Some Applications of Ion Beam Enhanced Deposition Techniques

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Ion beam enhanced deposition (IBED) is one of the newest techniques for film formation, and it has been widely applied in the field of surface modification of materials in last two decades. In our laboratory, a lot of work on the research and application of IBED techniques has been done in the past few years. In this paper, some different thin films, such as wear-resistant hard coatings, corrosion and oxidation protective coatings, biomaterial films, buffer layer for high temperature superconductor films, and oxygen sensitive films, synthesized by the IBED method, and some industrial applications of IBED coatings achieved in our laboratory were briefly reviewed.

I. INTRODUCTION

Ion beam enhanced deposition (IBED) is one of the newest techniques for film formation. It is a combination of ion implantation and vacuum deposition (PVD or CVD). Its originality is the energetic ion beam bombardment of a growing film. IBED technique has the advantages of improving adhesion to the substrate, easier control of composition and thickness of the film, and the possibility of synthesizing compound films and growing films at room temperature. At the interface between the substrate and the thin film there exists a mixed transition layer. The thickness of the transition layer is affected by the energy and the mass of ion used in the thin film synthesis process. In recent years, IBED method is developing very rapidly, and has attracted great attention for both scientific research and industrial applications. In this paper, some different thin films, such as wear-resistant hard coatings, corrosion and oxidation protective coatings, biomaterial films, buffer layer for high temperature superconductor films, and oxygen sensitive film, synthesized by the IBED method in our laboratory were briefly reviewed.

II. THIN FILM SYNTHESIS BY IBED

a. Wear-resistant hard coatings

The wear resistance of a material is dependent on the combination of its hardness and toughness. In recent years, many wear-resistant hard coatings, such as TiN, Ti(C,N,O), TiB_2, TiB_2/TiN, BN/Si_3N_4, β-C_3N_4, diamond-like carbon (DLC), etc., have been prepared by the IBED techniques in our laboratory.

Usually, TiN films preparation by IBED is based on the concurrent nitrogen ion bombardment on a growing titanium film. The maximum hardness of the N^+-IBED TiN film formed at room temperature is only about 1500kg/mm^2. In our laboratory, a new method, Xe^+-IBED, has been developed to fabricate TiN films. Superior TiN film was obtained by 40 keV Xe^+-IBED. The film is smooth, dense and composed of nanocrystallites. Microhardness of the TiN film formed by Xe^+ ion bombardment reached up to 2300kg/mm^2, which is much higher than that of N^+-IBED TiN film under the same preparing conditions and close to that of bulk TiN material (c.a. 2500kg/mm^2). This was attributed to the more perfect crystal structure of the Xe^+-IBED film because of the higher density of the energy deposition by a Xe^+ ion than that by a N^+ ion. The wear resistance of the specimen can be greatly improved by the Xe^+-IBED TiN coating. In Fig.1, the microhardness and wear rate of some 9Cr18 steel samples with or without N^+-IBED and Xe^+-IBED TiN coatings were compared.

b. Corrosion and high temperature oxidation protective coatings

The intermetallic compounds Ni_3Al and TiAl are good candidates for structure materials in space- or air-craft and automobile industries because they have high specific strength at elevated temperatures with a characteristic positive temperature dependence of strength over a certain temperature range. On the other hand, however, the oxidation resistance of these compounds at high temperatures in air or oxygen atmosphere has been reported to be very poor. And their corrosion resistance in aqueous solution is also not good. Some Si_3N_4 films have been synthesized by the IBED method for improving corrosion and high temperature oxidation resistance of these materials in our laboratory. Electrochemical experimental results showed that IBED Si_3N_4 film is effective for reducing the corrosion rate, improving the passivability and increasing the durability of these alloys in aqueous solution [1]. It was also found that the IBED Si_3N_4 coating on TiAl was very effective to protect this alloy from oxidation at 1300K for at least 600h [2], which is about 2 times longer than the best previous results, at 1300K for 200h, obtained by S.Taniguchi [3] who prepared an Al_2O_3 scale on TiAl by a more complicated procedure.

c. Biomaterial films

Low temperature isotropic pyrolytic carbon (LTI-carbon) and titanium alloys are usually used for fabrication of artificial heart valves because of their combination of blood compatibility and high resistance to degradation, wear and fatigue. The main problem of the clinically used mechanical heart valves made of LTI-carbon is their thrombogenicity. Life-time anticoagulant therapy is indispensable to minimize the risk of thromboembolic complications. Recently, some IBED biocompatible titania films were used for improving the blood compatibility of artificial heart valves in our laboratory [4,5]. The *in vitro* measurements showed that blood clotting time of IBED TiO_2 film is longer than that of LTI-carbon and other reference materials. The adherent platelet and aggregation of platelet on the surface of IBED TiO_2 are much lower than that on the surface of LTI-carbon and titanium alloy. *In vivo* investigation, by implanting small LTI-carbon disks with and without IBED titania coating into the aorta of a dog for two weeks, showed that the amount of thrombus adhered on TiO_2 coated LTI-carbon is only about 1/8 of that on the pure LTI-carbon.

d. Buffer layer for high Tc superconductor films

It is well known that the $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconducting thin films on single crystal substrates have critical current density (Jc) values of over $10^6 A/cm^2$. This high-Jc property is very attractive not only for small-size electronic devices, but also for large-scale applications. Practical large-area applications would be achieved if high-Jc YBCO thin films could be grown on some practical flexible polycrystalline substrates, such as, silver, stainless steel, or nickel-based superalloys. However, the superconducting properties of the YBCO films deposited directly on these substrates have proved to be very poor. It has been demonstrated that a well-textured yttrium-stabilized zirconia (YSZ) intermediate layer can yield YBCO films of higher quality. In our laboratory, (001)-oriented and in-plane aligned YSZ thin films have been successfully fabricated on polycrystalline Ni-Cr metallic alloy substrates using low energy IBED. X-ray pole figure and Φ-scan spectrum measurement results, as shown in Fig.2, demonstrated that our IBED YSZ films were highly textured. And YBCO thin films with Tc=88K and Jc=10^4 A/cm^2 (0T, 77K) have been synthesized on our IBED YSZ buffer layers using MOCVD method at 800°C.

e. Oxygen sensitive film

In recent years, there has been an increasing demand for various kinds of sensors, which are very important in automated systems. In particular, gas sensors have seen a great amount of scientific and technological activity and among these, oxygen sensors played a major role, esp. for the industrial and automobile exhaust pollution control. Since the discovery that the transport properties of oxide semiconductors may be influenced by the adsorption of gases on their surface, many semiconducting oxide materials have been investigated for the use of gas sensors. Among the oxygen sensors, both ZrO_2 and TiO_2 have been under the most intensive investigation. Recently, however, it has been reported that Nb_2O_5, esp. TiO_2-doped Nb_2O_5, can exhibit even better oxygen sensitive properties. In our laboratory, we have attempted to prepare the TiO_2-doped Nb_2O_5 films by the IBED method. It has been found that the conductivity of IBED Nb_2O_5 films are significantly dependent on the oxygen partial pressure, as shown in Fig.3. The optimum amount of the titania dopant was about 5mol%. It was also found that both the oxygen sensitivity and responding time can be evidently improved if a little amount of Pt (c.a. 0.3mol%) was added to the TiO_2-doped Nb_2O_5 films.

III. INDUSTRIAL APPLICATIONS

Our Xe^+-IBED TiN film has been successfully applied for protecting the scoring dies made of GCr15 steel which is used to make souvenir coins from gold and silver alloys. The life of the dies coated with Xe^+-IBED TiN films was increased 3-10 times in comparison with traditional Cr coated ones. The surface damage of the dies and the material pick-up from working pieces were greatly reduced by Xe^+-IBED TiN coatings.

The light tube forming dies, see Fig.4, work with molten glass and air surrounding. Because of the erosion and oxidation at high temperature, its service life is short as only 1-3 months. We try to improve its surface properties by using IBED Pt coatings. Light tube forming dies with a diameter of 230mm were coated with Pt film in a broad beam IBED system. These IBED coated dies have been succesfully used in industrial production lines. The application results showed that the dies coated with IBED Pt film could last more than 18 months.

The traditional technology to make backelectrode of silicon devices is to coat Ni film on the backside of wafer by plating with subsequent high-temperature annealing. It is easy to cause contamination which will consequently deteriorate the performance of device and lower the production efficiency. IBED Ag/Ni-Cr bilayer film was formed at room temperature without subsequent annealing in our laboratory. The IBED Ag/Ni-Cr double layer on silicon is of the advantages of low oxygen contamination, low internal stress, and good adhesion to the wafer. It has good conductance, durability, better performance in subsequent joining with chip holder. IBED Ag/Ni-Cr bilayer film can dramatically reduce the dark current and the voltage drop in positive direction of the diode. It has been successfully used in the fabrication of photosensitive diodes. 300,000 backelectrodes of photodiodes used in cameras have been fabricated by using this technique. The pass rate of product has been increased from 20% to 65%.

Shadow grid, see Fig.5, is a key part of traveling wave tube used in precision control of guided-missile launch. Electron emission from the grid, which may seriously limit the service life and even destroy the working condition of the traveling wave tube, must be suppressed in order to increase the service life of grid controlled guns for space applications. For this reason, amorphous carbon film was prepared in our laboratory by IBED. After this treating procedure, the electron emission from the grid was suppressed satisfactorily. The service life of one traveling wave tube with grid treated by IBED carbon films was increased from 70 hours to more than 1000 hours. The processing of IBED carbon film for suppressing the electron emission from grid of traveling wave tube has already been used in precision control system for guided missile launch. The system has been successfully tested.

IV. SUMMARY

IBED is a very promosing thin film deposition method because of its many advantages, such as excellent adhesion property of films to substrates, room temperature processing, ease of control over the composition and thickness of films, and so on, over the conventional techniques, It has been widely applied in the field of surface modification of materials in the last decade. In our laboratory, many kinds of thin films, such as wear-resistant hard coatings, corrosion and oxidation protective coatings, biomaterial films, buffer layer for high temperature superconductor films, and oxygen sensitive film, have been synthesized by IBED, and several industrial applications of the IBED films have been conducted.

References:

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Figure Captions:

Fig.1 Comparison of microhardness (a) and wear rate of 9Cr18 steel samples with or without N^+-IBED and Xe^+-IBED TiN coatings.

Fig.2 (111) X-ray pole figure (a) and (111) Φ-scan spectrum (b) of the highly-textured YSZ films synthesized by low energy IBED on a polycrystalline Ni-Cr substrate.

Fig.3 The dependence of electrical conductivity of an IBED deposited TiO_2-doped Nb_2O_5 film on oxygen partial pressure.

Fig.4 Photograph of a glass tube forming die.

Fig.5 Photograph of a molybdenum-based shadow grid used in a traveling wave tube.

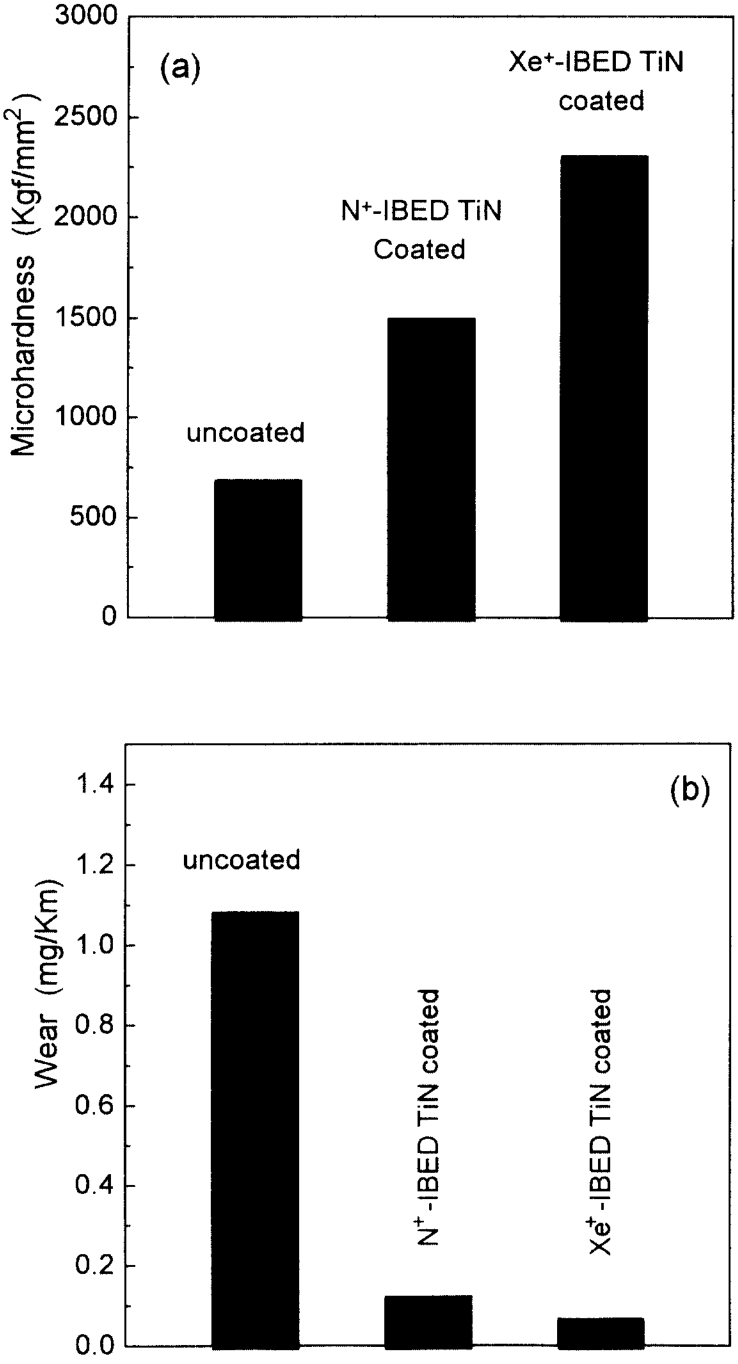
3000
2500
2000
1500
1000
500
0
Microhardness (Kgf/mm2)
(a)
Xe+-IBED TiN
coated
N+-IBED TiN
Coated
uncoated
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Wear (mg/Km)
(b)
uncoated
N+-IBED TiN coated
Xe+-IBED TiN coated

Fig.1

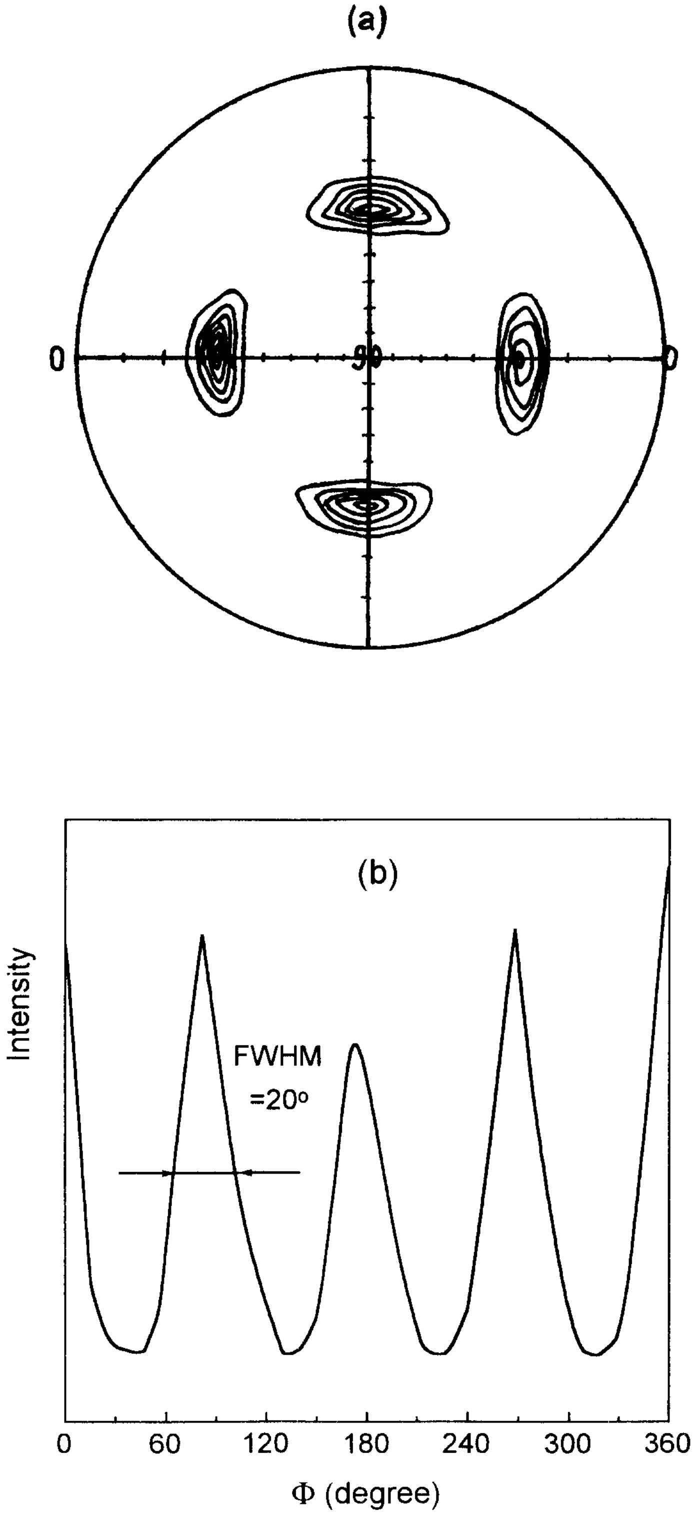

Fig.2

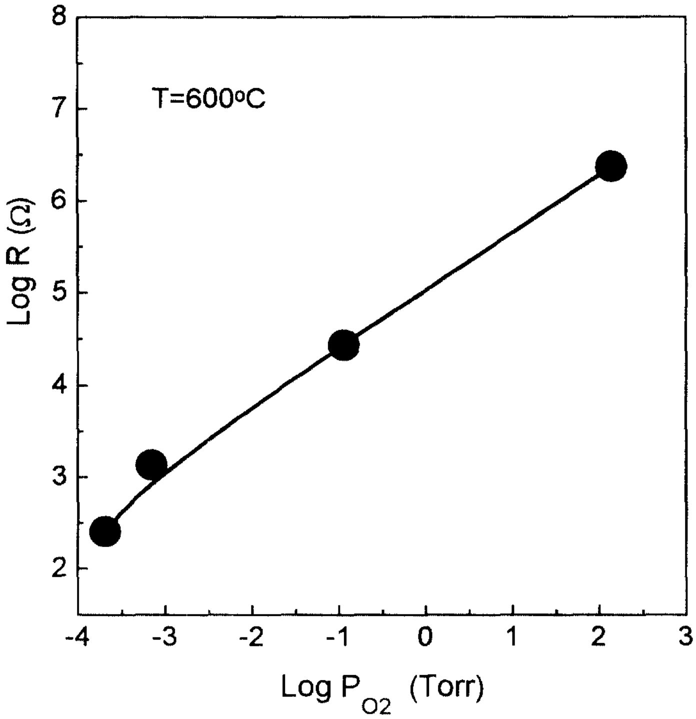

Fig.3

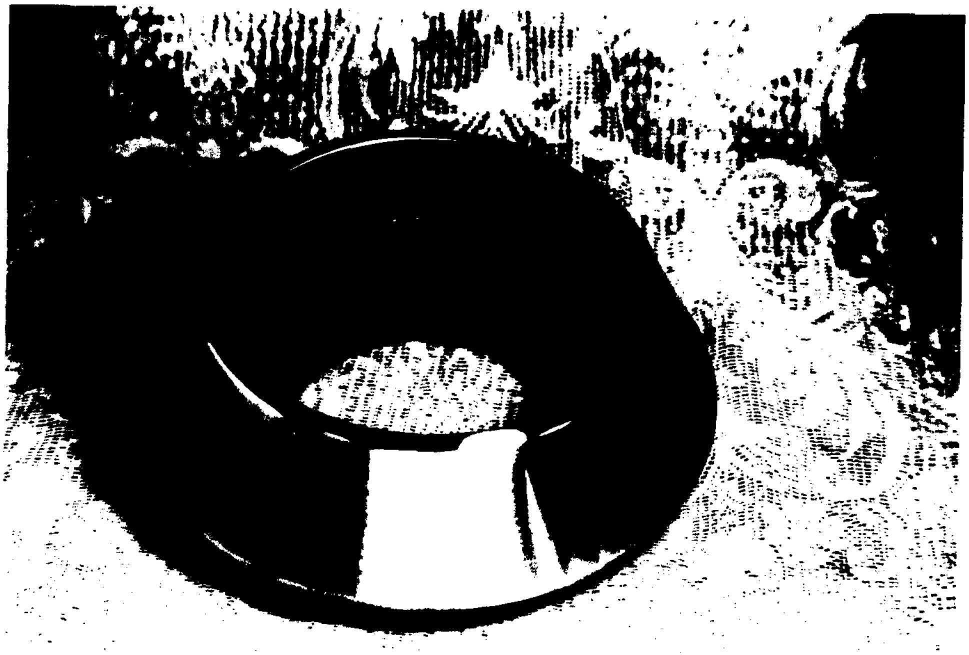

Fig.4

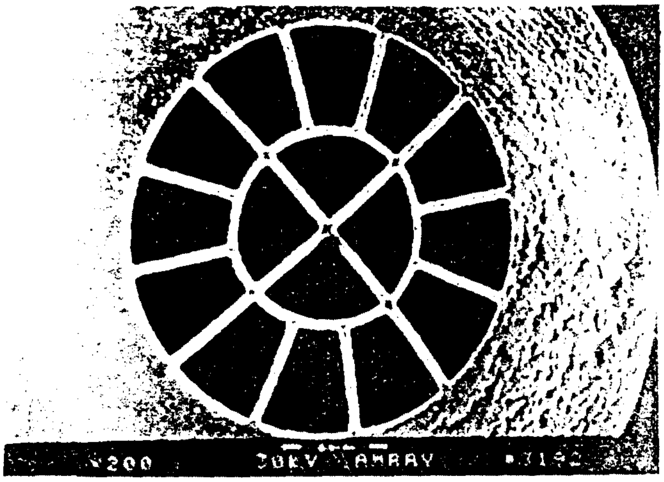

Fig.5