

# Improved Mechanical Properties of Al<sub>2</sub>O<sub>3</sub>/PTFE Layer by Metal Ion Implantation

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## Abstract

*In this work, metal ion implantation was employed to improve the mechanical properties of Al<sub>2</sub>O<sub>3</sub>/polytetrafluoroethylene (Al<sub>2</sub>O<sub>3</sub>/PTFE). Four metal ions (Al, Cr, Ni, and Ag) were selected as the implantation source, respectively, and the implantation process was optimized by SRIM method. Optimization results revealed that, among these four metal ions, implantation of Al ions exhibited the best modification for Al<sub>2</sub>O<sub>3</sub>/PTFE composite layer, when the particle distribution section, distribution range and energy exchange were concerned. Al ion implantation could minimize the damage of carbon skeleton and lamellar structure of Al<sub>2</sub>O<sub>3</sub>/PTFE substrate, which kept strong scattering of Al ions and obtained the thick and uniform coating on the surface of Al<sub>2</sub>O<sub>3</sub>/PTFE substrate. The uniformity of Al<sub>2</sub>O<sub>3</sub>/PTFE layer was improved with the increase in Al ions implantation dosage and the best dosage of Al ions was regarded as  $1 \times 10^{16}$  ions/cm<sup>3</sup> with the implantation energy of 20KeV. After implantation modification, the mechanical properties of Al<sub>2</sub>O<sub>3</sub>/PTFE layer were obviously improved. The hardness (H) of samples was detected to be 0.65GPa and elastic modulus (E) 2.2 GPa, with a higher H/E value of 0.295, which was 10 times higher than original PTFE.*

**Keywords:** Al<sub>2</sub>O<sub>3</sub>/PTFE Layer; Metal Ion implantation; SRIM; Mechanical property

## 1. Introduction

Polytetrafluoroethylene (PTFE) is widely applied in industrial production, As a kind of engineering material, due to excellent properties that many other engineering materials can not match.[1-6] but its poor wear resistance limits its application in the industrial field[7-14]. To explore and find effective ways and methods to improve the tribological properties of PTFE, The special software SRIM was selected to study this subject. Particle radiation cross-section and range distribution of four kinds of metal ion under different condition implantation into PTFE were studied by SRIM in the paper. based on SRIM optimization experiment, modified experiment of PTFE was completed by MEVVA80-10 ion implantation machine. Al<sub>2</sub>O<sub>3</sub>/PTFE nano-composite layer was fabricated. The mechanical property of Al<sub>2</sub>O<sub>3</sub>/PTFE layer samples before or after modified were tested by the nano- indentation test machine.

## 2. Experiment

### 2.1. SRIM Optimization Experiment

The special software SRIM of ion range and energy calculation was selected to study this subject about optimization experiment. The program was invented by Dr. James F. Ziegler of Yale University [15], and was a special software to study the molecular dynamics of simulating each element change in layer growth process. It also was a classic

program of simulating radiation damage of ion in the material and calculating resistance and range distribution of ion (10eV ~ 2GeV) in solid [16].

Fixed-point implantation method was used in optimization experiment. Ions implantation rate were 290-295 ions/min. Ion distribution curve could be obtained after Al ion implantation of 230 minutes approximately. Special notes: too large computation of simulation software would cause fault of system because of memory. In order to control the time of the experiment, simulation experiment of implantation dose of  $1 \times 10^{16}$  ions/cm<sup>3</sup> was conducted on the material surface of 40nm thickness. From the analysis of the experimental results, collected simulation characteristic value was enough to continue experiment. The incident angle was calculated by MACIC algorithm. Atomic binding energy  $E$ , atomic binding energy in the body  $E_b$ , atomic displacement energy  $E_d$  and atomic density  $\rho$  of substrate surface were set by SRIM, which was obtained from first principle calculations[17]: density of PTFE was 2.2g/cm<sup>3</sup>,  $E_{disp}$  is equal to 28ev and  $E_{surf}$  is equal to 2ev and  $E_{latt}$  is equal to 7.47ev for carbon atom .  $E_{disp}$  is equal to 25ev and  $E_{surf}$  is equal to 2ev and  $E_{latt}$  is equal to 3ev for fluorine atom .

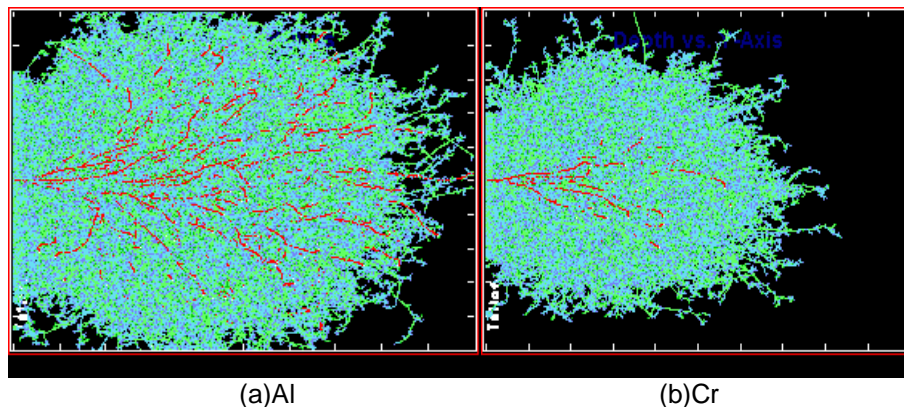
## 2.2. PTFE Modified Experiment

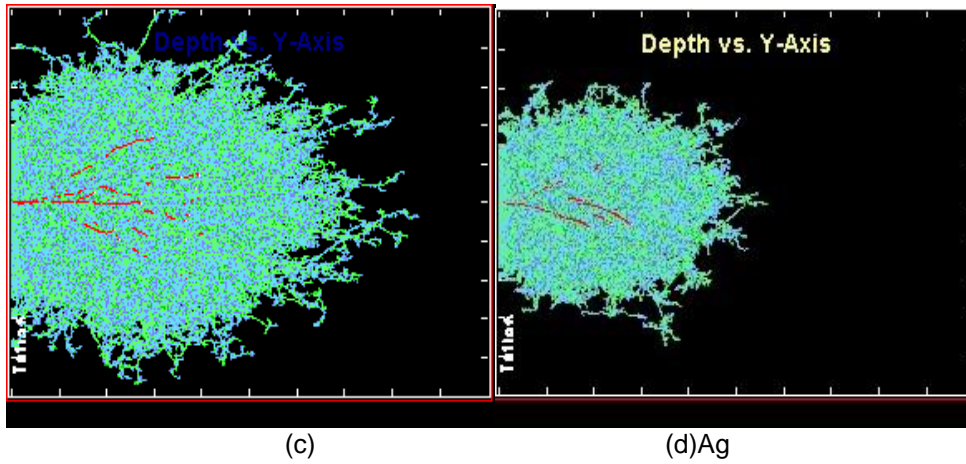
Al<sub>2</sub>O<sub>3</sub>/ PTFE nano-composite layer was fabricated in matal vacuum room of MEVVA by Bunch Plasma Beam Implantation Technology. the maximum acceleration voltage of ion implanter was 40KV. Aluminum ion energy was 20KeV. Three kinds of does for ion beam were  $1 \times 10^{15}$  ion/cm<sup>3</sup>,  $5 \times 10^{15}$  ion/cm<sup>3</sup> and  $1 \times 10^{16}$  ion/cm<sup>3</sup>, Current Density was 10uA/cm<sup>2</sup>. Al<sup>3+</sup> was implanted under pressure was  $2 \times 10^{-4}$ Pa, running pressure was  $3 \times 10^{-3}$ Pa.

## 3. Simulation of Particle Distribution Section

Figure 1 showed X-Y plane projection images of distribution trajectories of different ions (Al(a), Cr(b), Ni(c), Ag (d)) with the same implantation energy (20KeV) and the same implantation dose ( $1 \times 10^{14}$  ions/cm<sup>3</sup>). In these images, the red lines represented the motion trails of metal ions, and the green lines represented the motion trails of collided PTFE atoms.

It can be seen from Figure 4-1, (a), (b), (c), (d) were separately correspond to particle distribution sections of PTFE surface with implanting Al, Cr, Ni and Ag ions. The path of red points showed position changes of metal ions, and the green points showed position changes of PTFE matrix particles. It can be seen obviously that the collided particles were diffusing in radiation range and the areas which there were no metal ions implanted have also been enhanced with the effect of diffusion. With the comparison of (a), (b), (c), (d) in figure 1, it can be seen that Al ions represented the most intense radiation diffusion effects among the four kinds of metal ions when they were implanted to the same material with the same implantation dose of  $1 \times 10^{14}$  ions/cm<sup>3</sup> and the same implantation energy of 20KeV. It was very important for PTFE to get a good modification effect.



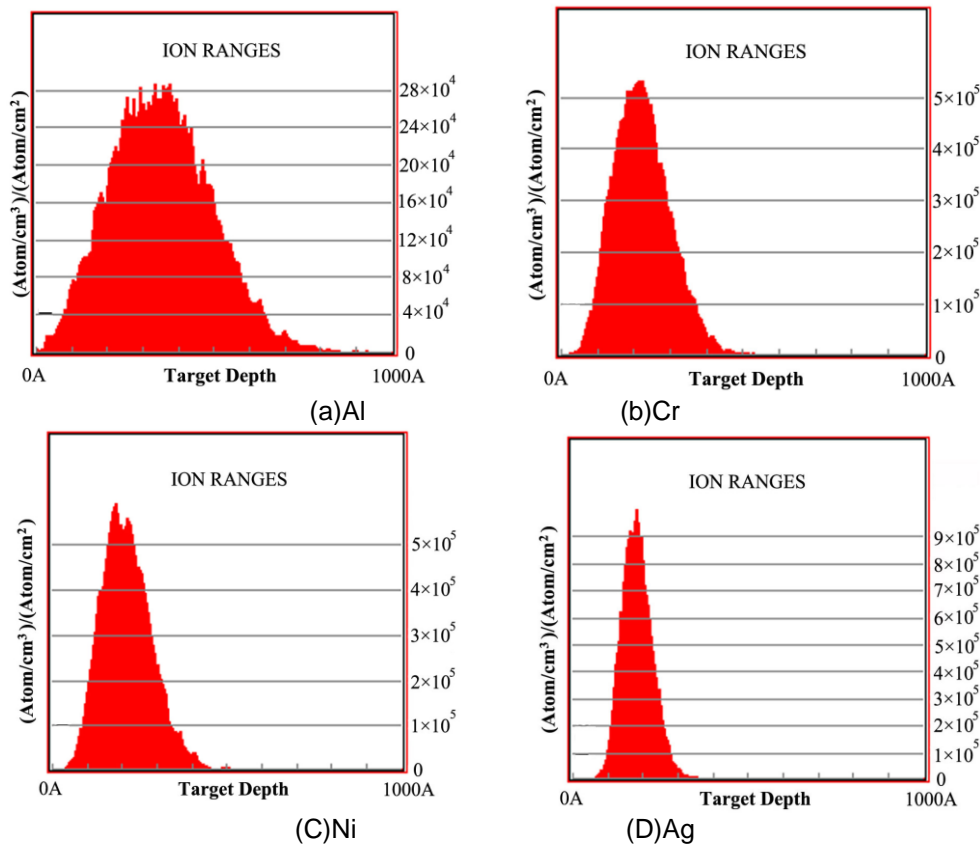


**Figure 1. Images of Particle Distribution Section when Implanted Different Ions (Implantation Energy and Dose were separately 20KeV and  $1 \times 10^{14}$  ions/cm<sup>3</sup>)**

#### 4. Simulation of Range Distribution

##### 4.1. Projected Range Distribution with Implanting Different IONS

Figure 2 showed images of projected range distribution, the abscissa represented the implantation depth and the ordinate represented the ion implantation dose of per unit section. It is noted that the unit in Figure 2 was atoms/cm<sup>2</sup>, multiply it by implantation dose was just the unit of impurities content.

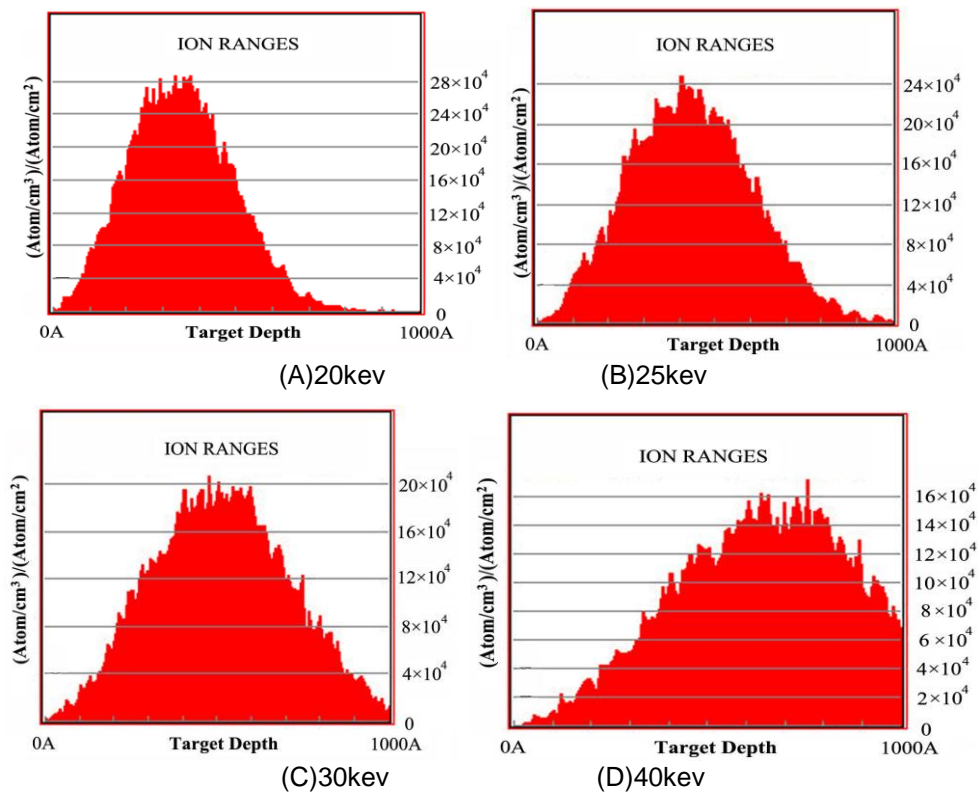


**Figure 2. Images of Projected Range Distribution with Different Metal Ions**

(Implantation energy and implantation dose were separately 20KeV and  $1 \times 10^{14}$  ions/cm<sup>3</sup>)

Figure 2 showed images of projected range distribution with implanting different metal ions under the condition of implantation energy of 20KeV and implantation dose of  $1 \times 10^{14}$  ions/cm<sup>3</sup>. Seen from figure 2, implantation range of Al(a) ions was 26.1nm and the average dose of impurities was  $2.8 \times 10^{19}$  ions/cm<sup>3</sup> (multiply ordinate by implantation dose), the half-peak width of particle number was 40 nm. Under the condition of the same implantation energy and dose, implantation range of Cr(b) ions was 22.8nm and average dose of impurities was  $45.6 \times 10^{19}$  ions/cm<sup>3</sup>, implantation range of Ni(c) ions was 21.2nm and average dose of impurities was  $42.4 \times 10^{19}$  ions/cm<sup>3</sup>, and implantation range of Ag(d) ions was 21.2nm and average dose of impurities was  $42.4 \times 10^{19}$  ions/cm<sup>3</sup>. The half-peak width with implanting Cr, Ni, Ag ions were all 20nm or less than 20nm, and their average doses of impurities were all higher than that implantation of Al(a) ions. So Al ions showed the best implantation effects. Because the implantation of metal ions to PTFE can change its surface structure, and introduce impurity particles to the transfer film which formed on dual plane in the process of material contacting with wear parts, then it could not only maintain part of the self-lubricating properties, but also could increase adhesive ability between the transfer film and wear parts. If the depth of implantation was too small, in the process of grinding with wear parts, the implantation layer would be transferred to dual plane, which could not increase the wear ability, but even aggravated the abrasion of the material. While implanted Cr(b), Ni(c), Ag(d) ions under the same conditions, they all formed high concentration of doping in the depth of 20nm, and such surface modified films were very likely to be detached by the mechanical forces, which was not conducive to resist wear. So Al ions showed the best modification effect among the four kinds of ions.

#### 4.2. Projected Range Distribution with Different Implantation Energies



**Figure 3. Projected Range Distribution of Al Ions with Different Implantation Energy**

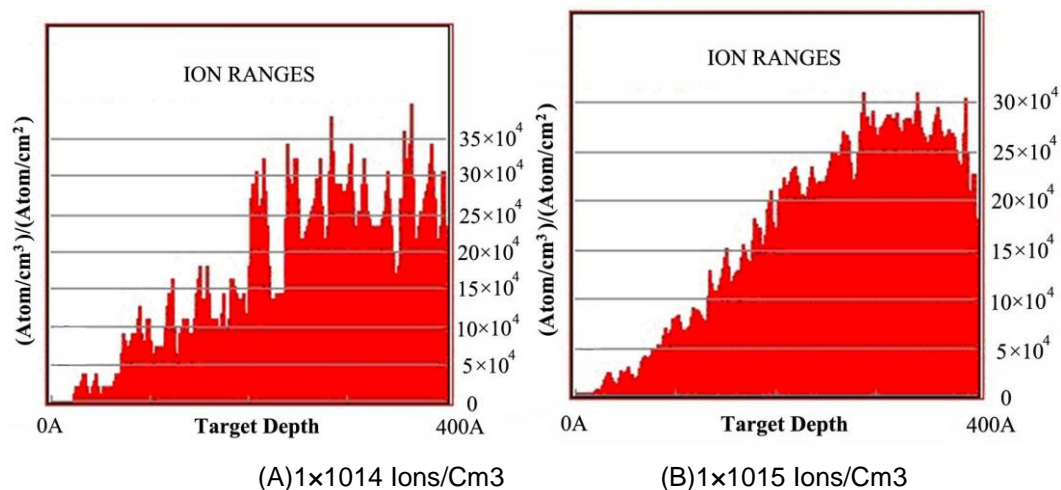
Figure 3 showed projected range distribution with different implantation energies under the condition of same implantation ions of Al and same dose of  $1 \times 10^{14}$  ions/cm<sup>3</sup>. When implantation energy was 20KeV, the implantation range was 26.1nm and average dose of impurities was  $2.8 \times 10^{19}$  ions/cm<sup>3</sup>. When implantation energy was 25KeV, the implantation range was 48.8nm and average dose of impurities was  $2.3 \times 10^{19}$  ions/cm<sup>3</sup>. When implantation energy was 30KeV, the implantation range was 61.0nm and average dose of impurities was  $1.9 \times 10^{19}$  ions/cm<sup>3</sup>. When implantation energy was 40KeV, the implantation range was 82.8nm and average dose of impurities was  $1.5 \times 10^{19}$  ions/cm<sup>3</sup>.

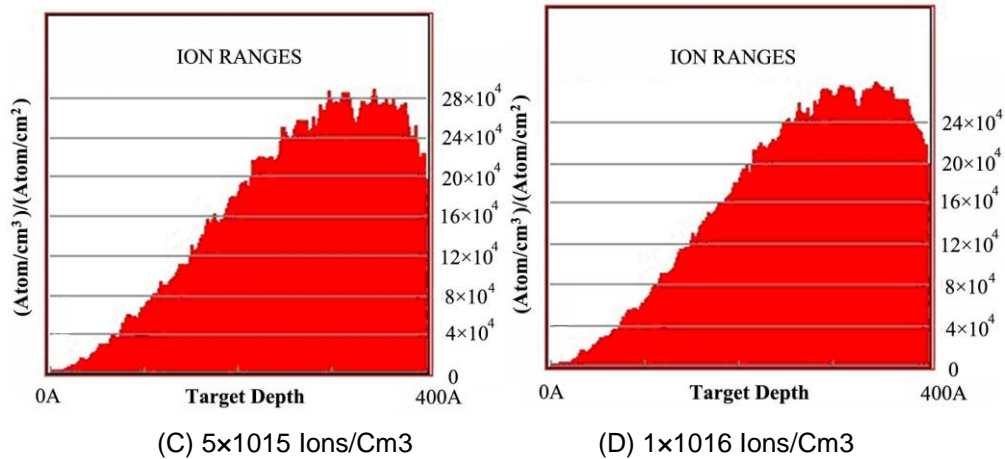
It can be seen from figure 3, the range of metal ions and the depth of implantation were gradually increased with the increasing of implantation energy. The radiation diffusion must be increased with the increasing of metal ion beam energy, then homogenized the particle distribution and decreased the average dose. In addition, the maximum of distribution peak of the doped particles would move right with the increasing of implantation depth. Because of the transfer film was in tens of nanometers from the surface, when the transfer film was peeled from the PTFE surface, the wear mechanism between PTFE matrix and the transfer film on dual plane would be changed. Then, the implantation energy was required to be limited in a certain range, or it would destroy the self-lubricating property of transfer layer.

#### 4.3. Projected Range Distribution with Different Implantations Doses

Figure 4 showed the projected range distribution with different implantation doses under the condition of same ions (Al) and same implantation energy (20KeV).

In order to ensuring that the maximum implantation dose could meet the requirements of experiment, this paper only considered the field which was in the top depth of 40nm from the surface of PTFE, then resulted in high levels of ions. In Figure 4(a), when the dose of implantation ions was  $1 \times 10^{14}$  ions/cm<sup>3</sup>, the implantation range was 28.8nm and the average dose of impurities was  $3.7 \times 10^{19}$  ions/cm<sup>3</sup>, which showed the best effects. In Figure 4(b), the dose of implantation ions was  $1 \times 10^{15}$  ions/cm<sup>3</sup>, the average dose of impurities was  $3.2 \times 10^{19}$  ions/cm<sup>3</sup>. In Figure 4(c), the dose of implantation ions was  $5 \times 10^{15}$  ions/cm<sup>3</sup>, the average dose of impurities was  $2.9 \times 10^{19}$  ions/cm<sup>3</sup>. In Figure 4(d), the dose of implantation ions was  $1 \times 10^{16}$  ions/cm<sup>3</sup>, the average dose of impurities was  $2.7 \times 10^{19}$  ions/cm<sup>3</sup>. With the gradually increase of the implantation ions dose, the range of implantation ions had only a very small fluctuations. However, because of the aggravated of diffusion by radiation, the volume of doped ions was increased and then resulted in a decrease of implanted ions concentration on the surface of matrix. As can be seen from the curves, increasing of the implantation dose could homogenize the distribution of implanted ions.





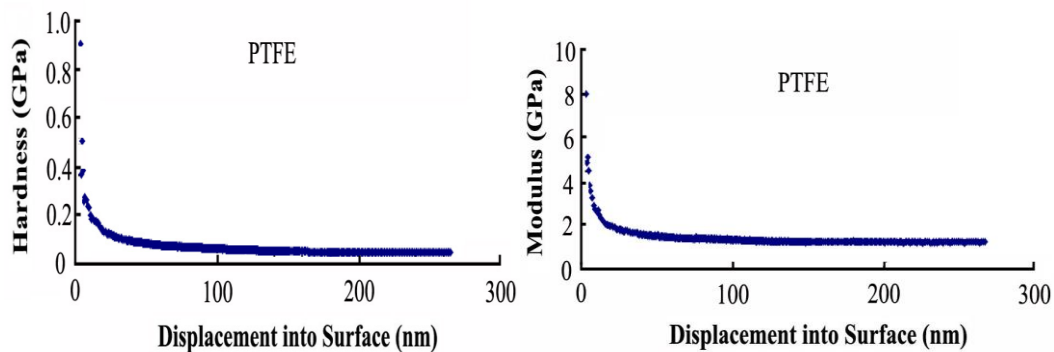
**Figure 4. Projected Range Distribution with Different Implanting Doses**

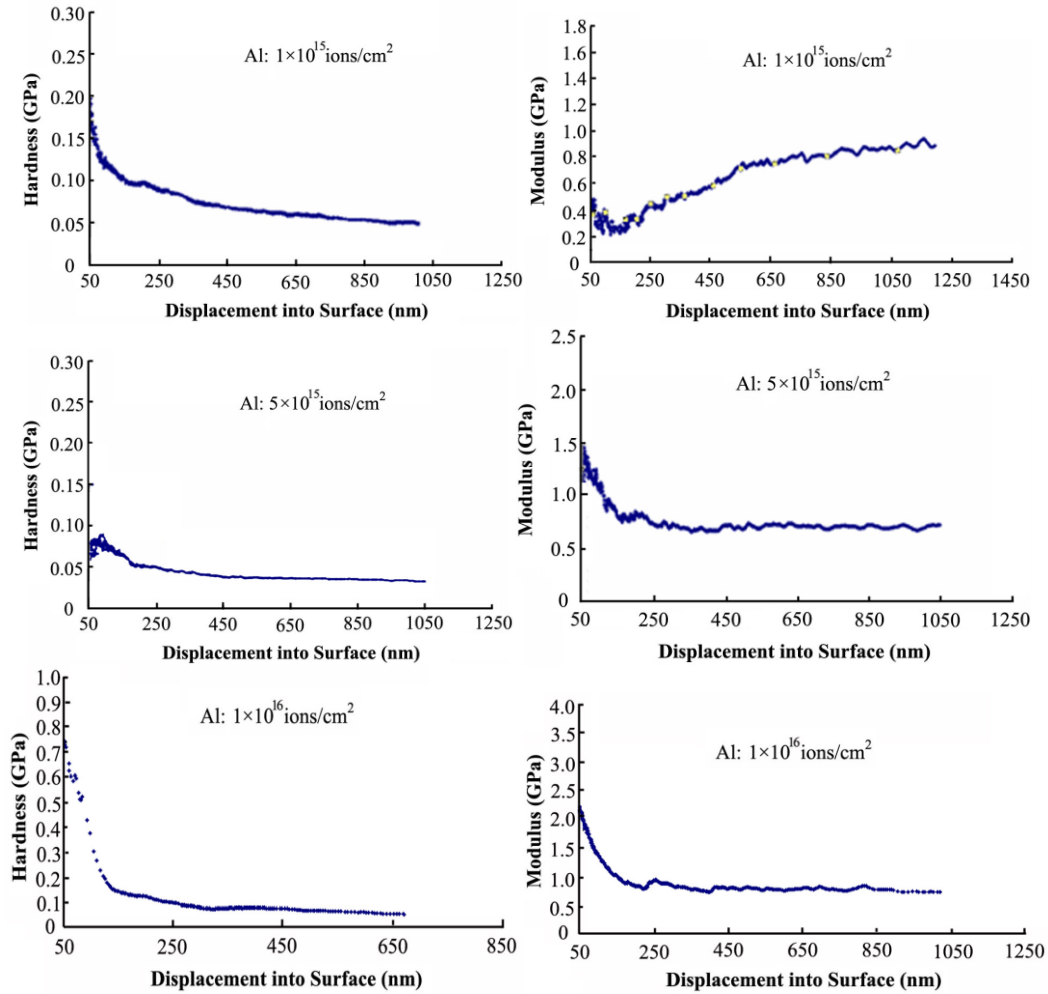
### 5. Al<sub>2</sub>O<sub>3</sub>/PTFE Mechanical Property Before or After Modification

By testing mechanical property of Al<sub>2</sub>O<sub>3</sub>/PTFE layer sample before or after modification using nano indentation test machine, it was found that the hardness(H) of implantation samples (1X10<sup>15</sup>, 5X10<sup>15</sup>, 1X10<sup>16</sup>) was correspondingly 0.15Gpa, 0.19Gpa and 0.65Gpa. The hardness of PTFE before modification was 0.04Gpa. This shows that after modification, all samples have increased their hardness. With film thickness increasing, the hardness of Al<sub>2</sub>O<sub>3</sub>/PTFE layer will increase 5-6 times than original value. See Figure 5.

When the implanting element was aluminum, implantation dose was correspondingly 1X10<sup>15</sup>ion/cm<sup>2</sup>, 5X10<sup>15</sup> ion/cm<sup>2</sup> and 1X10<sup>16</sup> ion/cm<sup>2</sup>, The elastic modulus E was correspondingly 0.9, 1.5 and 2.2. The former two are lower in modulus E than that of before modification which is 2.0, in these two cases, it is benefit to improving the adherence wear ability. The later one is higher in modulus E, it is unfavorable in improving the adherence wear ability, See Fig 5.

The H/E values of Al<sub>2</sub>O<sub>3</sub>/PTFE layer are 0.165, 0.127 and 0.295 respectively, while the H/E value of unprocessed PTFE is 0.02. It can be concluded that the Al<sub>2</sub>O<sub>3</sub>/ PTFE layer has low plastic deformation and can increase elastic deformation. So the Al<sub>2</sub>O<sub>3</sub>/ PTFE layer had higher adherence abrasion- resistance ability after beam aluminum ion implantation. When implantation dose was 1X10<sup>16</sup> ion/cm<sup>2</sup>, effect of modification was best, it was more 10 times than before, average effect of modification was as 5-6 times as before.





**Figure 5. Hardness and Elastic Modulus Comparison of Implanted And Non-Implanted PTFE**

## 6. Conclusions

(1) The results of simulation experiment showed that, *four kinds of metal ion* with same dose and energy were implanted on the surface of substrates, Al ion had more intense radiation diffusion and larger area scattering, the damage on C skeleton and lamellar structure of PTFE substrates were minimum, and was beneficial to keep the self lubrication of material. Scattering of Al ions was more strong, so that the films were thicker and more uniform, the wear resistance ability of PTFE was improved.

(2) When metal ion implantation were Al ions and implantation dose were  $1 \times 10^{14}$  ions/cm<sup>3</sup>, implantation depth not only could be kept enough at 20KeV among four kinds of implantation energy (20, 25, 30, 40KeV), and implantation range was about 26.1nm, but also the damage could be controlled to a lesser degree, and average impurity concentration was about  $2.8 \times 10^{19}$  ions/cm<sup>3</sup>, which was best modification effect. With the increase of the Al ions implantation dose, nano composite films were more uniform and more consistent performance in the same ions and energy, and modification effect of PTFE was the best at implantation dose of  $1 \times 10^{16}$  ions/cm<sup>3</sup>. The best metal ion was Al, implantation dose was  $1 \times 10^{16}$  ions/cm<sup>3</sup>, implantation energy was 20KeV by SRIM optimization.

(3) The results of modification experiment showed that, the hardness of Al/PTFE nano-composite layer ( $1 \times 10^{15}$ ,  $5 \times 10^{15}$ ,  $1 \times 10^{16}$  ions/cm<sup>3</sup>) were 0.15, 0.19, 0.65Gpa, respectively, elasticity modulus were 0.9, 1.5, 2.2 Gpa at 20 KeV, with a higher value of H/E, which

was  $0.295 (1 \times 10^{16} \text{ ions/cm}^3)$  after implanting Al ions. The best modification effect was 10 times than original PTFE, which was helpful to reduce the plastic deformation of PTFE and improve the elastic deformation ability. So that PTFE of aluminum ion implantation with beam line type had a higher ability to resist adhesion wear.

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