properties.

## 5. Effect of ion sputtering on tissue response to biological implant materials

It is now generally accepted that the surface morphology is one of the most important factors which affect the biological tissue response to an implant material (after implantation into the body). In order to develop clinically acceptable materials, the influence of the surface morphology of biomaterials on the biological response must be understood. Different problems, such as changes in the healing process that result from the presence of an implant, a firm attachment of the surrounding tissue (or thrombus) to the implant material, etc must be considered depending on whether the implant is used in soft or hard tissue or in contact with the blood. Preliminary tissue response data have been obtained and described by several authors. Short [54] and extensive [4] reviews of biomedical applications of ion beam processing were also presented in the literature. Several important examples describing the influence of the surface texture of biomaterials on tissue response are discussed below.

Xenon–ion-textured titanium and MP35N (cobalt–nickel–chromium–molybdenum alloy) dental implants were tested in beagles. The experimental results indicated a minimal tissue inflammatory or foreign body response and a close adaptation of interfacial tissue with the implant material [49]. Also canine tests have been performed to evaluate zirconia coated cobalt–chromium–molybdenum dental implants in which the surface texture was either smooth or pitted by ion sputtering through the screen mesh mask. The implant test periods ranged from 6 weeks to 1 year. The results of clinical evaluation of the performance of the implants showed success to failure ratios of 0.6 for the pattern textured (pitted) and a 2.3 for the smooth surface implants. The increased failure rate of the pitted surface implants can be characterized by gross mobility, inflammation, hyperplasia, etc [4]. Natural textured MP35N, tantalum seed textured pure titanium and pattern textured aluminium oxide implants have also been evaluated as canine dental implants. Results of experiments indicated no statistically significant difference in the clinical performance or mechanical retention of the implants and prevented any statistically significant conclusions as to whether a closer simulation of cementum morphology resulted in an improved dental implant performance. Recently it appeared that a greater emphasis must be placed on the examination of the use of textured surfaces at the gingival percutaneous location rather than at the osseous level. This statement was based on information indicating that a significant fraction of dental implant failures occurs as a result of peridental disease resulting from an ineffective percutaneous seal rather than problems associated with the anchorage in bone [4].

Concluding this part of the results which concern the ion textured hard tissue implants, it can be stated that the ion processing of these materials rather profitably influences the tissue response. On the other hand, it is difficult to say anything definite about the mechanical retention of ion sputtered implants. Experimental results obtained after implantation of sputtered orthopedic and dental implants indicate no statistically important differences of some mechanical properties of sputtered and unsputtered samples. The application of the ion textured hard tissue implants will require additional knowledge of the short and long term consequences.

The second part of the experimental results relates to the so-called soft tissue implants, i.e. for example, cardiovascular implants, peritoneal implants or percutaneous connectors. Cardiovascular implants of segmented polyurethane were implanted against the inside walls of canine femoral and carotid arteries [55]. The results of the experiments indicate significant differences in the blood response between the ion sputtered and untreated implants. The initial thrombus growth (after 1 h of implantation) was accelerated when compared to the growth on unsputtered samples. However, the final thrombus thickness (after 4 days of implantation) was the same for both ion sputtered and untreated samples.

Flat implants of PTFE, alumina, Haynes 25, Ti-6,4 and 316 stainless steel were pattern textured and tested in the dorsal subcutaneous soft tissue of rats. After an implantation duration of 6 weeks, the implants were investigated for mechanical attachment by means of a "pull out" test. The results indicated an increase in the tissue attachment to ion sputtered samples compared to untreated implants. There was no evidence of an inflammatory cell response in the tissue surrounding the implants.

Peritoneal implants have been used to evaluate cellular response to biomaterials [52]. The peritoneal cavity of a rat is a convenient environment for the observation of the characteristics of cellular interactions with foreign surfaces. Untreated and sputtered PTFE samples, consisting of ion beam polished, natural textured and pattern textured samples, were implanted in rats for periods ranging from 30 min to 14 days. In general the smooth surfaces attracted less cells than ion etched samples – ion sputtering increased the cell attachment by an order of magnitude over the smooth (ion polished or untreated) surface of PTFE. The ion processing was observed to enhance not only cell attachment but also multinucleated giant cell to cell contact, and fibrous capsule formation.

Implants of PTFE and Delrin (polyoxymethylene) have been implanted into the intercostal musculature of rats to investigate the tissue response to both ion sputtered and untreated samples [4]. It has been stated that ion beam processing induced the following modifications in the mononuclear phagocytes adjacent to the implant surface: increased cell adhesion, metabolism, acid phosphatase activity, increased vacuolization and filopodia formation and increased foreign body giant cell formation. Some experiments have also been performed with exudate extracted from within hollow cylindrical subcutaneous implants having smooth and natural textured surfaces. The results of these tests indicated increased cell growth activity for exudate extracted from textured implants within approximately the first week of implantation.

A very interesting problem, in the case of soft tissue implants, is the influence of surface texture on attachment kinetics. This can be approached in several ways. If one considers the electrostatic repulsion theory [52], then the energy of repulsion for two surfaces decreases with decreasing radius of curvature (assuming the surface potential of the untreated and ion textured surfaces does not change). This theory would suggest that for a cell interacting with textured surface, less work would be required to overcome the repulsion barrier during attachment. The energy of attraction, however, is not enhanced but reduced with the reduction in the radius of curvature. The repulsion term is generally the larger of the two, thus the reduction in the repulsive term would be greater than that of the attractive one.

The ion sputtered (textured) surfaces of biomaterials have lent themselves to some new applications. Results of experiments suggest that the avid adherance of cells to the surface texture could be used to extract them from body fluids in either diseased states such as leukemia or the routine removal in separation from plasma. Gradations in texture could also be utilized to evaluate diseased states characterized by the lack of adherence to the surface. There is also a need for further work that investigates cell interactions with materials of different morphologies.

Numerous biomedical applications have been identified and/or are now in various stages of experimental evaluation, i.e. for example:

(a) the use of transfer cast biopolymers peeled from ion beam textured surfaces as blood contacting surfaces (microvascular grafts, left ventrical assist devices),

(b) the feasibility of using ion beam sputter ventilated microtubules to shunt cerebrospinal fluid directly from the lateral ventricals upward to the subarachnoid space,

(c) the research for an optimal transfer cast pillar morphology to utilize this surface structure in the design of functional percutaneous connector devices,

(d) the possibility of application of an artificial ureter and a colostomy device.

It is worth noting that several experiments have also been performed in a sphere of biological derived materials [19, 56–59]. Reports in the literature have indicated that the ion sputtering can be applied to reveal subsurface features of biological tissues. This process in combination with scanning electron microscopy could be used as a diagnostic technique for pathological discrimination. However, contrary to the initial optimistic opinions expressed for instance by Stewart *et al.* [56], Hodges *et al.* [57] concluded that the ion sputtering was unlikely to be of much value with soft biological tissues. There have been some difficulties in distinguishing intercellular structures from artefacts produced by the ion processing. This inability to distinguish cellular structures from features produced by ion sputtering suggests that a better understanding of the ion sputtering of the organic materials is required before this technique can be used for the recognition and investigation of biological cell and/or tissue types and structures.

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