THE NEW TYPE BROAD BEAM ION SOURCES AND APPLICATIONS

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ABSTRACT

The broad beam ion sources of hot filament plasma type have been widely used for modifications of materials and thin films, and the new type intensive current broad beam metal ion source including reactive gaseous ion beams is needed for preparing the hard coating films such as DLC, β-C_3N_4, Carbides, Nitrides, Borides etc.. Now a electron beam evaporation (EBE) broad beam metal ion source has been developed for this purpose in our lab. CN film has been formed by the EBE ion source. Study of the CN film shows that it has high hardness(HK=5800kgf/mm ^{2}) and good adhesion. This method can widely changes the ratio of C / N atom's concentrations from 0.14 to 0.6 and has high coating rate. The low energy pocket ion source which was specially designed for surface texturing of medical silicon rubber was also developed. It has high efficiency and large uniform working zone. Both nature texturing and mesh masked texturing of silicon rubbers were performed. The biocompatibility was tested by culture of monocytes, and the results showed improved biocompatibility for the treated silicon rubbers. In addition, the TiB_2 film synthesized by IBED is being studied recently in our lab. In this paper, the results which include the hardness, thickness of the films and the AES, XRD analysis as well as the tests of the oxidation of high temperature and erosion will be presented.

1. Introduction

IBED (Ion Beam Enhanced Deposition), also called IBAD (Ion Beam Assisted Deposition) combines both the PVD and ion implantation technology together and has great potential of industrial applications. This method has widely developed in CSSAR since 1984. Up to now it has been extended to synthesis the hard coating films, such as DLC, β-C_3N_4, Carbides, Nitrides, Borides and to treat biological materials, for example, medical silicon rubber. However the key step for developing the IBED is the successful applications in industry and the most important thing is to develop the efficient ion sources which have better treatment ability.The broad beam ion sources of hot filament plasma type have been widely used in IBED to improve the production efficiency. But it still have some problems which have to be solved.

1. The efficiency of preparing films with IBED.
2. The extractive intensive beam current at low energy.

In order to avoid serious crystal damage of material, we have to use the low energy ions instead (typically 100-200 eV called energy window). But, according to Child- Langmuir Law, it is difficult to extract intensive beam current at such low energy.

3. To extract a variety of intensive metal ion beams and mixture of both gaseous and metallic ions.

In order to satisfy all demands, the EBE (Electron Beam Evaporization) metal ion source is developed. Different from the MEVVA ion source which is just used for implantation, the

EBE ion source is designed for deposition at selectively low energy to improve the deposition rates.

Our lab has being worked on these subjects for many years and several achievements have been obtained. A low energy as low as 10 eV Kaufman type of gaseous ion source was developed for producing intensive beam current, a low energy pocket Kaufman type ion source was specially designed for surface texturing of medical silicon rubber in order to improve the biocompatibility of the medical material has been also developed. CN film has been formed by EBE ion source. TiB_2 and B_4C, B-C-Ti films were prepared in our laboratory by IBED, and medical silicon rubber has been treated by using ion beam texturing. All of these will be introduced here briefly.

2. CN film preparing by EBE

The schematic diagram of EBE ion source is shown in Fig.1. It is consisted of discharge chamber, anode, cathode, crucible and applied magnetic coils. The discharge of the EBE consisted of two parts, the first part was occurred between refractory filament and anode, the electrons emitted by filament bombard gas atoms to cause the discharge and heat the discharge chamber to avoid the vapor condensation on the chamber wall, the discharge was also occurred between filament and crucible. The electrons generated by discharge is focused to form an electron beam with high beam current density and bombard the metal in the crucible by applied magnetic field. A very high temperature area can be obtained in the crucible center and a high density of metal vapor was formed. The metal vapor was ionized in the discharge chamber and the ions were extracted by a two grid or three grid extraction system.

Table 1 The deposition rates of a variety of metals

Beam voltage (KV)	Beam current density (mA/cm^2)	Max deposition rate (Å/s)		
		C	Mo	Ti
2	2 - 3.5	80	25	30

Ions of C, W, Ta, Mo, Cr, Ti, B, Ni, Cu, Al, N_2, etc. have been produced by the EBE ion source, and the deposition rates have been greatly improved (shown in Table.1). Another feature

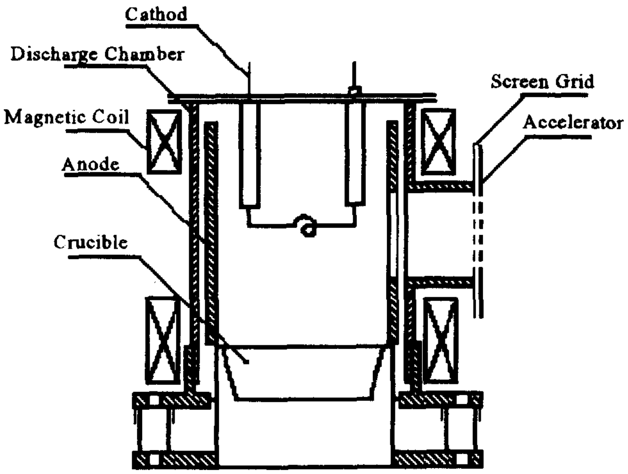


Fig. 1 The schematic diagram of EBE ion source

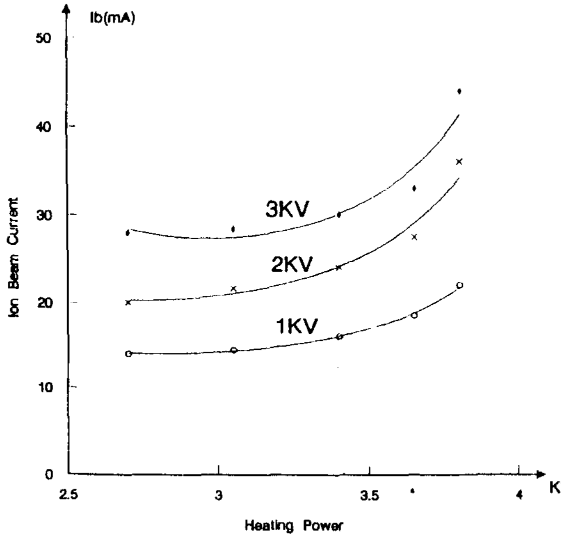


Fig. 2 Extraction character of W ions

of the EBE ion source is that it can be operated in different discharge voltages to obtain high charge state of ions. In order to obtain the high charge state of ions for implantation and making inter-mixted interface, the high discharge voltage was applied previously at high extraction voltage, then the low energy ions was followed for coating and improving the coating rates. The extraction character of W ion is shown in Fig.2. The beam current density profiles of C ions are shown in Fig. 3.

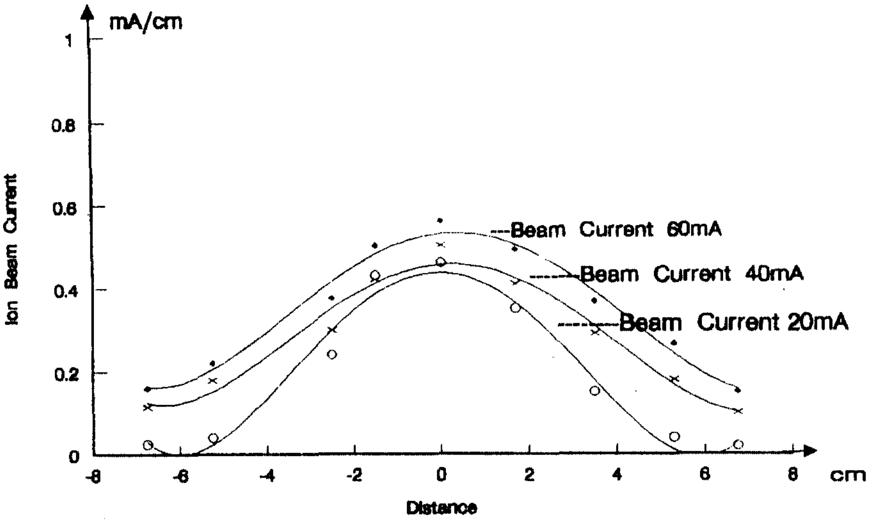


Fig. 3 Distribution profile of C ions

Table 2 The hardness of CN on the WC plate

Sample	Extraction Voltage (KV)	Beam Current (mA)	N_2 flowrate (sccm)	Deposition Time (min)	Load (g)	Hardness (kgf/mm^2)
1	4	40	1.26	35	20	3100
2	4	40	1.86	60	20	4157
3	4	40	2.09	70	20	5300-5800

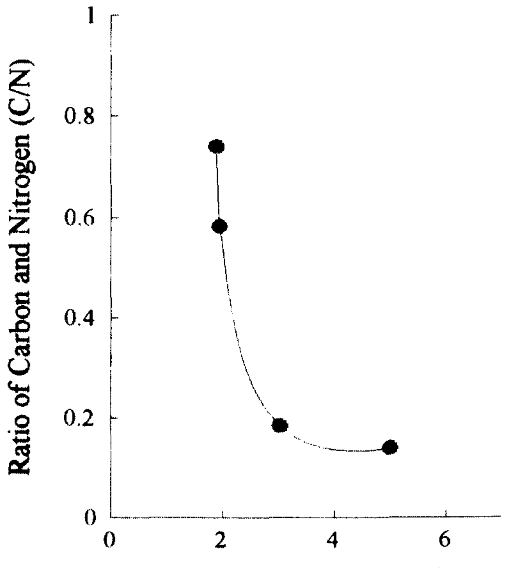


Fig. 4 Affection of N_2 flowrate on C/N

CN film can be formed on the substrate of Tungsten Carbide where nitrogen and metal ions bombard by introducing N_2 into discharge chamber of ion source, and if the flowrate of N_2 was modulated from 1.80 sccm to 5.04 sccm, the ratios of C/N atom concentrations will be changed from 0.14 to 0.6 (see Fig.4) .The microhardness was shown in Table. 2. The hardness of CN films on the WC substrate was Hk=3100-5800 kgf/mm^2 . The hardness of CN film is increased with increasing the flowrate of N_2 from 1.26 to 2.09 sccm at extraction voltage 4 kV and bombardment current of 40 mA. The AES depth profile of C, N on Si substrate was shown in Fig. 5. The good mixed zone can be found in this figure. The depth of mixed zone is about 30 nm, which is double deeper than the expected penetration depth at this energy will ensure that the film has good adhesion. The participation of the high charge state of ions will be confirmed, and the microstructure of CN film will be studied further.

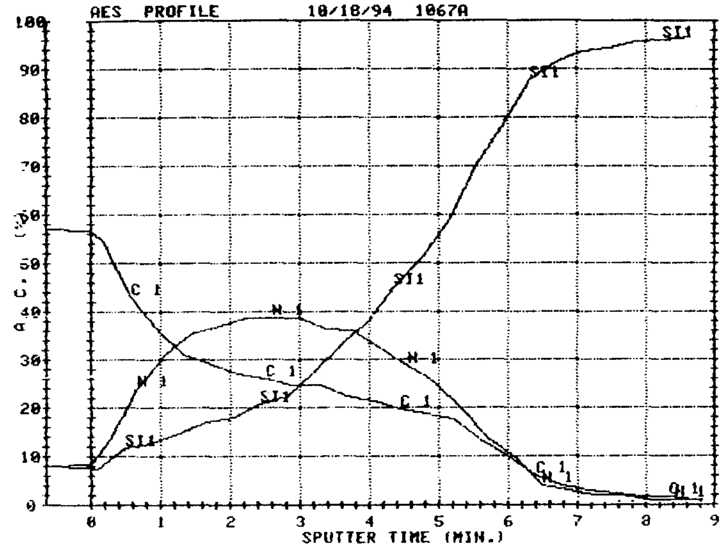


Fig. 5 The AES profile of C,N on Si

3. B-C, B-C-Ti, and Ti-B films prepared by IBED

These films are prepared in the dual ion beam sputtering systems. The B-C film was bombarded by low energy Ar^+ ions (0-6 KeV) and the Ti-B film by intermediate energy Ar^+ ions (10- 40 KeV). The sputtering targets are sintered by boron with graphite powder and titanium with boron powder, respectively. The composition and structure of the film were characterized with AES, XRD and TEM.

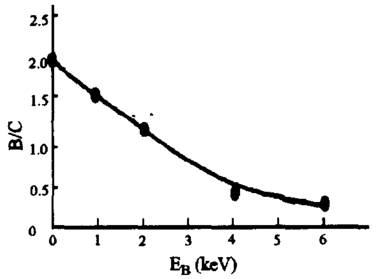


Fig. 6 B/C atomic ratio on boron carbide films versus bombarding energies

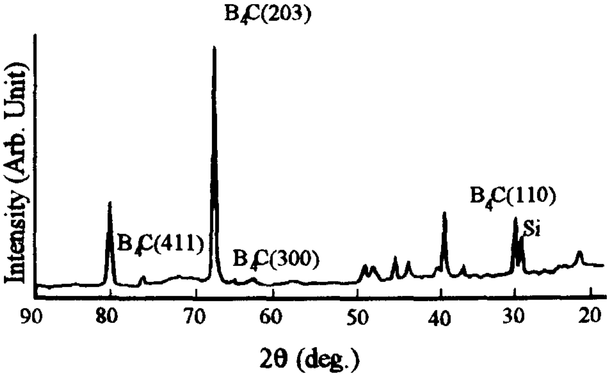


Fig. 7 XRD chart of boron carbide film

The hardness was measured by Knoop Hardmeter, and the tribological test of films were performed in the SRV Tester. The sliding ball which was 10 mm in diameter and made of hardened AISI 5,2100 steel grinds back and forth on the surface of coated disk over a 4 mm track length. The reciprocating frequency of the ball was 10 Hz. The load was 2-5 N. The friction coefficient was continuously monitored during test and the volummetric wear of the disks was measured by using surface profimeter. The B/C atomic ratio on BC films versus bombarding energies was shown in Fig. 6. The XRD chart of boron carbide film was shown in Fig. 7. The microhardness of BC films versus bombarding energy is shown in Fig. 8. The SRV Wear-out chart of Ti-B-C was shown in Fig. 9. The B content decreased with the increase of bombardment energy. It is suggest that the Boron was volatile and preferentially sputtered. The diffraction peaks of B_4C and other Boron carbides were observed by XRD. Bombarded by Ar^+ with more than 6 KeV energy, the film was amorphous. The Hk of the as-deposition BC film was 1200 kgf/mm^2. The hardness Hk increased with the energy of Ar^+ and reached the highest value of 3200 kgf/mm^2 as the bombarding energy was 4 KeV. It could be perceived that crystallization would be of benefit to the hardness of some materials of ceramic. In order to

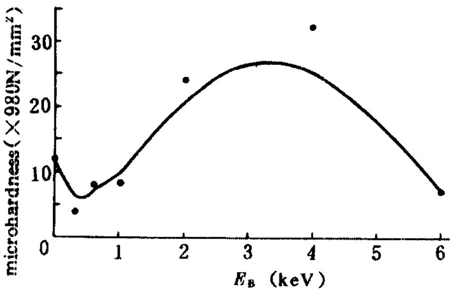


Fig. 8 Microhardness of boron carbide films versus bombarding energies

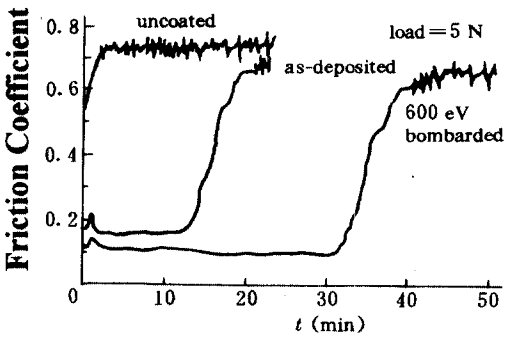


Fig.9 The wear-out chart of Ti-B-C

improve the toughness of the films, the Ti-B-C film is also prepared. The SRV wear out test shows that the Ti-B-C film formed by IBED has lower friction coefficient (~0.1) than the as-deposited one. The microhardness reached the highest value of 2700kgf/mm^2 for the film was bombarded by Ar$^+$ with the energy 600 eV, and rapid dropped to 1200 kgf/mm^2 as the bombarding energy increased to 900 eV.

Table 3 The hardness of TiB_2 films

Sample	Bombarding Parameters		Thickness (μm)	Hardness (kgf/mm^2)
	Voltage (KV)	Current (mA)		
1	0	0	1.6	1600
2	20	5	1.3	2421
3.	20	10	1.6	2980
4	20	15	1.6	3269
5	40	10	1.6	3370

TiB_2 film has high hardness and good inertness to erosion. In addition to its applications for wear and corrosion resistant coating, TiB_2 film has a potential application in microelectronics as diffusion barriers between metallic contacts and silicon substrate. The AES profile of TiB_2 film on the Si by using 20 KeV, 5 mA Ar$^+$ bombarding was shown in Fig. 10. The composition of this film was near stoichiometric TiB_2 as shown. The XRD chart of the asdeposited and bombarding with different Ar$^+$ energy were shown in Fig. 11. We can conceive that from this figure the crystallization is enhanced with the bombarding energy and current of ions. The hardness of TiB_2 film was listed in Table 3. The hardness will increase with crystallization content. The tribological test result was shown in Fig. 12 and the profile of volummetric wear was obtained with greatly improving.

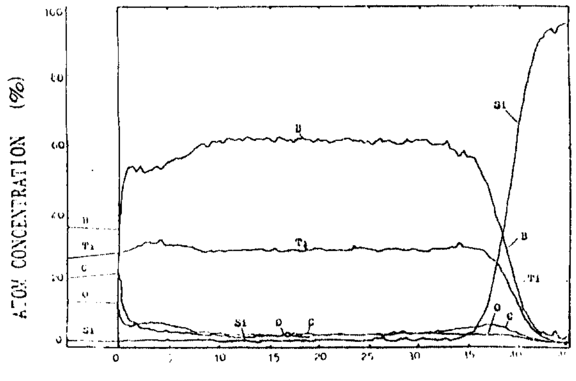
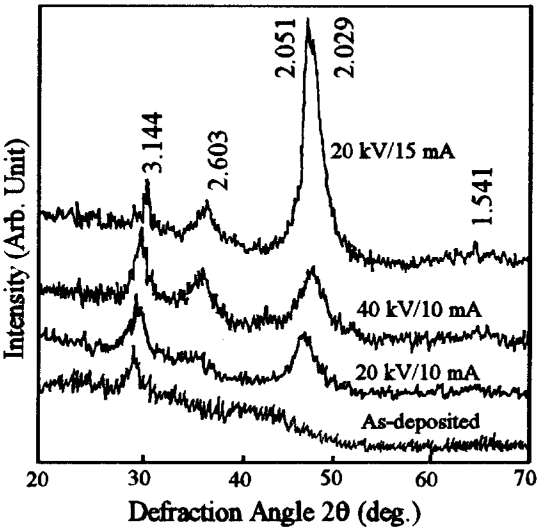


Fig. 10 AES profile of TiB_2 films

The weight gain of oxidation at high temperature of the TiB_2 film were shown in Fig 13, and



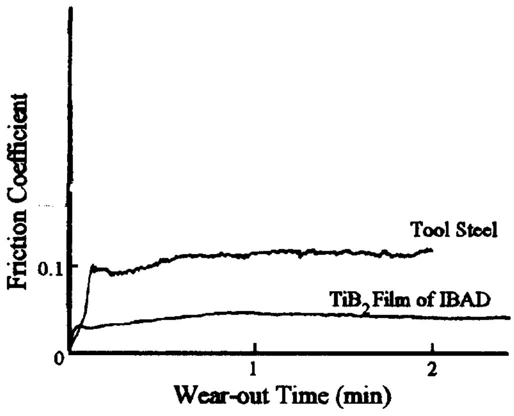


Fig. 11 XRD chart of TiB_2 films

Fig. 12 Wear-out test results of TiB_2 films

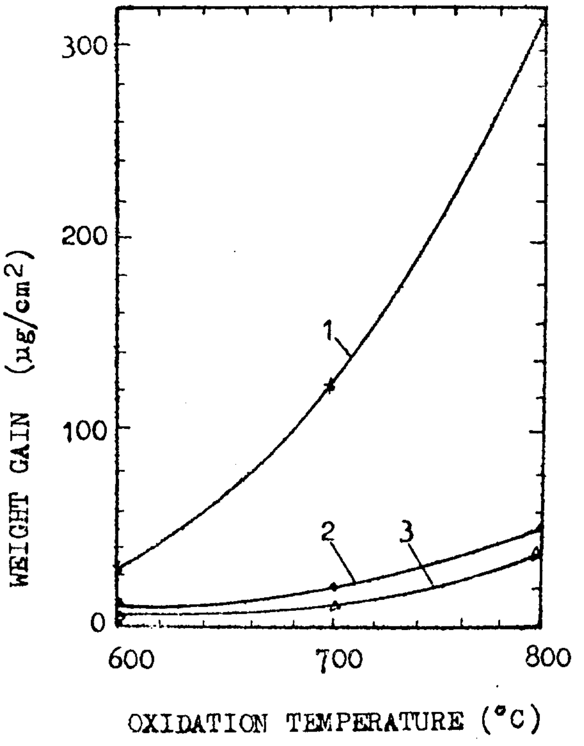
the electrochemical erosion test in 1 N H_2SO_4 solution at room temperature was shown in Table 4. These data indicate that TiB_2 has been synthesized by dual beam sputtering deposition, the composition of the film is of B/Ti=2:1. The characterization by XRD revealed that the as-deposited film is amorphous, and the IBED films have crystalline structure. The structure and the hardness of TiB_2 films depend on the energy as well as beam current of Ar^+. The films of TiB_2 have good ability to resist oxidation of high temperature and erosion.

4. Pocket ion source and ion beam texturing of medical silicon rubber surface

A 3 cm diameter ion beam ion source was specially designed for ion beam texturing of medical silicon rubber. The pocket ion source has some features:

- No discharge chamber, just an anode to avoid sputtering contamination.
- Plug-in mounting.
- Compact mechanical structure.
- Small grid holes and divergent ion optics, so large uniform working zone has been obtained. See the Photo 1 and Fig. 14.

The magnetic circuit configuration was special, (see Fig. 15). The front magnetic pole piece is smaller than the anode diameter so that the integrated magnetic field between virtual anode and virtual cathode increased. it



1---copper, untreated
2---TiB_2, as deposited
3---TiB_2, by IBED

Fig. 13 Weight get of oxidation for TiB_2 film at high temperature effectively confines the primary electrons and improves the discharge efficiency.

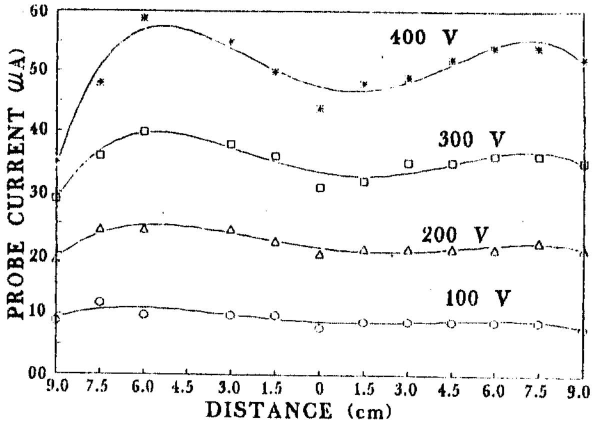


Fig. 14 The ion beam density distribution

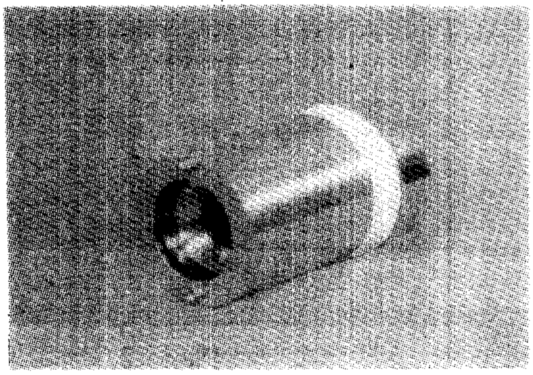


Photo 1

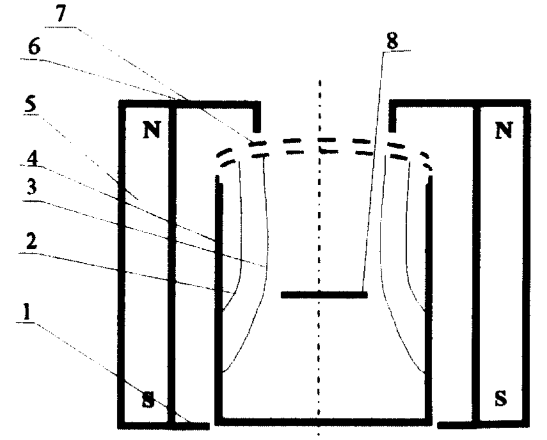
Table 4 The results of electrochemical test

Sample	i_{corr} (nA/cm^2)	i_p (nA/cm^2)	i_c (nA/cm^2)
Copper substrate	4.7×10^4	1.1×10^8	3.0×10^8
TiB_2 as-deposited	1.6×10^3	2.0×10^7	6.3×10^7
TiB_2 by IBED	5.0×10^2	7.6×10^6	1.1×10^7

i_{corr} corrosion current density; i_p passivation current; i_c critical current density

Artificial organ technology was composed of medicine, biology and material. The medical material play a important role. Silicon rubber has long been considered as good candidate for prostheses, because of its superior physical, mechanical, chemical and medical features. It is believed that the surface texturing of medical silicon rubber by ion beam sputtering, which can improve the biocompatibility of silicon rubber.

Surface texturing, will change the morphology of the surface, and will be benefit of nutrition feeding for neighbour cells. It also will stimulate the cells growing and absorbing to the surface. Ar^+ ions extracted from the 3 cm ion source were used for the surface texturing of silicon rubber. After a series of experiments, the optimum parameters for the ion beam texturing were chosen as follows: ion beam energy is near 1000 eV, current density is 800-1500 μA/cm^2, the dose of irradiation is 10^{24} - 10^{25} Ar^+/cm^2, and the incident angle of ions is 0°. Both nature texturing and mesh mask texturing were performed. the silicon rubber sample of nature texturing after cell culturing test of 20 hours is shown in Photo 2. As shown in the photo, the growing of the cells speeds up, the activity of the cells increases also and some of the cells starts to divide as well. The morphology shows that there are a lot of particles, pilars, pits and crests on the surface. The roughness scale is about 100-1000 Å. The morphology of the mask



1. Rear pole piece. 2. Virture anode. 3. Virture cathod. 4. Anode. 5. Permenet magnetes. (AlNiCo5) 6. Frout pole piece. 7. Grids. 8. Cathod.

Fig. 15 The magnetic structure of the pocket ion source

Photo 2

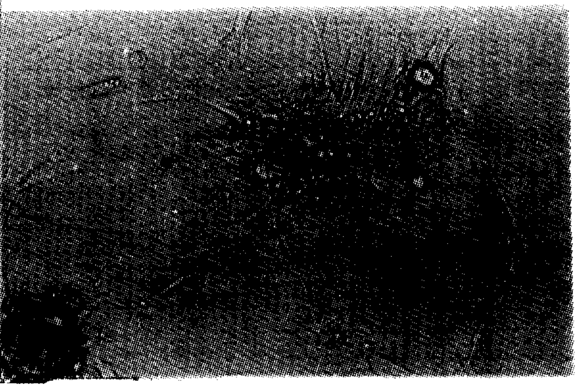


Photo 3

texturing of the silicon rubber was shown. That corresponding to the width of stainless steel mesh mask, the width of the pit is about 50 μm, the depth of the pit is about 10 μm and a lot of particles, pillars, pits and crests on there resemble the nature one. But some string were developed, corresponding with the anisotropy of the material. The photo of the cell's culture of the mask texturing after 43 hours was shown in Photo 3. As shown in the photo the compatibility of the material was greatly improved. Implantation experiment in animals will be done further.

5. Summary

The new type of broad beam ion source of EBE was successfully developed in CSSAR. A series of films were prepared such as metal compound and ceramic. The C-N films can has a variety of ratios of C/N because of EBE source feature. B_4C & TiB_2 films were also prepared by dual ion beam sputtering. Finally the medical silicon rubber was textured by specially designed pocket low energy ion source, and was shown better biocompatibility after cell's culture testing.

Reference:

1. F.Fujimoto and K.Dgata Jpn.J.Appl.phys, 32(1993) L420
2. M.Y.Chen, X.Lin, V.P.Dravid, J.Vac.Sci.Technol, All(3) 1993.521
3. A.Y.Liu & M.L.Cohen, Science, 24(1980) 244
4. Y.C.Feng etc."Prepare the films of High C and CN by using EBE Intense metal Ion source" "Chinese Journal of Materials Research" to be published.
5. Y.Z.Kuang, D.W.You. etc. "The performence of the study of TiB_2 by IBED" "Chinese Journal of Materials Research" to be published.
6. J.P.Riviere, P. H. Guesdon, J.Delafond, Nucl. Instrum. Methods B59/60 (1991) 273
7. Orrman-Rossiter K.G, Mitchell DRG, Donnelly SE etal Phil., Mag. Lett, 1990; 61 :311
8. Olsson M. Stridh B. Mater. Sci. and Eng. , 1988. A105/106 :453
9. D. W. You etc. "Chinese Journal of Dialysis and artificial organs" 1992. V3. No2 P59
10. O.Auceills: "Ion Bombardment Moditication of surface" pp 399-460
11. G. J. Picha "NASA-CR-159819"