Ion Bombardment Treatments for Metallic and Polymeric Bio-medical Materials

Rafael J. Rodríguez

Centro de Ingeniería Avanzada de Superficies, AIN, E-31191 Cordovilla-Pamplona (Spain).

PRESENTATION

1 Ion implantation in the frame of advanced surface treatments

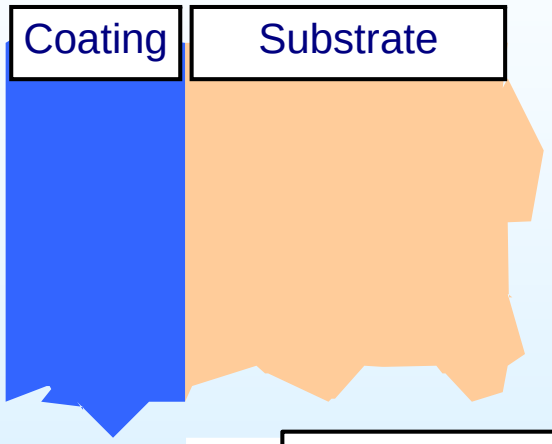
2 Ion implantation treatment of metal alloys

3 Ion implantation treatment of polymers

4 Conclusions on bio-medical applications

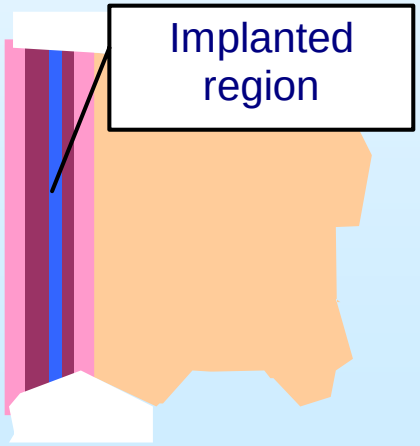
TREATMENT STRATEGIES

COATINGS



Coatings always change the dimensions of the pieces and have an abrupt transition

ION IMPLANTATION



Ion implantation does not change dimensions and has a smooth transition to the substrate

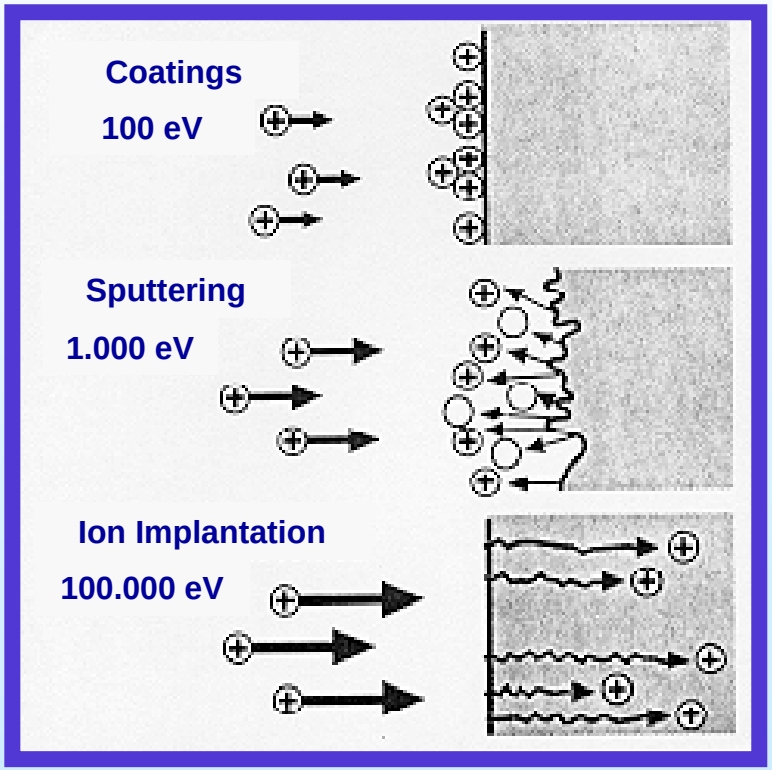
EFFECTS OF ION BOMBARDMENT

Ion Implantation is a ballistic treatment.

Depending on the bombardment energy, the dominant effect on the surface can be very different:

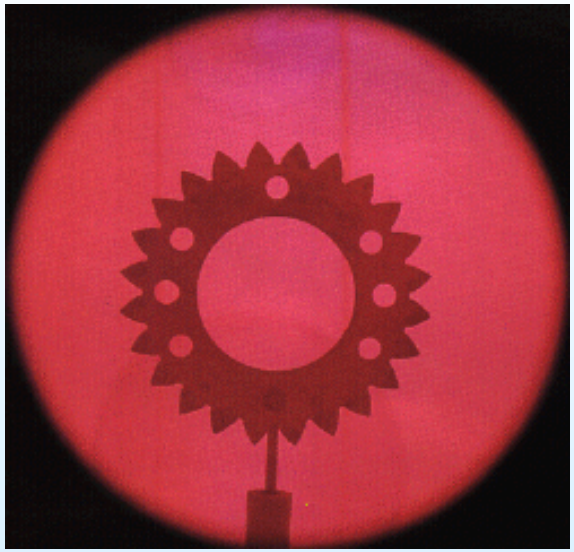
- **Coatings (E < 100 eV)**
- **Sputtering (100 eV < E < 1000 eV)**
- **Implantation (E > 10.000 eV)**

Typical energies for Ion Implantation industrial surface treatment are between 10.000 eV and 200.000 eV



ION BOMBARDMENT STRATEGIES

ION BEAM IMPLANTATION (II)

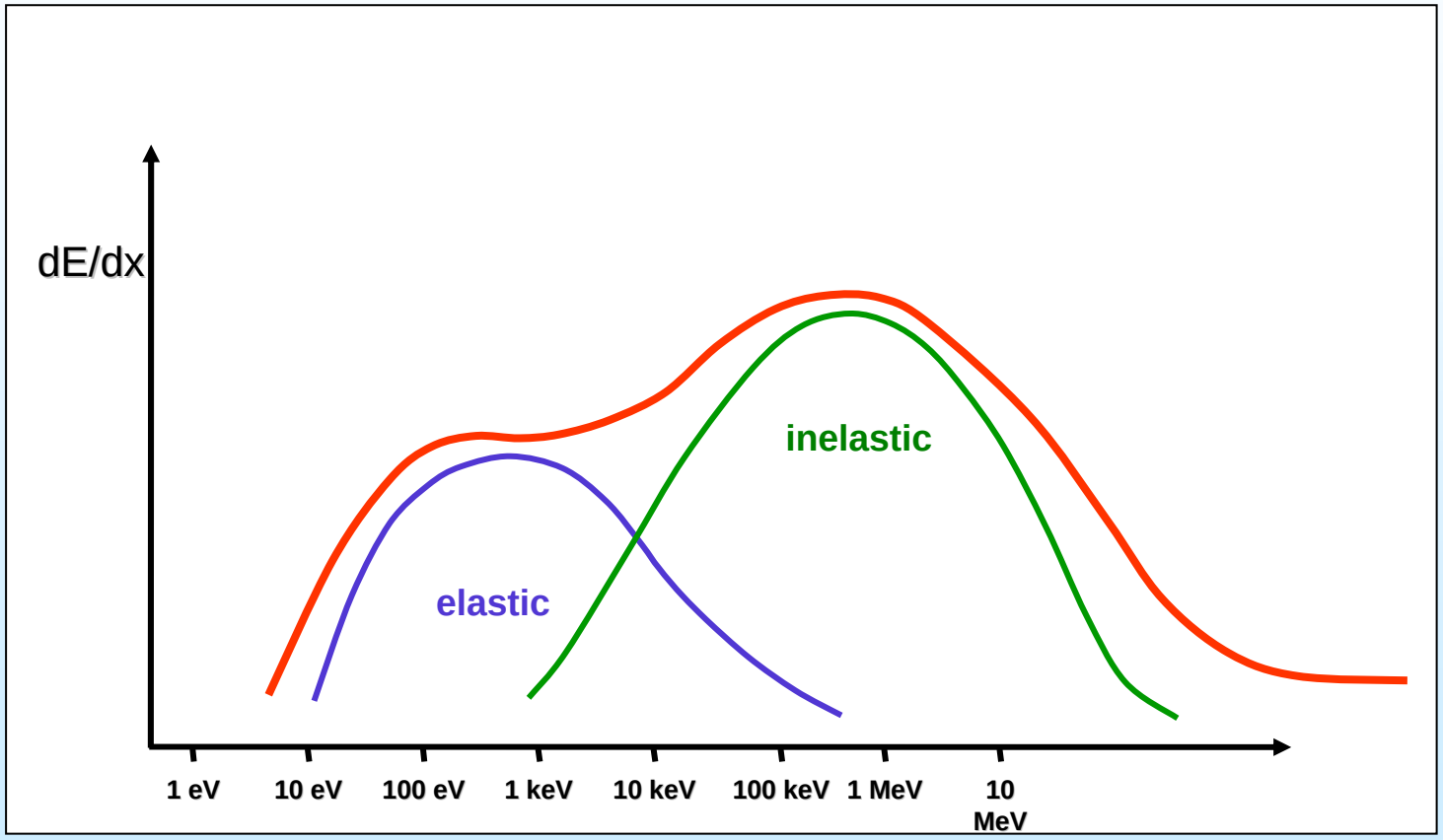


PLASMA IMMERSION IMPLANTATION (PI^3)

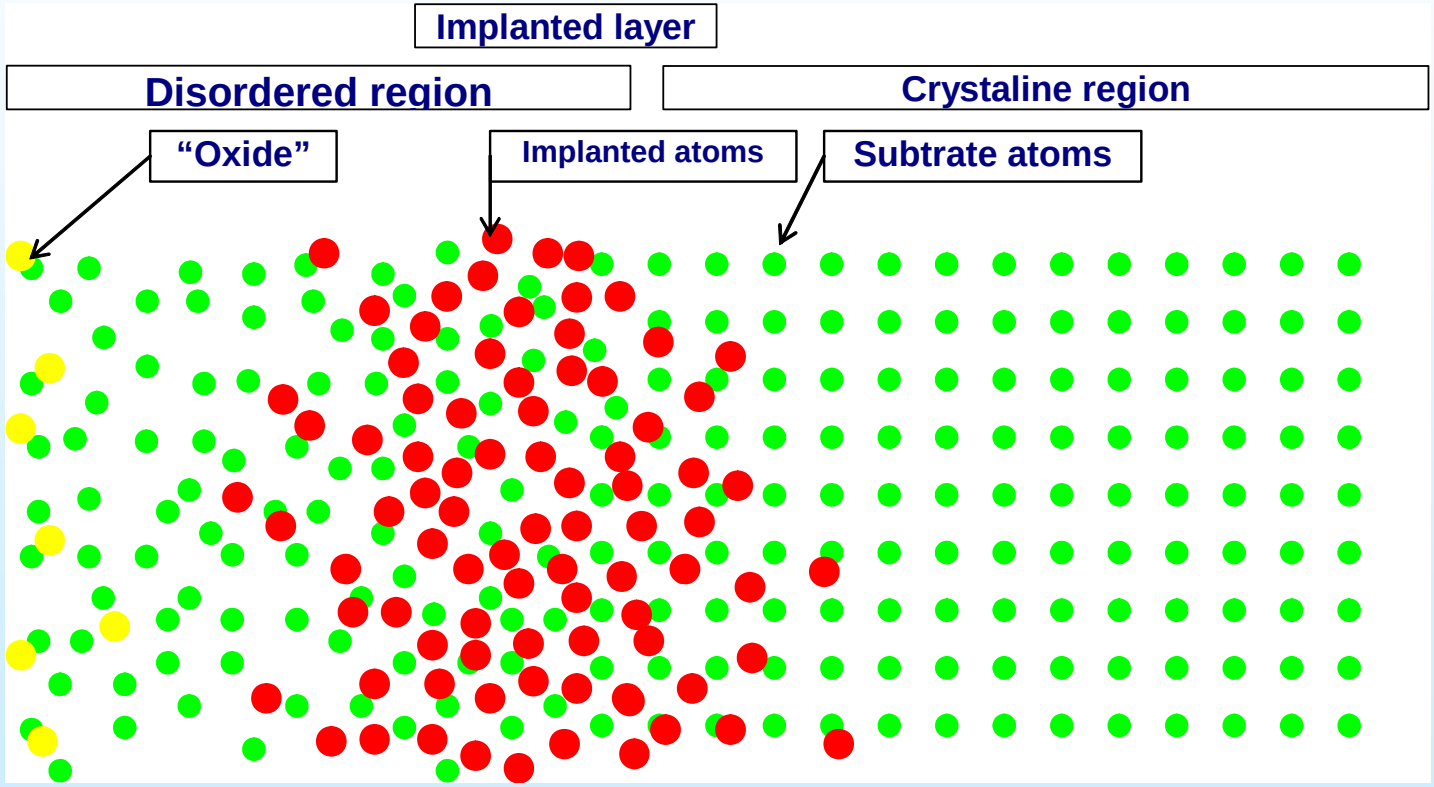
In all cases, the relevant parameters are:

- **Ion(s) to be implanted**
- **Energy**
- **Dose**

STOPPING POWER



ION IMPLANTATION RESULT

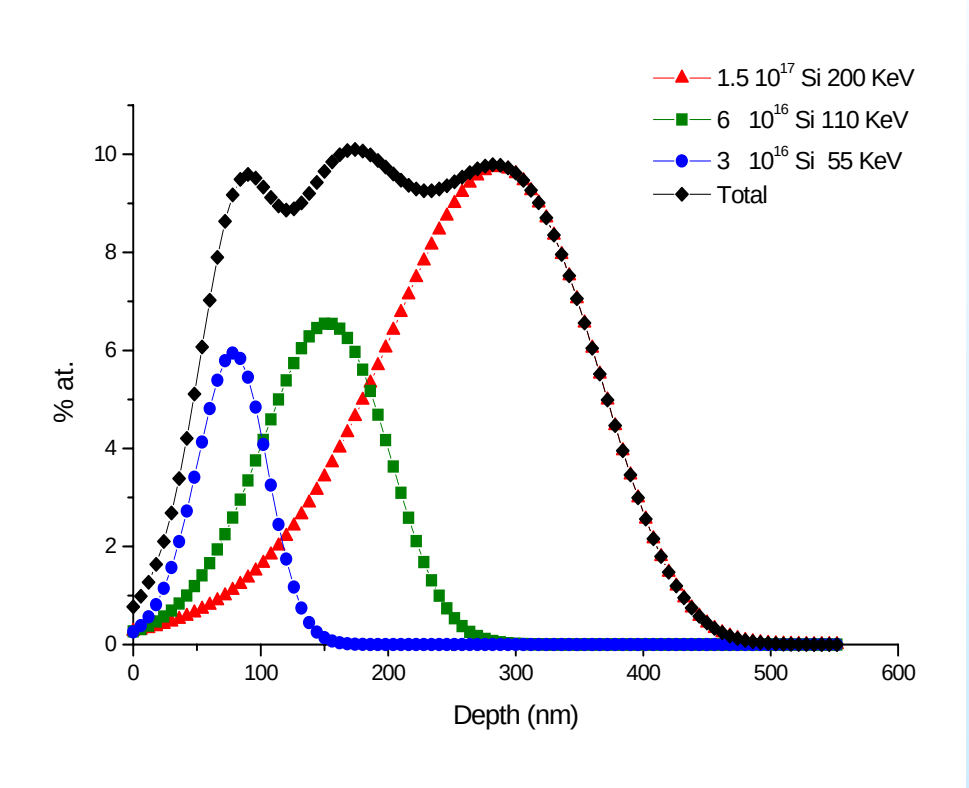


SIMULATION OF THE ION IMPLANTATION RESULT

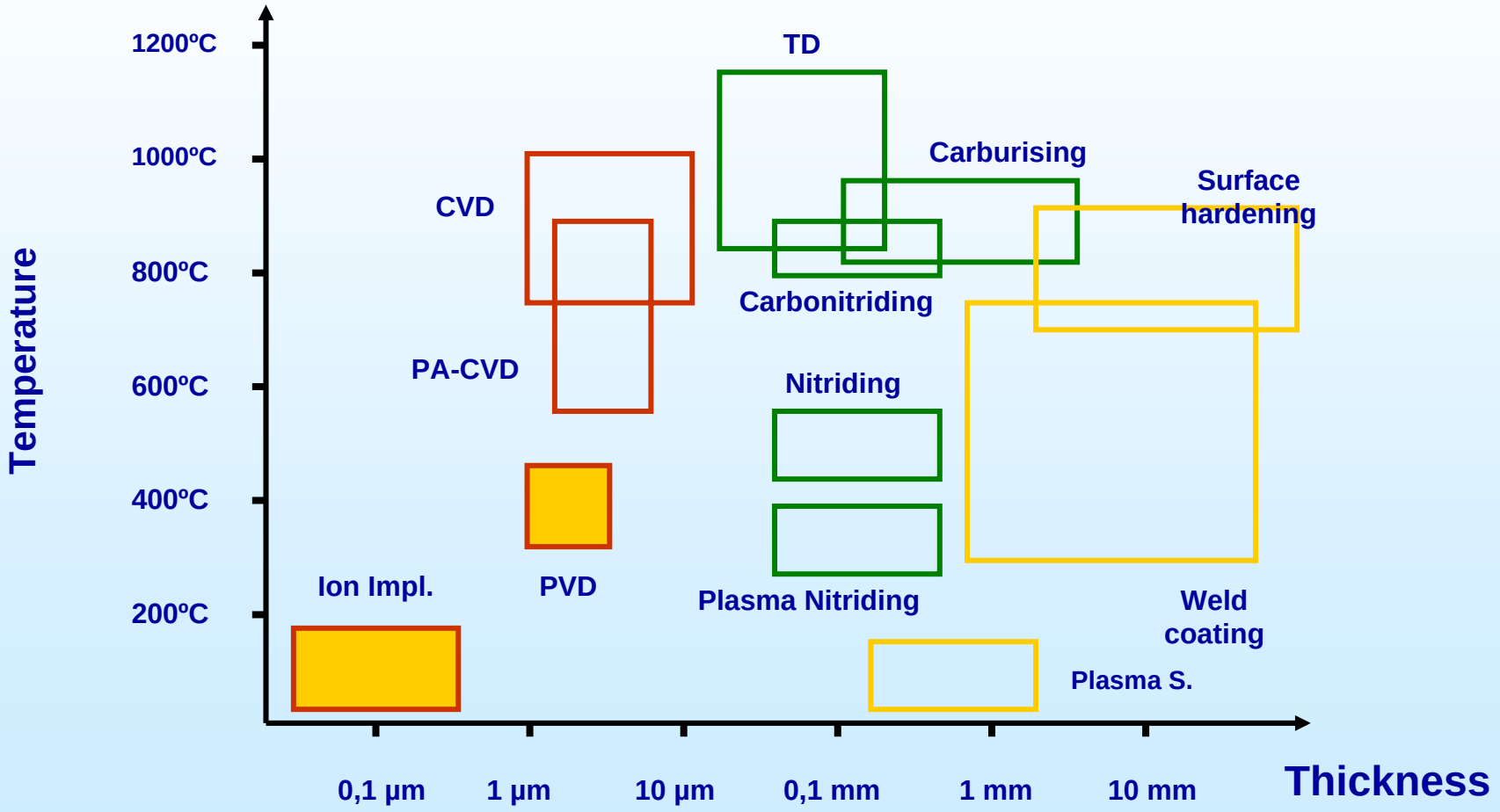
Range and distribution of implanted ions can be calculated by using TRIM or PROFILE codes.

Codes help to:

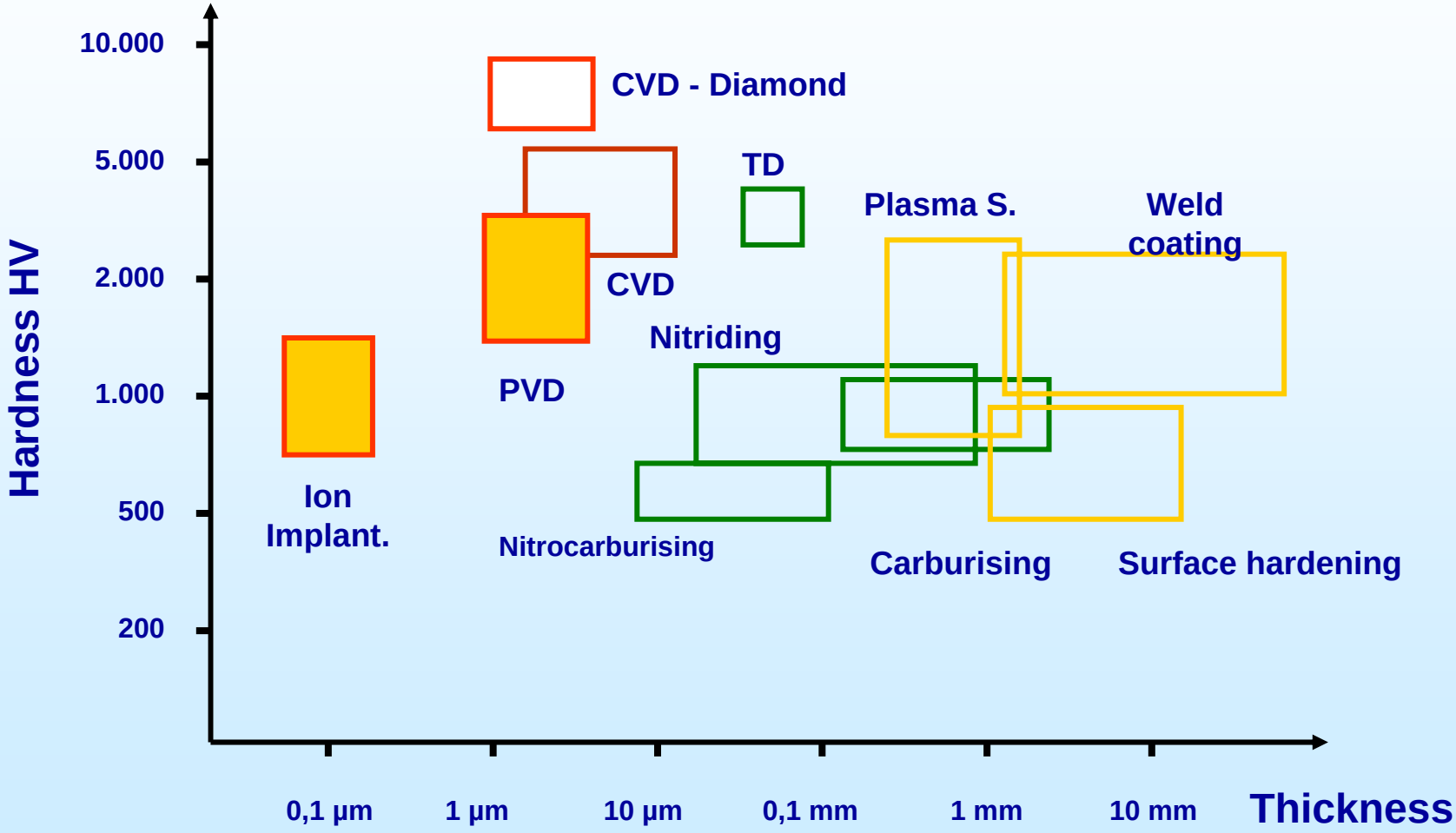
- design the implantation
- design co-implantations
- estimate saturation limits
- estimate other effects:
  - sputtering
  - ionization...



TEMPERATURE vs. THICKNESS



HARDNESS vs. THICKNESS

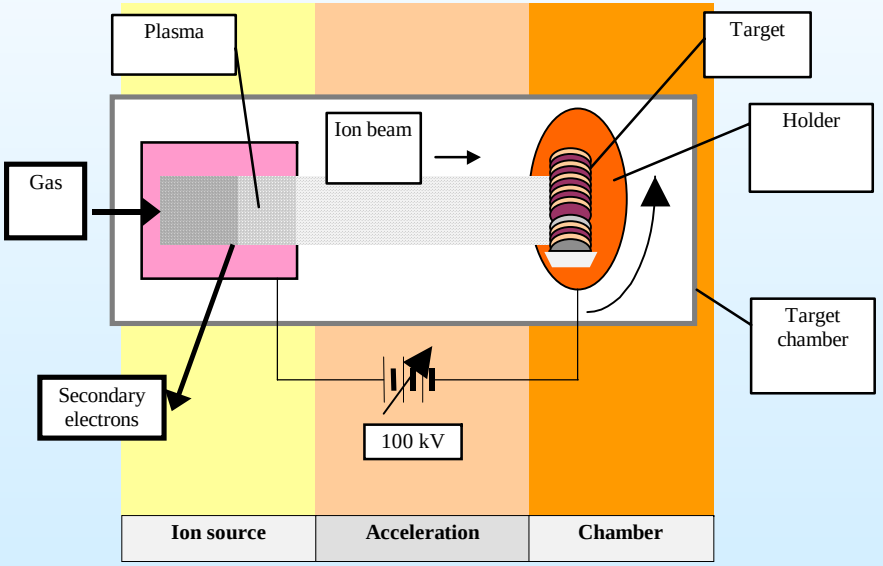


NO MASS SEPARATION INDUSTRIAL ION IMPLANTER

For Nitrogen or other gas implantations it is enough to have:

- Gas ion source
- One acceleration step (100 keV)
- A target chamber with mechanical scanning

Again, the equipment operates at high vacuum (10^{-6} mbar)



NO MASS SEPARATION INDUSTRIAL ION IMPLANTER

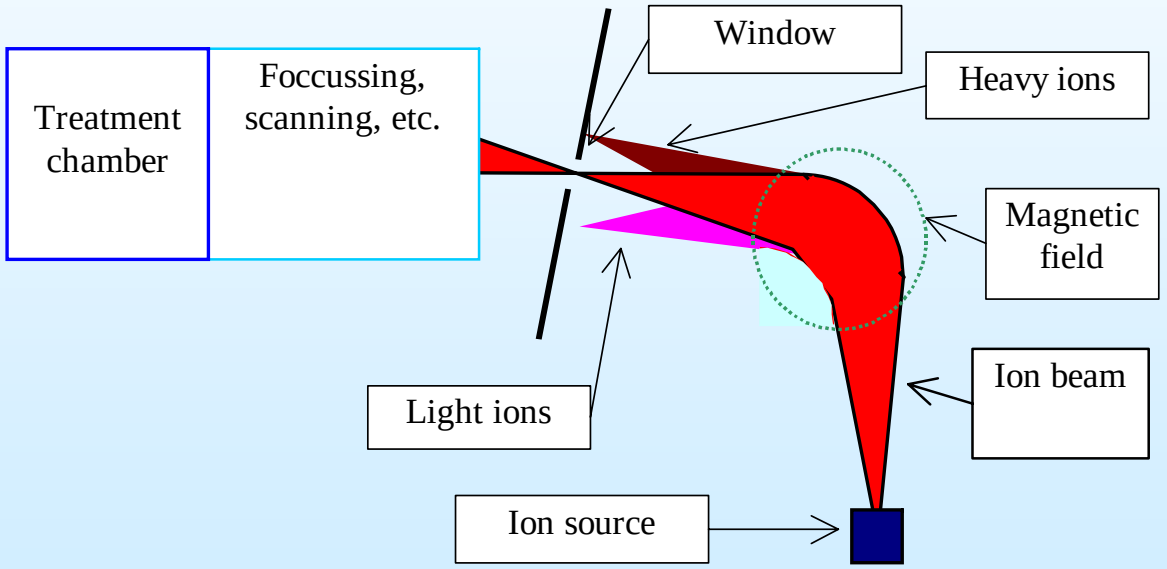
TECVAC 223 Implanter

- Gas ion source
- No mass separation
- Beam intensities up to 3 mA
- Energies up to 100 keV
- Turbomolecular vacuum
- 2 axis mechanical scanning
- Automated control

MASS SEPARATION INDUSTRIAL ION IMPLANTER

For all species implantation, a mass separation system is needed.

That lead to more complex and expensive equipment.



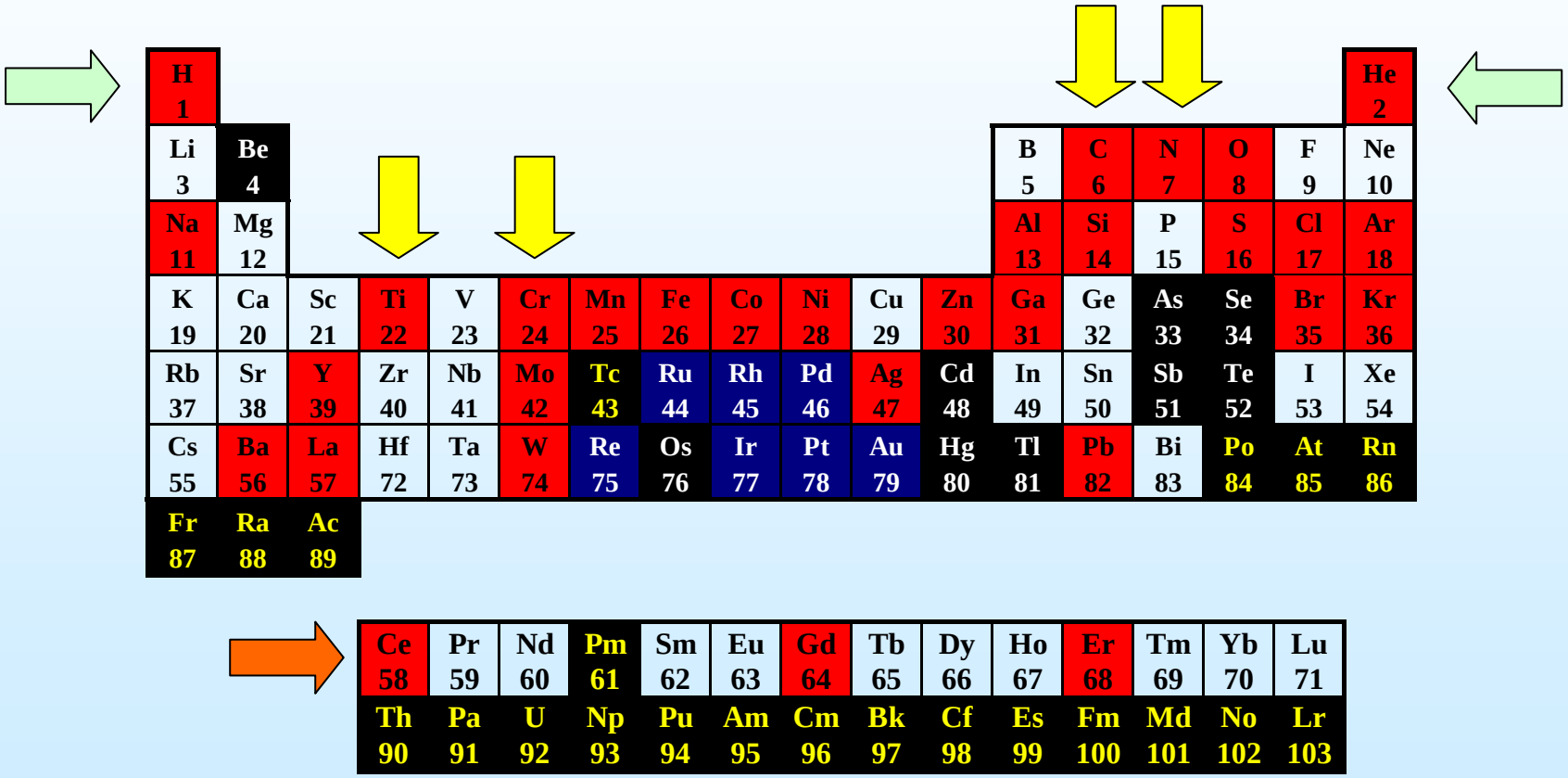
MASS SEPARATION INDUSTRIAL ION IMPLANTER

WHICKHAM IBS

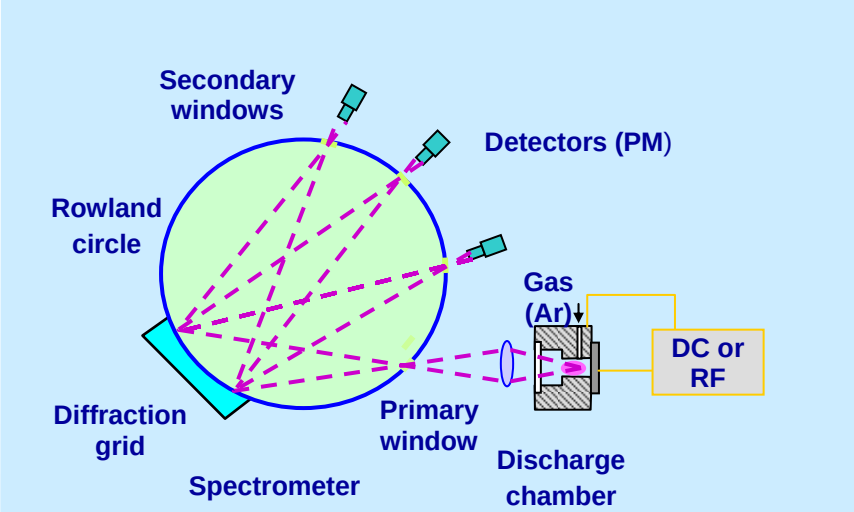
AIN - ion implanter

- Freeman ion source
- Mass separation
- Beam currents up to 5 mA
- Beam energy up to 200 keV
- Cryogenic vacuum
- 5 axis mechanical scanning
- Automated control

TYPICAL ELEMENTS TO BE IMPLANTED

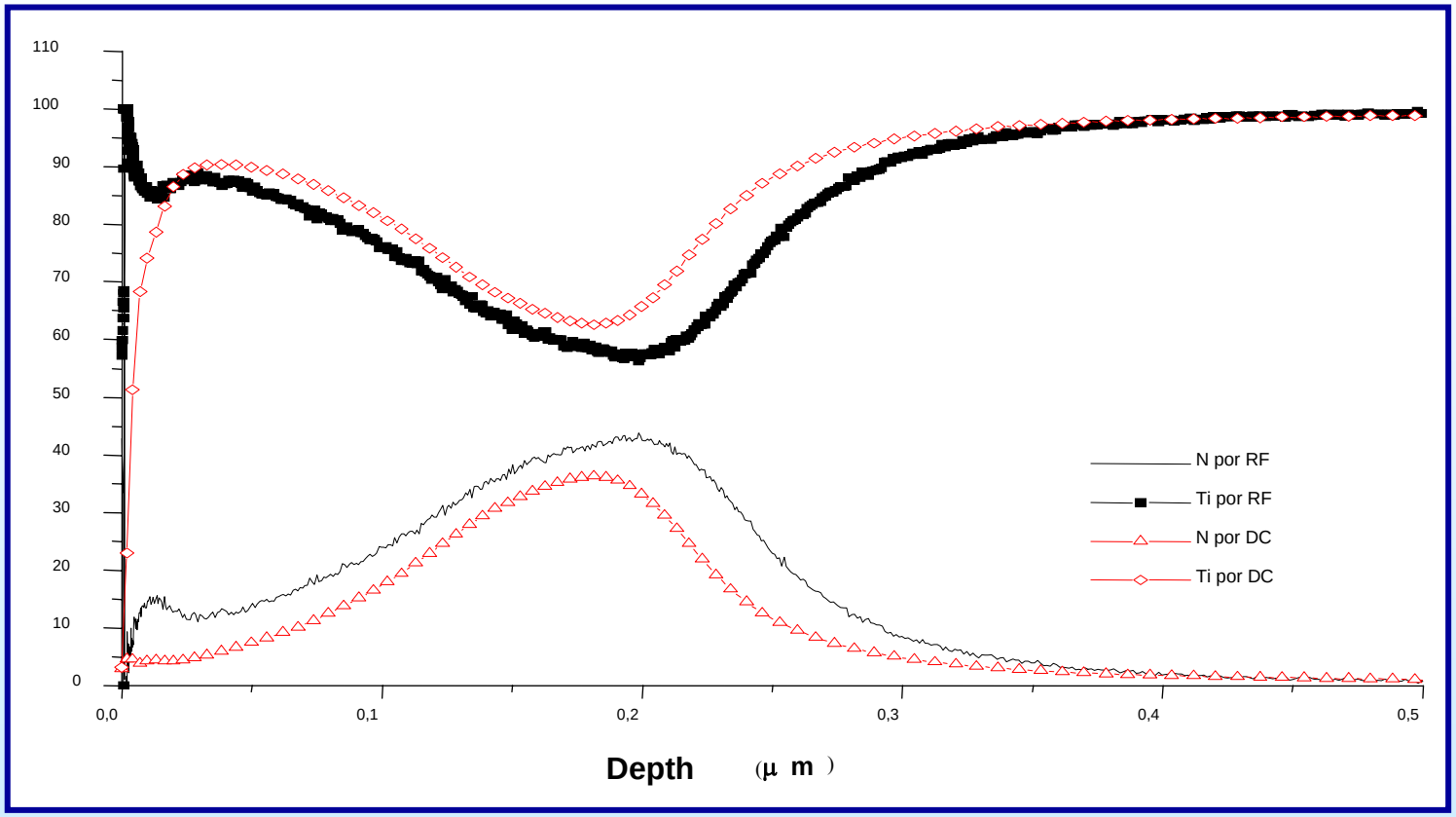


PRACTICAL SURFACE ANALYSIS: GD-OES



Glow Discharge Optical Emission Spectroscopy (GD-OES) allows to obtain precision quantitative composition profiles in few minutes. No UHV is required. Just well polished flat implanted samples.

PRACTICAL SURFACE ANALYSIS: GD-OES



GD-OES analysis of a Ti sample implanted with $8*10^{17}$ N_2^+

EFFECTS ON THE IMPLANTED MATERIALS

INCREASE OF HARDNESS

- Precipitation of nitrides, carbides, etc.
- New alloys formation
- *Cross-linking* of polymers

BETTER TRIBOLOGICAL BEHAVIOUR

- More homogeneous / coherent oxide layers

RESISTANCE TO ROLLING FATIGUE

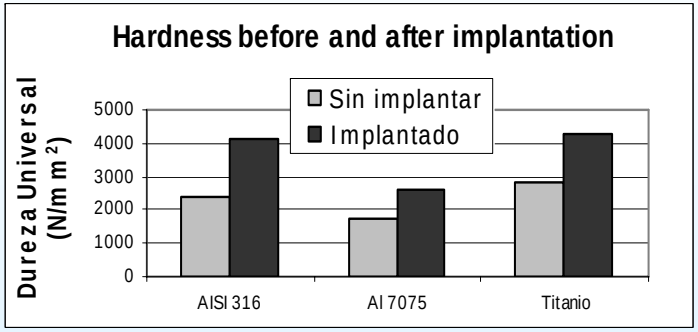
- Compressive tensions at the surface

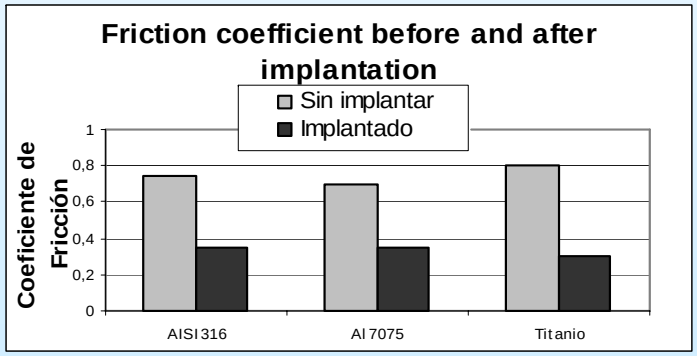
CORROSION RESISTANCE

- New alloys with better resistance
- Better adhered and compact oxide layers

OXIDACION RESISTANCE

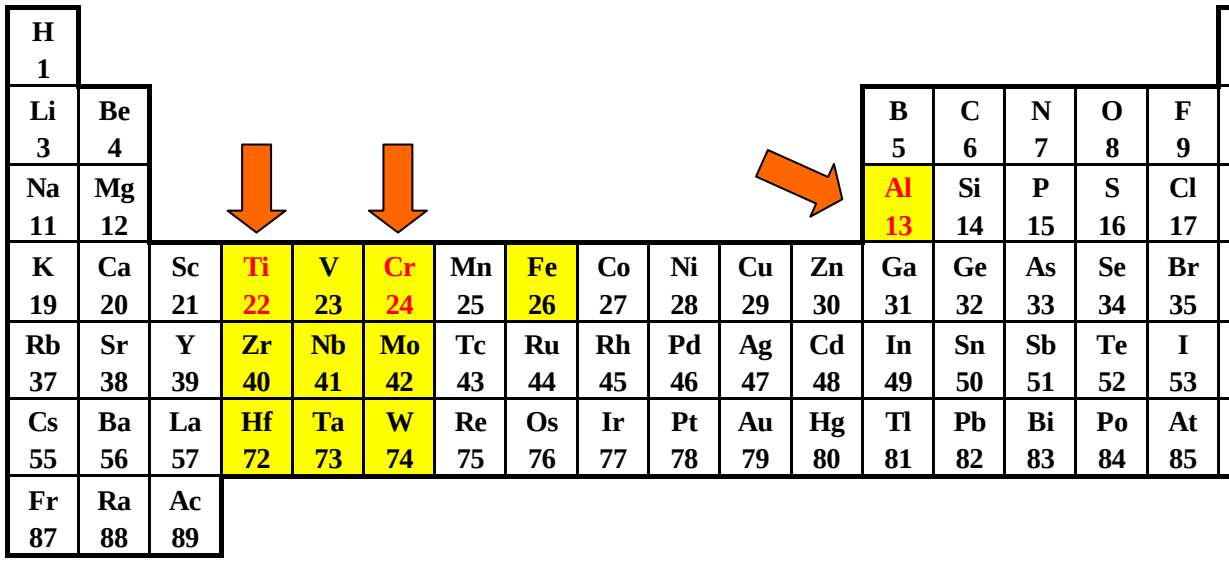
- Surface doping with lanthanide elements





R. Rodríguez, A. Sanz, A. Medrano and J.A. García-Lorente. **Tribological properties of ion implanted Aluminium alloys.** *Vacuum* **52** (1999), 187.

ELEMENTS THAT CAN BE IMPROVED BY NITROGEN IMPLANTATION



SURFACE MECHANICAL PROPERTIES: HU and E

Universal Hardness (HU) can be measured from 1mN, till 1000 mN of maximum load by using a **Fischeroscope** microindentation equipment. At 2mN, the indentation depth in metals is less than 0,2 microns

Elastic and plastic hardness as well as elastic modulus can be obtained from the load – unload curves.

UNIVERSAL HARDNESS TESTS ON IMPLANTED SURFACES

LOW LOADS:

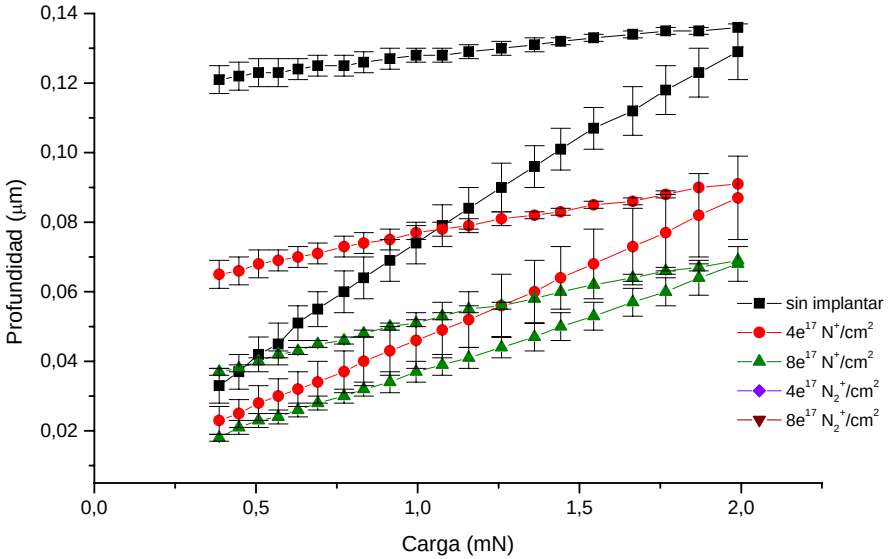
Low indentation loads are needed because the implanted region is thinner than few tenths of micron.

DEFFECTLESS SURFACES:

Hardness tests can be carried out only on mirror polished surfaces.

BETTER ON SOFT METALS:

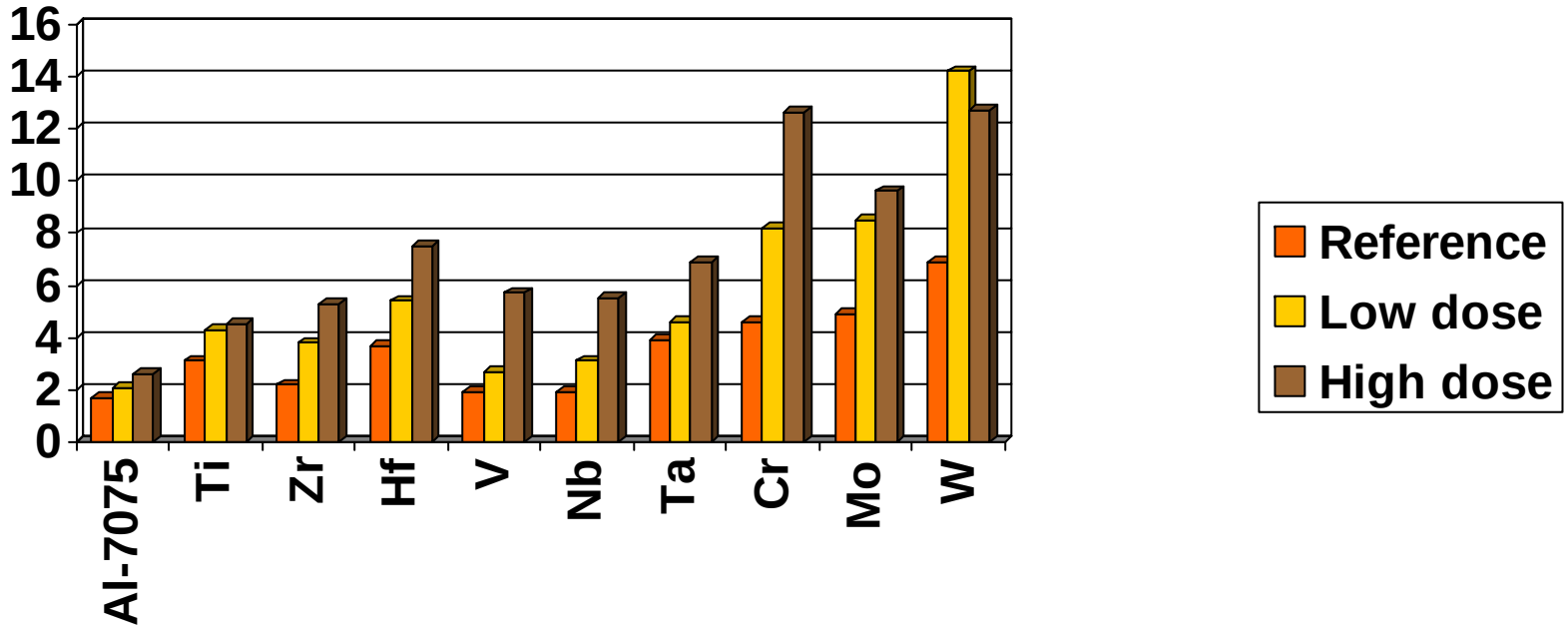
Changes in hardness are more visible on soft metals.



N^+ Implanted Zirconium at different doses

J. A. García, A. Guette, A. Medrano, C. Labrugere, M. Rico, M. Lahaye, R. Sánchez, R. Martínez and R. J. Rodríguez: **Nitrogen ion implantation on Group IV metals: chemical, structural and tribological study,** Vacuum **64**, 343 (2002).

HARDNESS (GPa) OF NITROGEN IMPLANTED METALS

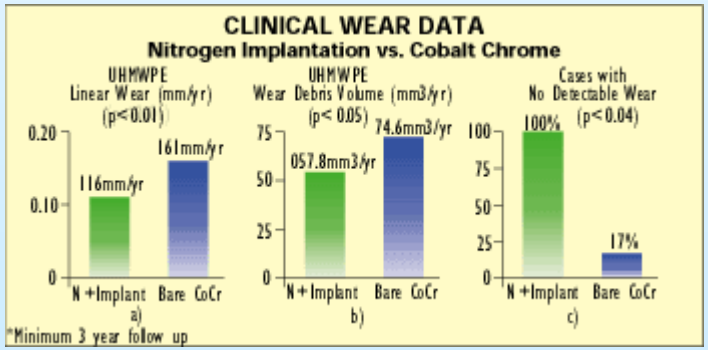


J. A. García, A. Guette, A. Medrano, C. Labrugere, M. Rico, M. Lahaye, R. Sánchez, R. Martínez and R. J. Rodríguez
Nitrogen ion implantation on Group IV metals: Chemical, structural and tribological study. *Vacuum* **64** (2002), 343.
J. A. García, R. J. Rodríguez, A. Medrano, R. Sánchez, M. Rico, R. Martínez, B. Lerga, C. Labrugere, M. Lahaye, and A. Guette
Study of the tribological modifications induced by nitrogen implantation on group V metals. *Surface and Coatings Technology* **158-159** (2002), 653.
R. Martínez, J. A. García, R. J. Rodríguez, B. Lerga, C. Labrugere, M. Lahaye, and A. Guette
Study of the tribological modifications induced by nitrogen implantation on groupVI: Cr, Mo and W. *Surface and Coatings Technology* **174-175** (2003), 1253.

APPLICATIONS FOR HIP AND KNEE PROSTHESIS

IMPLANT SCIENCES CORPORATION

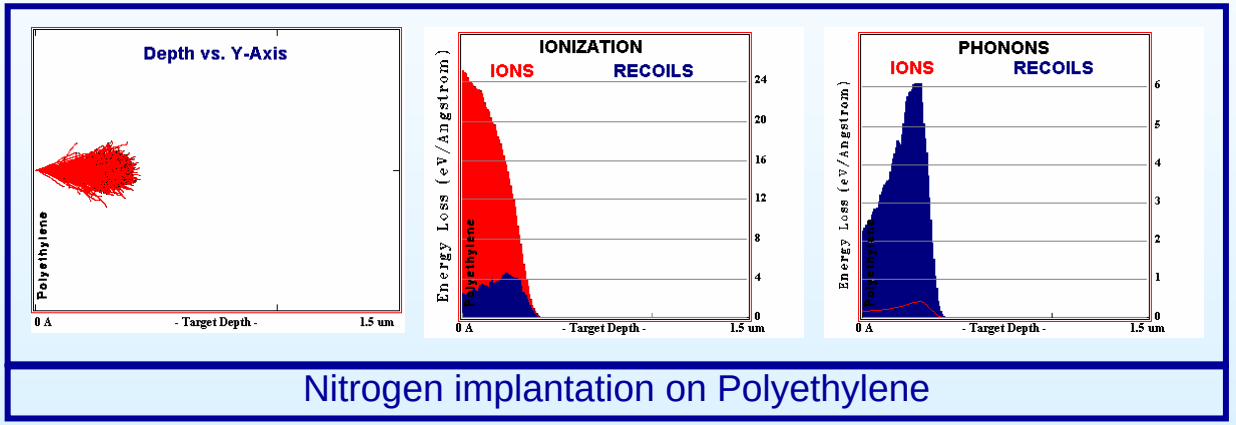
spire Biomedical



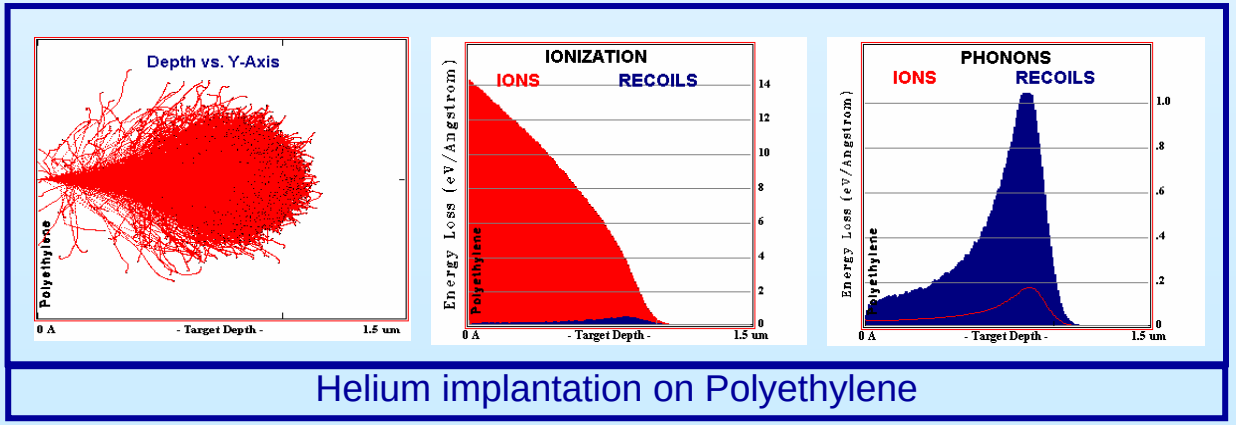
ION IMPLANTATION ON POLYMERS

The main effect of ion implantation on polymers is the increase in hardness due to the cross linking of polymer chains because the ionisation produced by ion bombardment.

The effect is more intense for light and energetic ions because they loss energy preferentially by ionisation (inelastic stopping power), have minor chain breakage effects (elastic stopping power) and goes deeper.



Nitrogen implantation on Polyethylene



Helium implantation on Polyethylene

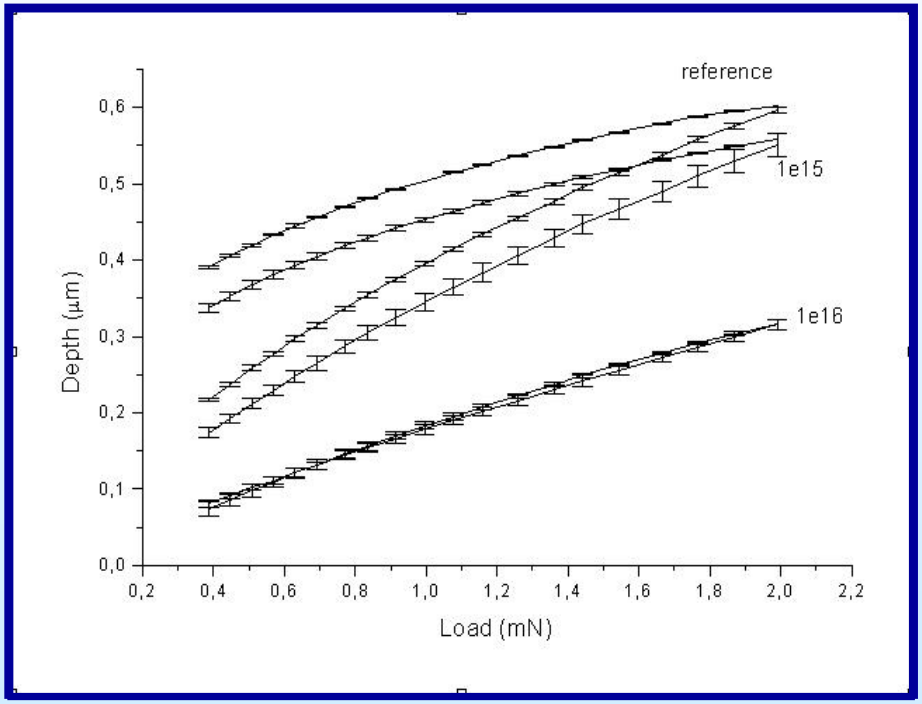
INCREASE OF POLYMER HARDNESS BY HIDROGEN IMPLANTATION

LOW DOSE IMPLANTATION ON POLYCARBONATE:

A low dose implantation is enough to produce a dramatic increase of hardness.

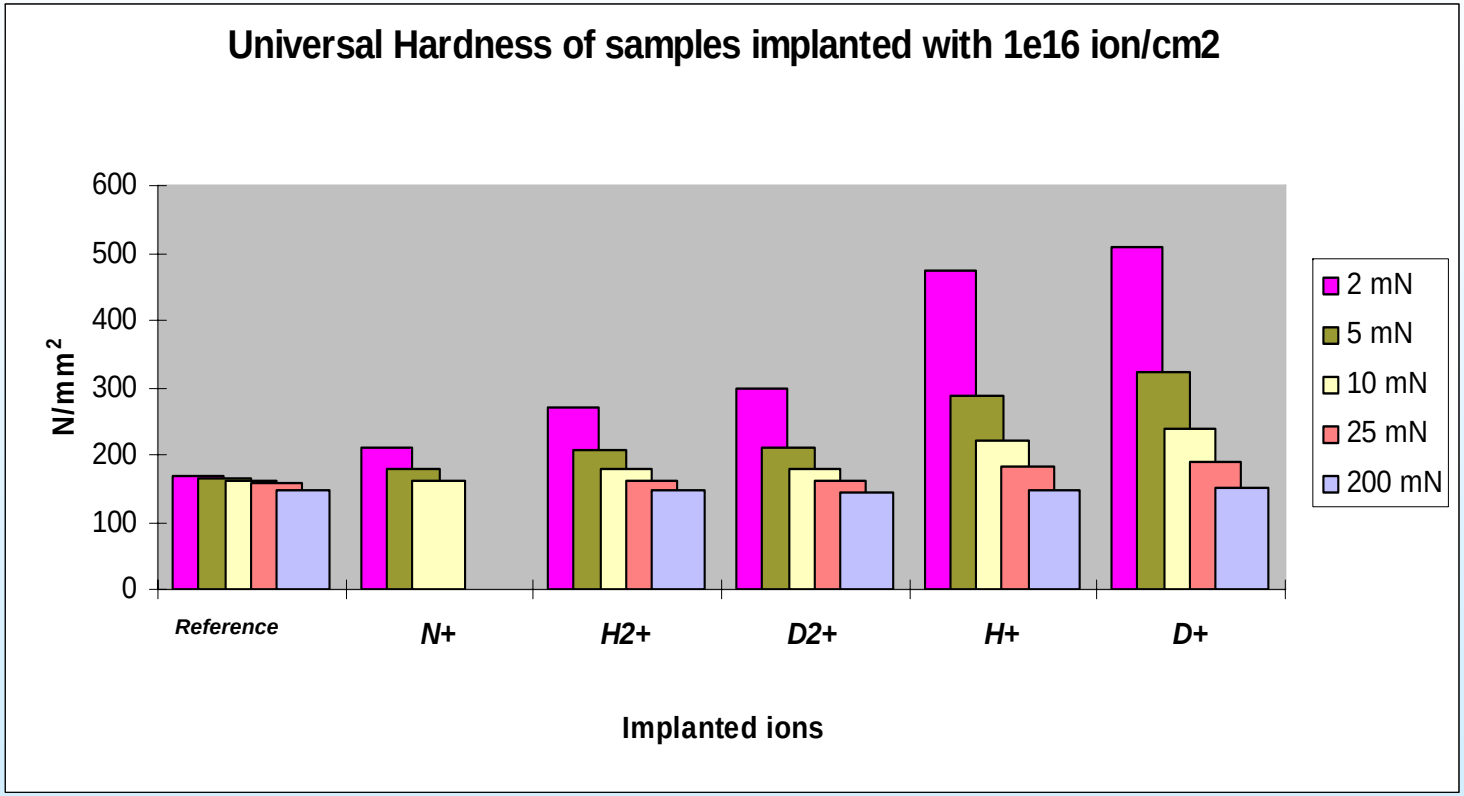
HU vs. HV:

Elastic recovery reach the 100% for a implanted surface. That would lead to an apparently infinite HV.



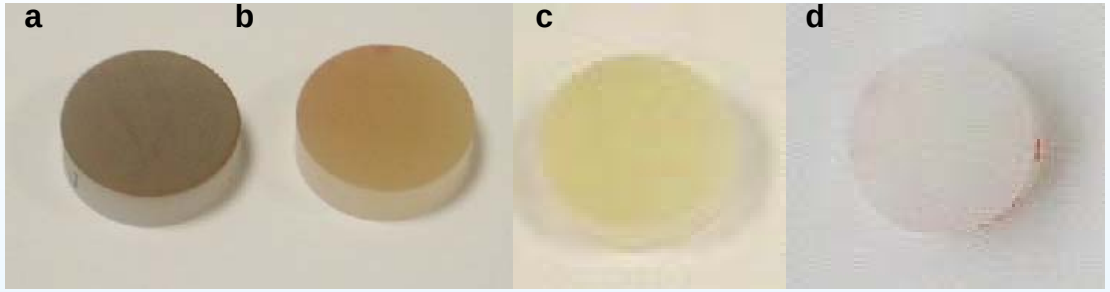
R. Rodríguez, J. A. García, R. Sánchez, A. Pérez, Blas Garrido and J. Morante: **Modification of surface mechanical properties of polycarbonate by ion implantation.** *Surface and Coatings Technology* **158-159** (2002), 636.

ION IMPLANTATION OF POLYCARBONATE



R. Rodríguez, J. A. García, R. Sánchez, A. Pérez, Blas Garrido and J. Morante:
Modification of surface mechanical properties of polycarbonate by ion implantation.
Surface and Coatings Technology **158-159** (2002), 636.

IMPLANTATION OF UHMPWD SAMPLES



UHMWPE SAMPLES AFTER IMPLANTATION

a) UHMWPE sample implanted with $1x10^{16}$ ions/cm^2 of N.

b) UHMWPE sample implanted with $5x10^{15}$ ions/cm^2 of N.

c) UHMWPE sample implanted with $5x10^{15}$ ions/cm^2 of He.

d) Untreated UHMWPE sample.

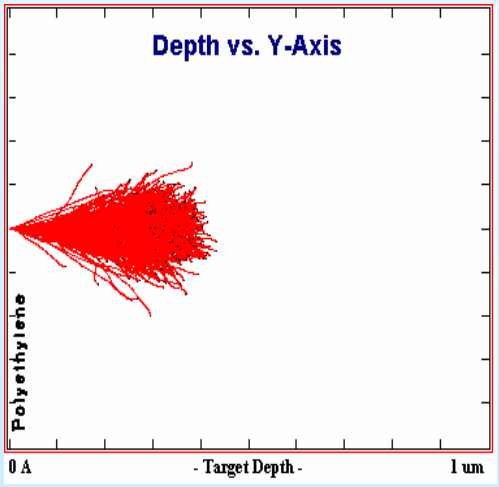
Visual inspection of samples after the implantation with different doses and ions shows that:

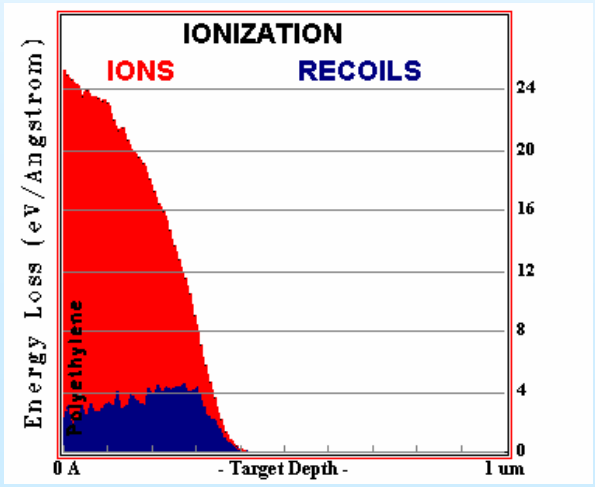
- After the treatments a change in the surface color was observed, the higher the dose the darker the color.
- Nitrogen implantation produced a darker surface than Helium.

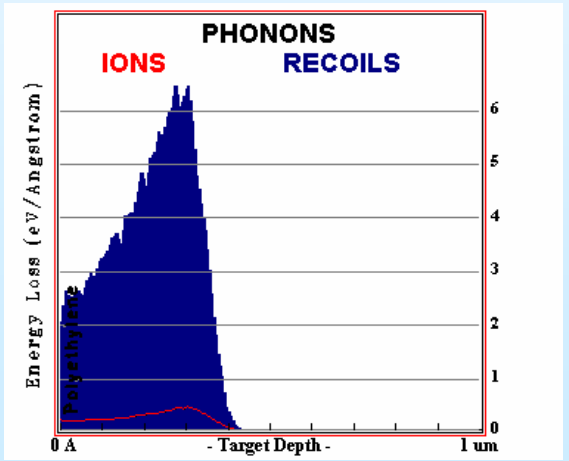
NITROGEN EFFECTS ON UHMWPE

The TRIM stopping power calculations shows that:

- **The range of Nitrogen implantation on UHMWPE, at 90 keV, is about 400 nm.**
- **A 80,5% of the bombardment energy is lost through inelastic mechanism and lead to ionization of the polymer chains.**
- **The other 19,5% of the energy is lost through elastic mechanism, leading to chain breakdown.**





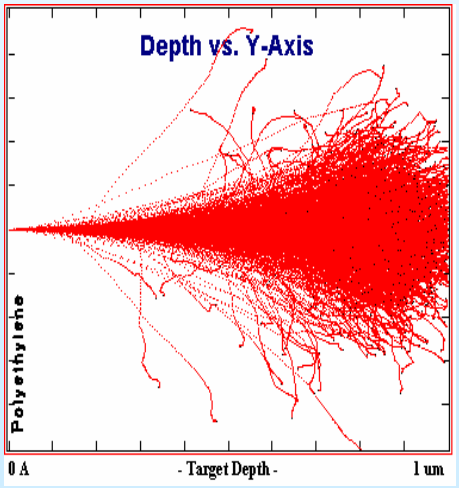


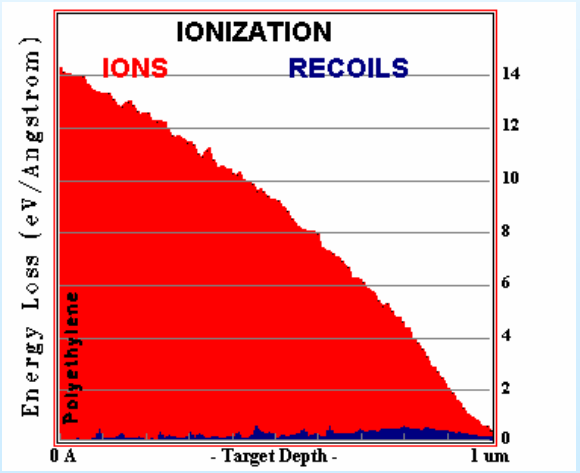
TRIM CALCULATION OF THE NITROGEN RANGE ON UHMWPE AND ENERGY LOSS MECHANISMS

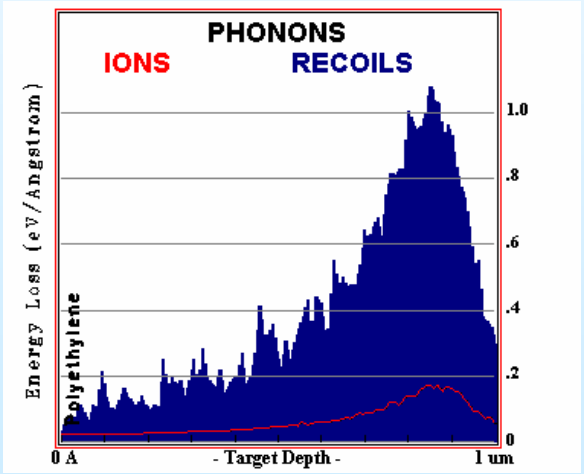
HELIUM EFFECTS ON UHMWPE

The TRIM stopping power calculations shows that:

- **The range of Helium implantation on UHMWPE, at 90 keV, is about 1000 nm.**
- **A 94,5% of the bombardment energy is lost through inelastic mechanism and lead to ionization of the polymer chains.**
- **The other 5,5% of the energy is lost through elastic mechanism, leading to chain breakdown.**

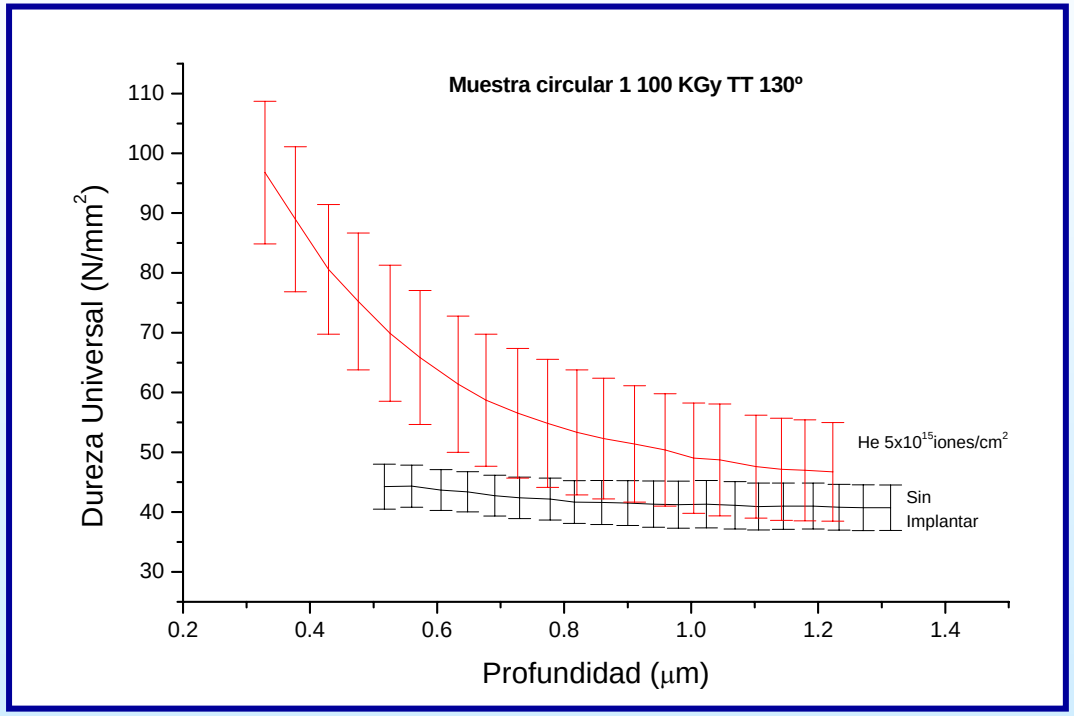






TRIM CALCULATION OF THE HELIUM RANGE ON UHMWPE AND ENERGY LOSS MECHANISMS

RESULTS OF INDENTENTION TESTS

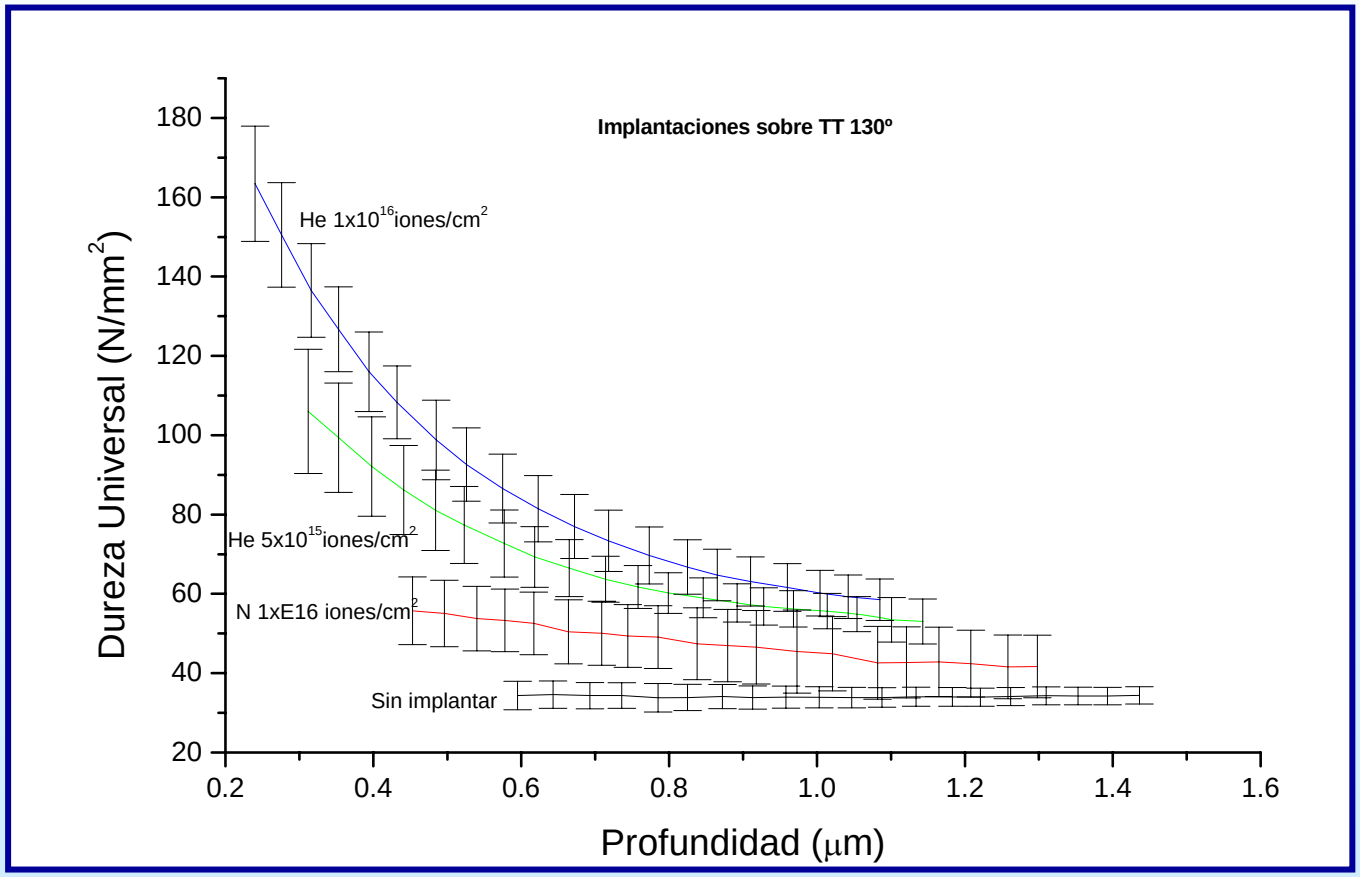


PROFILE OF HARDNESS vs. DEPTH FOR IMPLANTATION 4 AND UNTREATED SAMPLE

UNIVERSAL HARDNESS IN (N/mm^2)	
SAMPLE	**2 mN**
UNTREATED	34 ± 2
IMPLANTATION 1 - N $5x10^{15}$	43 ± 4
IMPLANTATION 2 - N $1x10^{16}$	42 ± 8
IMPLANTATION 3 - He $5x10^{15}$	53 ±6
IMPLANTATION 4 - He $1x10^{16}$	59 ± 5
IMPLANTATION 5 - He $2x10^{16}$	40 ± 9

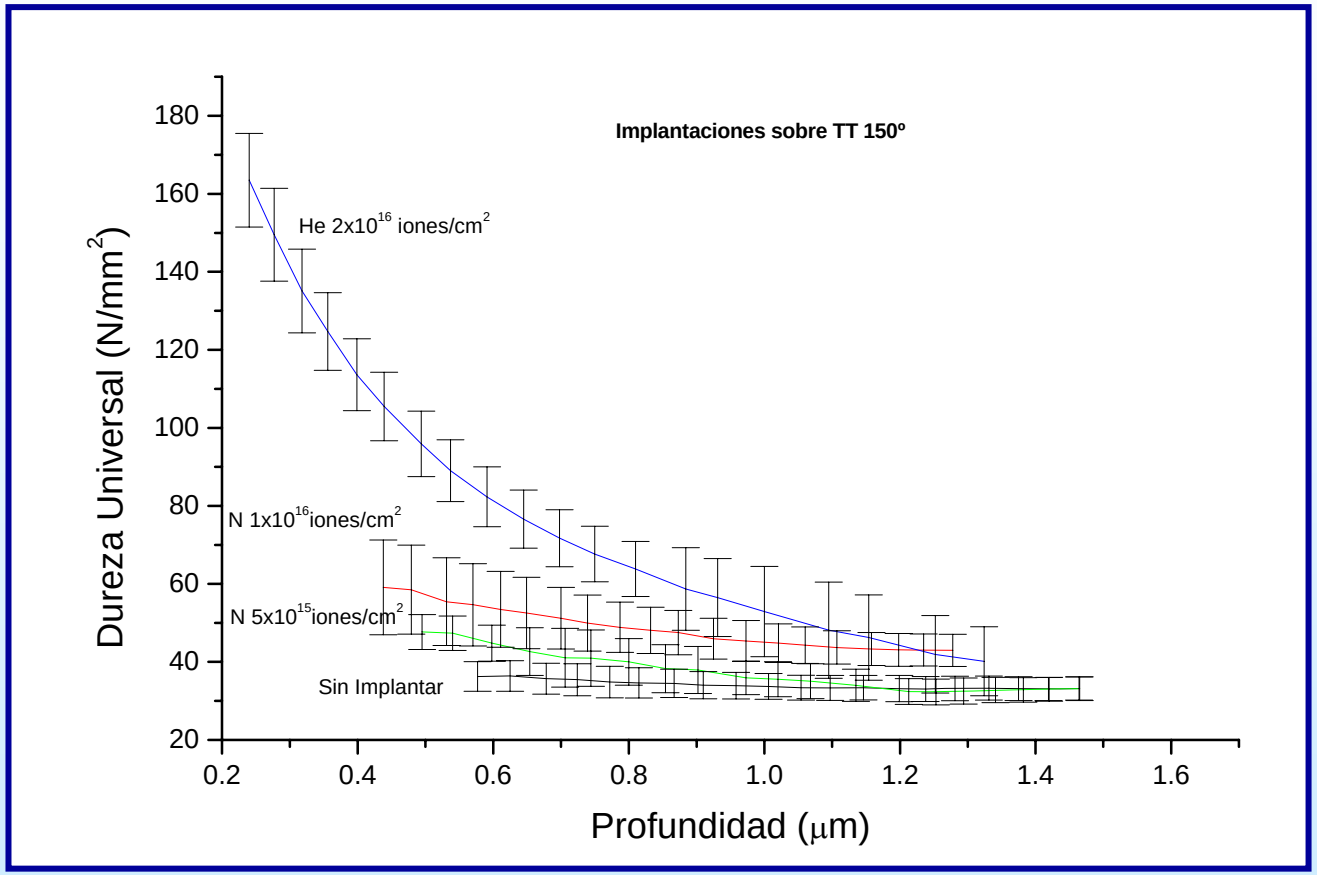
HU at 2mN OF FINAL LOAD

RESULTS OF INDENTENTION TESTS



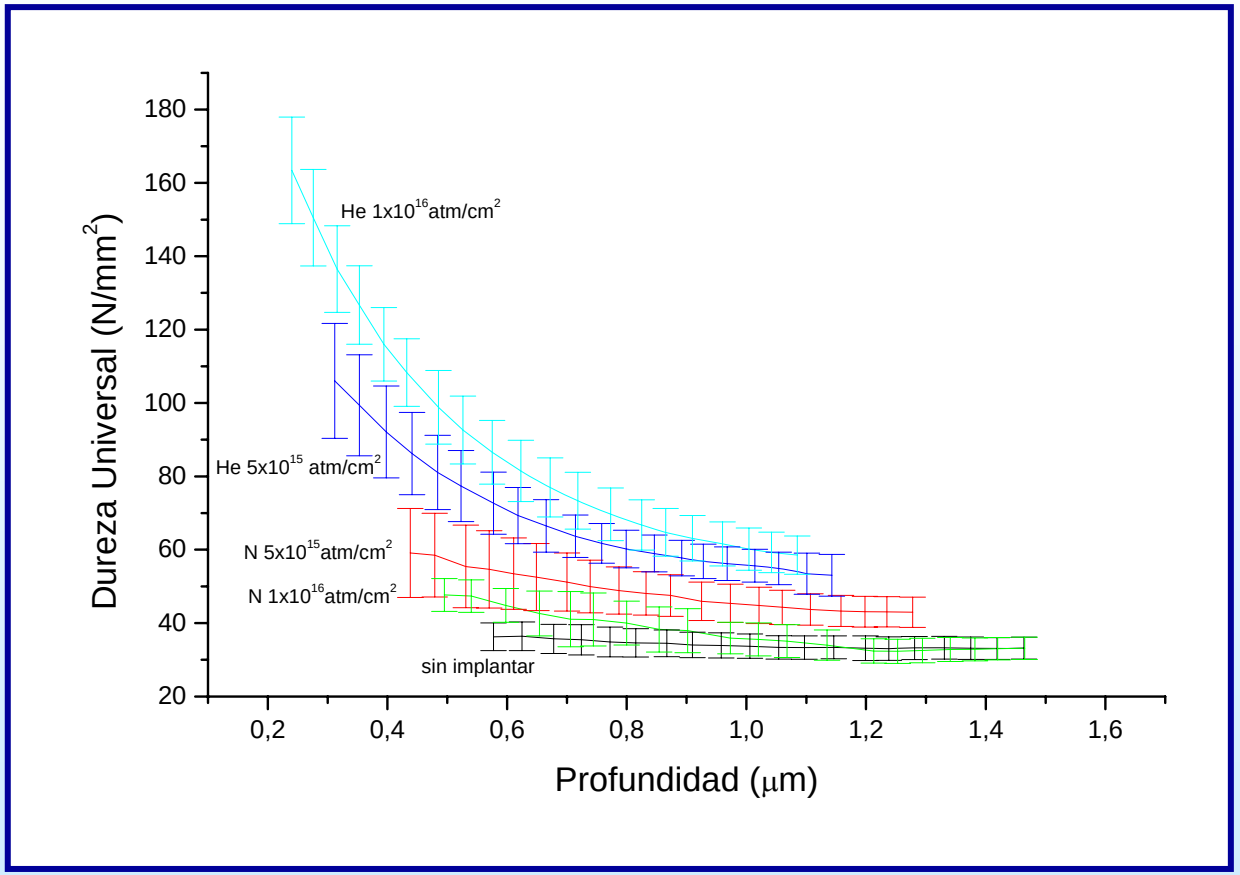
COMPARISON OF HARDNESS PROFILES OF THE IMPLANTATIONS CARRIED OUT ON UHMWPE SAMPLES WITH PRETREATMENT AT 130ºC

RESULTS OF INDENTATION TESTS



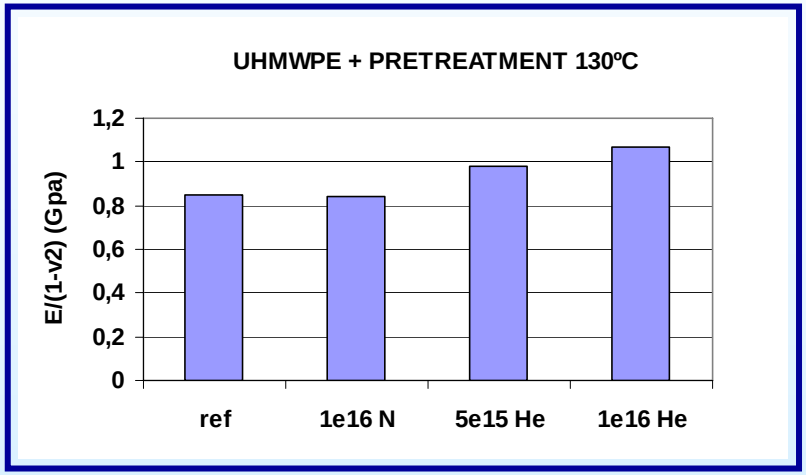
COMPARISON OF HARDNESS PROFILES OF THE IMPLANTATIONS CARRIED OUT ON UHMWPE SAMPLES WITH PRETREATMENT AT 150ºC

RESULTS OF INDENTENTION TESTS

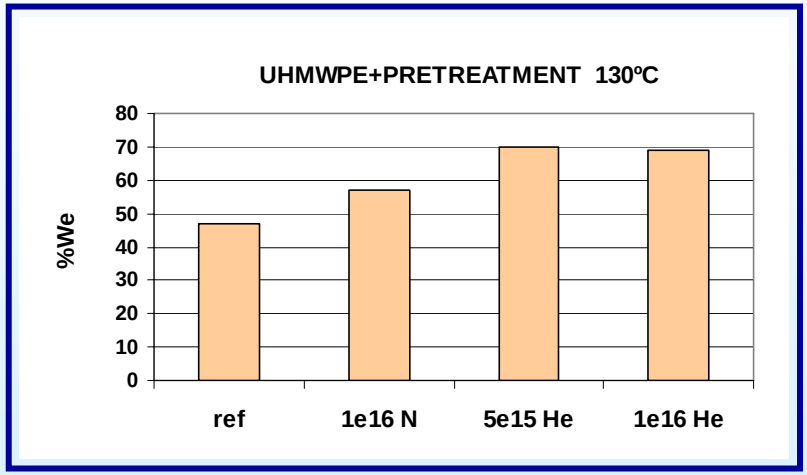


COMPARISON OF HARDNESS PROFILES OF THE IMPLANTATIONS WITH ALL THE DIFFERENT DOSES AND IONS

ELASTIC MODULUS AND ELASTIC WORK



a



b

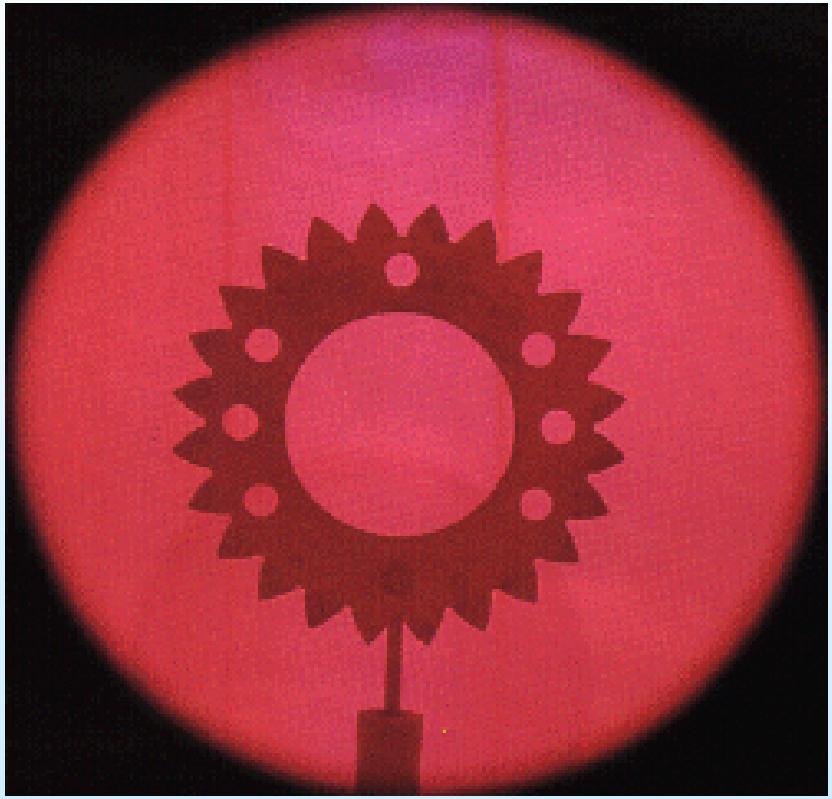
(a) ELASTIC MODULUS AND (b) % OF ELASTIC WORK OF THE IMPLANTED SAMPLES, MEASURED AT FINAL LOAD OF 2mN.

PLASMA IMMERSION ION IMPLANTATION

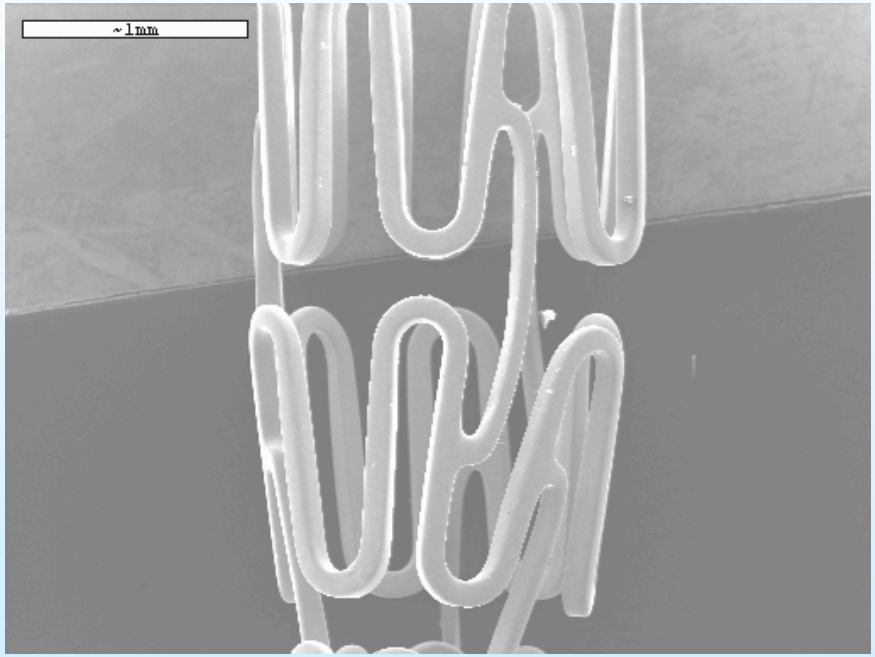
Plasma Immersion Ion Implantation (PI^3) has been claimed as the future solution of the ion implantation problems (line-of-light process, sequential process...).

The no directional intense bombardment can increase the temperature. That would lead to a combined ballistic - diffusional process.

PI^3 is an excellent alternative to conventional processes for treating large series of small complex shape components like stents



APLICATIONS ON STENTS

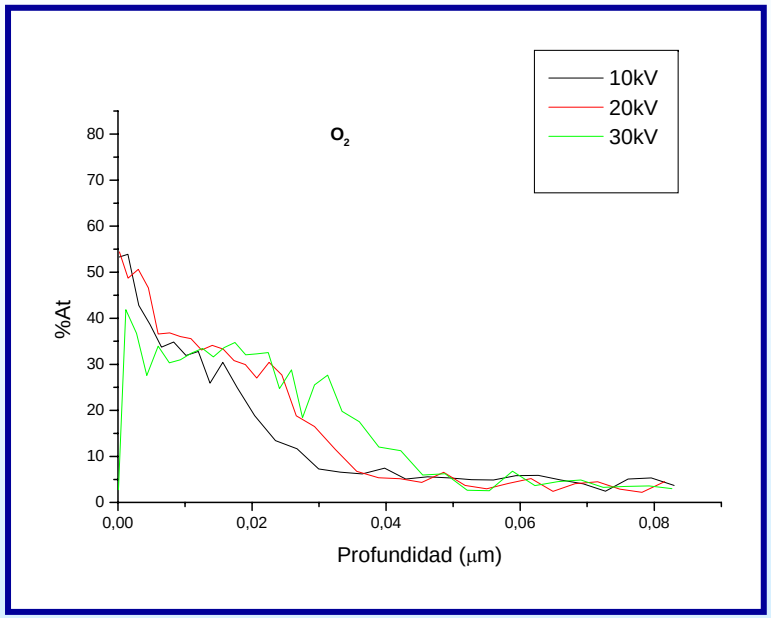


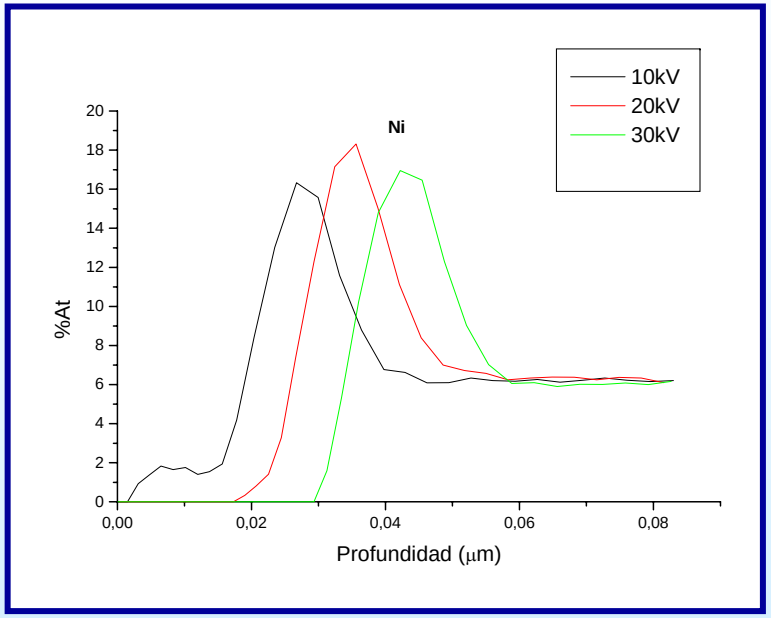
Stents are being extensively employed in many surgical operations.

There are some concerns about the stability of stents that have to remain implanted in the human body. It is worth to mention the effects of metal ion migration (possible toxicity).

To prevent the migration of undesired ions, (e.g. Nickel) a possible technique is the creation of an oxide barrier. Ion implantation of Oxygen could be a good strategy, but the ordinary line-of-sight ion implantation process is not adequate to implant thousands of small components.

OXYGEN PLASMA IMMERSION IMPLANTATION ON STEEL

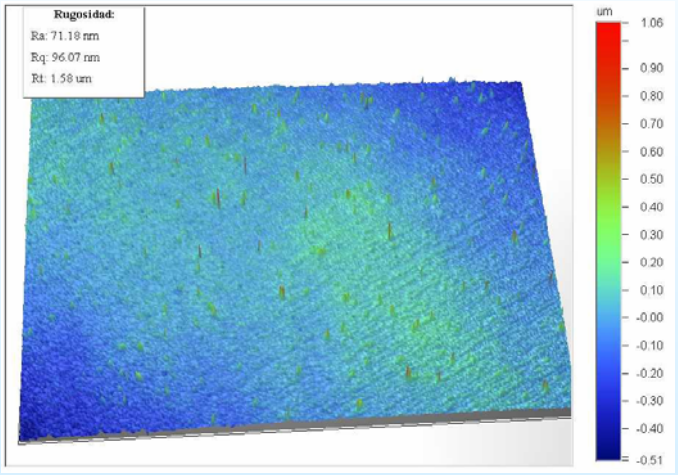




PI^3 leads to saturated implantation profiles, which goes deeper as a function of the energy.

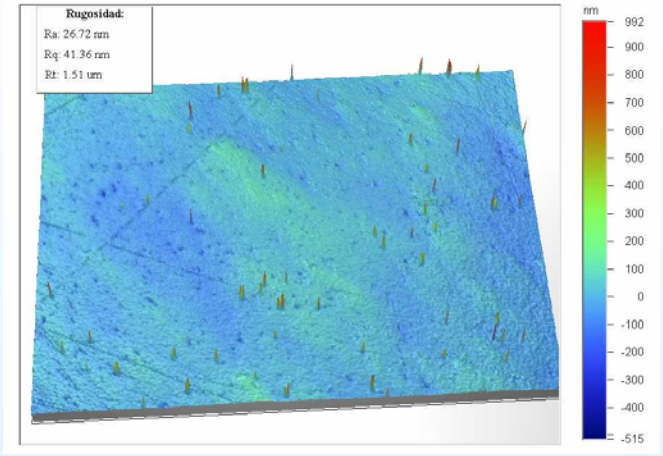
In the case of Oxygen implanted on stainless steel, it can be shown how the oxide barrier confines the Nickel at increasing depth.

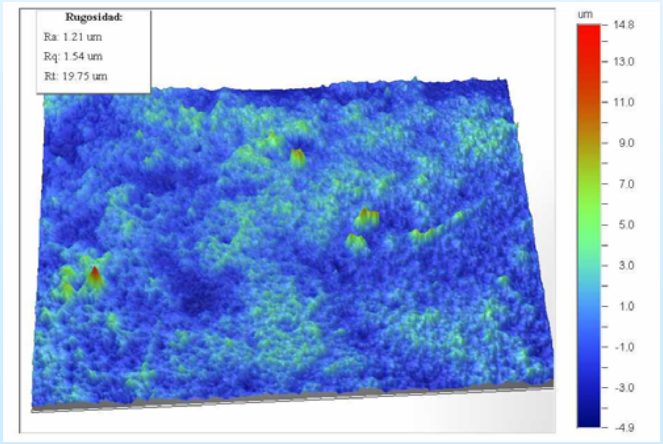
PLASMA IMMERSION ION IMPLANTATION



II

PI^3





In spite of its functional advantages, PI3 can lead to more relevant surface heating as well as to increases of roughness (e.g., more than 10 times in the case of Al alloys)

FINAL REMARKS

- Ion Implantation has demonstrated to be an effective technique for the prevention of wear, excessive friction and some oxidation and corrosion problems of metal alloys employed in medical implants and devices (stainless steel, Titanium alloys, CrCo, NiTinol...).
- In addition, other benefical effects of ion implantation have been reported: implantation of CO^+ ions seems to facilitate the bone growth and integration. The implantation of Ag^+ has bacteriocide effects. The implantation of oxigen allows to create difusional barriers for toxic ions...
- The ion implantation treatment of polymers is still more promising, and the required dose is 10 – 20 times smaller.
- Ion implantation is economically affordable when size and geometry collaborate to short times of treatment per unit. Future developments like PI^3 could lead to even cheaper treatments.

AIN - Centre of Advanced Surface Engineering

- Private technological center, founded in 1963
- Association of 157 companies
- Employees (2005): 121 (15 AIN - CIAS)
- Clients (2005): 1085 (90 AIN - CIAS)

e-mail: surfatec@ain.es