DOD Sample Phase I Proposal

SUPERADHERENT HARD COATINGS BY ION BEAM ENHANCED DEPOSITION

(FIGURES AND TABLES ARE UNAVAILABLE ON THIS WEBSITE.)

1. COVER SHEET (see attached)

2. IDENTIFICATION & SIGNIFICANCE OF THE OPPORTUNITY

The objective of this proposal is to demonstrate the feasibility of producing superadherent protective coatings at low processing temperatures using energetic ion beams in conjunction with conventional deposition techniques. This process, coined Ion Beam Enhanced Deposition (IBED), is depicted in Figure 1 and promises a new generation of exotic coatings with superior adhesion, near theoretical densities, very high hardness, and, at the same time, capable of being deposited at low temperature. T he effect of the ion beam (e.g., N) is to initially "intermix" the deposited atoms (e.g., Ti) with the substrate for superior adhesion as well as to provide energy to the grown layer for effectively "high temperature" processing at low substrate temperatu res. Highly adherent coatings of "TiN" with low friction (Figure 2) have already been demonstrated by Kant et al(l) at Naval Research Laboratory by N-bombardment of deposited Ti. This proposal is to extend the range of protective coatings produced by IBED to include HfN, AI203 and to characterize such films for mechanical and chemical properties as well as microstructural analyses. Evaluation of mechanical properties will include adhesion tests and wear tests. Initially laboratory pin-on-disc tests will be used for screening purposes with in-situ component tests planned for later. Microstructural analyses deemed necessary include 1) sputter Auger electron spectroscopy for compositional analysis, 2) sputter ESCA for composition and chemical bonding information, 3) glancing x-ray analysis for lattice structure, 4) ion backscattering for nondestructive composition vs. depth information, and 5) SEM and TEM for grain structure and lattice microstructure information.

Hard, extremely adherent hard coatings synthesized by the ion beam enhanced deposition technique will be of immediate use to SDI. Primary candidates for these (ultra) thin coatings would be for i) precision aerospace bearings and ii) precision micropositioning platforms where a very thin (i.e., 0.1-0.5 micrometer) antifriction antiwear coating could be used without remachining or respecifying dimensions of critical components. Besides being an end-of-line process not requiring production changes, IBED coatings promise a convenient retrofit to existing tribological problems involving precision mechanisms.

2.1 BACKGROUND

There is an acute need for development of high quality, low temperature thin film deposition techniques that can achieve thin film qualities found in high temperature processes. Present low temperature thin film deposition techniques sometimes result in inferior microstructural features within the film such as columnar growth and not the preferred equiaxed grain structure ordinarily found in high temperature processes. Conventional methods of laying down films result in a greater or lesser degree of departure from bulk material properties (density, grain structure, etc.) depending, among other things, on the energy of the atoms as they arrive at and arrange themselves on the substrate surface.

Table I shows the typical energy ranges associated with various physical vapor deposition and ion beam based techniques.

The three PVD processes in the table above, namely evaporation, sputtering, and ion plating are discussed here briefly since eventually any coating produced by a new method, such as IBED, will have to be compared with those in common usage. (2)

Evaporation can be done directly in a high vacuum to provide an extreme range of deposition rates with extreme versatility in the coating composition obtainable.

Sputter deposition, in general, has lower deposition rates than either evaporation or ion plating, however, high throughput production units utilizing magnetron type sputtering are being used industrially. In general, the adherence of films deposited by sputtering are better than by simple evaporation because of their higher energy. The wide variety of geometries employed for various applications by sputter deposition has been recently reviewed by Thornton. (3)

Ion plating is a process largely developed and recently reviewed by Mattox (4) in which the substrate and/or the deposited film is bombarded by energetic (10-100eV) particles. This particle bombardment can significantly affect film characteristics such as: adhesion, morphology, stress and surface coverage. The process is typically carried out in an inert gas plasma discharge with a potential applied to the substrate, although many other variations of the technique have been developed including reactive ion plating. One early benefit recognized for this process is that the atoms in the plasma often undergo considerable scattering and are able therefore to reach surfaces not accessible to line-of-sight processes such as high vacuum evaporation as well as an enhancement of diffusion and chemical reactions without the need for high bulk temperatures. It is interesting to note that the origin of these benefits was at first poorly understood and somewhat controversial, although in intervening years, the importance of the kinetic energy of the bombarding particles and the degree of ionization has been recognized.

2.1.1 ION BEAM ENHANCED DEPOSITION - EFFECTS OF ION BEAMS ON FILM GROWTH

The lack of control as well as understanding of the role particle energy and ionization played in these various PVD processes just mentioned was motivation for at least some workers to conduct deposition experiments where one has independent control of the ion energy and ion type as well as the rate of bombardment(5-11). Several aspects of film growth that have been influenced by ion bombardment during deposition are listed in Table 2.

TABLE 2. FILM GROWTH CHARACTERISTICS AFFECTED BY ION BOMBARDMENT DURING DEPOSITION

1. Superior Adhesion
2. More Uniform Nucleation and Growth Kinetics
3. Lowered Tensile Internal Stresses
4. Improved Morphology
5. Controllable Composition

Greene and Barnett (12) have recently reviewed the area of ion surface interactions during crystal growth from the vapor phase. Most of the work done in this area thus far has been associated with semiconductors using low energy ions (1 keV), to avoid lattice damage. One common goal is to promote lower temperature epitaxial growth of semiconductor films and to incorporate desired impurities for doping purposes. Optical coatings, as mentioned previously, is another current application area for ion beam assisted deposition of this films. Here one objective is to increase the packing density (13) and thereby make the films more stable since they pick up less water from the atmosphere. The following examples of ion bombardment effects on film growth are directed towards non-semiconductor applications, which is the thrust of the present proposal.

Pranevicius (6) demonstrated the effect of ion bombardment on nucleation during Al deposition, done both with and without simultaneous 5 keV Ar+ bombardment. Electron microscopy measurements showed that ion bombardment increased the density of nucleation sites by 2X-4X and that the size of the Al island structures were 3X-15X less in the case of bombarded films.

Adhesion measurements, taken on the AI films discussed above, showed that improved adhesion results from both surface cleaning and interfacial mixing. Others have seen significant improvements in film adhesion and stress using concurrent ion bombardment. In one such study, Franks et al., (14) used 5 keV Ar+ ions before and during the first stages of film evaporation of Au on a number of substrates including Si, Ge and Cr, with improvements of adhesion seen in all cases. With regard to stress, Hoffman and Gaerttner (I5) found that simultaneous irradiation of evaporated Cr with 11.5 keV Xe+ ions caused a sharp transition from tensile to compressive stress for relative concentrations of Xe exceeding 0.3 at %. At about 1 at % concentration the stress is maximum, and on the order of the yield strength. This stress reversal was accompanied by an increase in the optical reflectance of the this Cr film.

Ion bombardment during deposition has also been shown to produce quite drastic changes in structure. For example, Bunshah (16) has reported that ion bombardment changes a normally columnar morphology of metals into a more dense, isotropic structure.

Perhaps the most striking change in structure has been the deposition of carbon films with “diamond-like” properties observed either after ion bombardment of carbon films or the deposition of energetic ionized hydrocarbons. It was first seen in 1971 by Aisenberg and Chabot (I7) and later by many other groups. The carbonaceous films produced by these methods (termed i-C denoting the role of ions) appear transparent with a high refractive index, quasi- amorphous, very hard, and have high electrical resistivity. Weissmantel et al. (9) have reviewed this area of producing hard coatings by ion bean techniques, including the production of i-BNx in attempts to produce cubic-BN, another extremely hard material second only to diamond in hardness. Weissmant el et al. (9,18) evaporated pure boron in a residual atmosphere of nitrogen, and subsequently ionized and accelerated the resultant species at 0.5-3.0 keV onto various substrates. IR absorption spectra confirmed that B-N bonding states predominate, while transmission electron microscopy and selected area electron diffraction patterns indicate a quasi-amorphous structure; however, high energy deposits contained small crystallites of about 100 A diameter which had a lattice constant corresponding to cubic BN.

Shanfield and Wolfson (19) present hardness, x-ray, and Auger analysis data supporting the production of dispersed cubic BN by using an ion beam extracted from a borazine (B(3)N(3)H(6)) plasma. Satou and Fijimoto (20) have also reported similar results by using simultaneous boron evaporation and (40 keV N2+) nitrogen bombardment. Using electron diffraction, they have identified microcrystallites of CBN after using specific boron to nitrogen ion fluxes.

Figure 3 shows the hardness of these i-C and i-BN coatings. Although very hard and adherent, the i-C coatings have very high compressive stress which gives rise to cracking and lift-off. Weissmantel (21) suggests using laser glazing or use of graded metal/i-C composite coatings to alleviate this. Such i-C composites, produced by RF discharge, are being tested for both tribological applications (wear resistant coating on video recorder heads) and corrosion protection (electrochemical electrodes).

Studies of the i-BNx system are by comparison in a much earlier stage and appear particularly amenable to the use of ion beams. Coatings of i-BNx have not yet shown a maximum in hardness when using increasing bias voltages in an ion plating system (22) . Hence, energetic ion beams offer a promising way to further explore and develop i-BNx and composite i-BNx coatings of optimal composition and structure.

The roles of ions in thin film growth has been recently reviewed by Takagi. (23) He concludes that the presence of ions produces a remarkable effect on chemical activity, particularly on the critical parameters of the condensation process.

2.1.2 CHOICE OF COATING SYSTEMS

The choice of what protective coating to be used for a particular application depends on a number of factors including in part: i) relative coating/substrate thermal expansion, ii) chemical stability of coating, iii) coating hardness, iv) required deposition temperature. The following systems have been chosen to cover a wide variety of anti-wear applications in actual practice.

One principal reason for initially studying TiN is that it serves as a benchmark for any new process, since it is being deposited by a variety of other PVD (physical vapor) and CVD (chemical vapor deposition) techniques for a variety of applications. Secondly, even though such TiN coatings are improving in adherence at lower processing temperatures, there still remain many critical applications where current temperature or adherence criteria are not satisfied.

HfN has a significantly higher hot hardness (i.e. 800-900 kgf mm (-2)at 1000 degrees C) than does TiN (200 kgf mm (-2)) and is of interest for high temperature cutting application. Its preparation should be a natural succession to TiN because of similar chemical reactivities.

A principal reason for studying Al(2)0(3) is because of the tremendous difference in its theoretical and actual performance. Kramer (24) points out that Al(2)O(3) coatings falls short of achieving theoretically expected lifetimes, as a high temperature curring tool coating, by three orders of magnitude, whereas other coating lifetimes (TiN, TiC) are in reasonable agreement with theory. Another reason for studying AI(2)0(3) involves its relatively poor adherence to substrates, like many other oxides. The adherence of ceramic coating; are definitely expected to be improved by ion beams, (25) and any improvement in microstructure is expected to help its deficiency in lifetime. (24) AI(2)0(3) has also been prepared by the ARE technique, however, high substrate temperatures (1000 degrees C) are required(2) to avoid growth defects that adversely effect microhardness. It is possible, because of higher surface diffusion during bombardment, that significantly lower temperatures will be required to produce dense AI (2)0(3) coatings by the IBED technique.

3. PHASE I TECHNICAL OBJECTIVES

The overall objective of the proposal is to develop the energetically enhanced deposition process and to investigate the quality of the coatings synthesized by this process. The specific objectives of the program can be enumerated as follows:

1. Modify and adapt a commercial electron beam evaporation source to fit inside Spire's metal ion implanter.
2. Operate the simultaneous thin film deposition - ion implantation system and obtain the optimum process parameters for the deposition of hard coatings.
3. Characterize the morphology and microstructure of selected coatings as a function of process parameters.
4. Investigate the mechanical properties of the coatings as a function of process parameters. These include hardness and adhesion properties as well as friction and wear behavior.
5. Compare their tribological properties and their microstructures to coatings produced by other (higher temperature) processes like CVD and PVD.

4. PHASE I - WORK PLAN

Phase I research will be restricted to showing feasibility of producing TiN and HfN. Investigation of Al(2)0(3) will be undertaken in Phase II.

The Phase I work plan will include the following tasks for achieving the stated objectives:

4.1 TASK I - ELECTRON BEAM EVAPORATION SOURCE INSTALLATION AND TEST

In this task, a commercial electron beam evaporation source will be modified as necessary to allow for incorporating it into the vacuum work station of Spire's Metal Ion Implanter.

After the new source is reassembled inside the work station, the components of the system will be tested and operated simultaneously. This task is expected to take one month after receipt of the evaporation source.

4.2 TASK 11 - TIN AND HFN PREPARATION

Initially TiN will be studied, but since TiN and HfN are chemically similar, it is planned that the HfN work will start two months after the TiN commences. This anticipated tasks for HfN are the same as for TiN, hence the outline below pertains to both.

First, the optimal N ion bombardment conditions and Ti (Hf) deposition parameters to achieve stoichiometric TiN (HfN) will be determined. This will include taking into account the following:

a. Sputtering (ion energy, target geometry, substrate composition)
b. Substrate reactivity (substrate temperature, incorporation of background vacuum constituents such as N2 and hydrocarbon contaminants)
c. Film growth processes (grain size, nucleation, internal stresses)

The following measurements will be made in the efforts to produce TiN (HfN):

> Ti (Hf) will be evaporated at various rates (A/sec) with respect to the arrival rate of nitrogen ions.
> It will be necessary to increase the Ti (Hf) deposition rate to compensate for the sputtered particles.
> The sputtering rate will also depend on geometry (approximately as 1/cos ( ) where (is the angle of incidence with respect to the normal.

The variables to be studied for TiN include:

1. Effect of substrate temperature on grain size and on microhardness
2. Effect of geometry on grain size (if any)
3. Effect of ion energy on grain size, adhesion, and composition

X-ray diffraction and TEM will be used to study the micro-structure of the coatings produced. Sputter ESCA profiling will also be available on a service basis. Coatings to be examined by Rutherford backscattering for stoichiometry will be deposited on pyrolitic graphite to allow low background in the spectra.

The mechanical properties (density, morphology, hardness, adhesion, wear resistance, scratch resistance) of the thin films developed in Task 11 will be measured at the Tribology Laboratory of Spire's Surface Modification Center. The optimum process parameters will be identified. A flow chart like the one shown in Figure 4 will be used for this purpose.

4.3 REPORTING

In addition to day-to-day informal contacts with the program monitor, monthly technical progress reports will be submitted with a complete Technical Progress Report being submitted at the end of each program year, as requested.

5. RELATED WORK

The Principal Investigator has been involved in pursuing ion beam enhanced deposition for the past two years. At his previous place of employment he was responsible for the conceptual design of a commercial IBED machine and ran a prototype machine for R&D activities on hard coatings (TiN) as well as for commercial service. The PI is in cose contact with other researchers exploring the IBED technique for hard coatings for example (21,22).

6. RELATIONSHIP WITH FUTURE RESEARCH OR RESEARCH AND DEVELOPMENT

Anticipated improvements in coating adhesion and morphology will be of immediate use where conventional (PVD) coating techniques currently have limitations at lower temperatures. The proposed Phase I work will determine the fundamental IBED parameters to produce adherent, low stress hard coatings in production line lots during the Phase II effort.

7. Commercialization Strategy

The use of hard protective coatings produced by both PVD and CVD processes is steadily growing in the cutting tool industry as well as for decorative purposes. The trend is towards lower temperature PVD processing generally with an accompanying loss of adherence or desirable structure of the coating. Successful application of IBED processing will eliminate both of these concerns and open up new applications especially for dimensional and temperature sensitive applications such as for precision aerospace bearings.

8. KEY PERSONNEL

JAMES K. HIRVONEN
Senior Scientist

EDUCATION:

Ph.D., Physics, Rutgers University, N.J. 1971.
M.S., Physics, Rutgers University, N.J. 1968.
B.S., Physics, Syracuse University, 1964.

CURRENT POSITION AND RESEARCH:

Dr. James K. Hirvonen is a Senior Scientist within the Materials Modification division of Spire Corporation. He is responsible for overseeing government R&D contract relating to aerospace applications of ion beam modification of materials and for monitoring process development and control for commercial implantation services. He has more than 18 years of experience involving ion implantation in materials.

RELEVANT EXPERIENCE:

Prior to joining Spire Corporation, J.K. Hirvonen was a founder, V.P. and Director of Research for Zymet, a start-up company dedicated to the production of ion implantation equipment for metals. There he was responsible for process control in the service laboratory and was responsible for the conceptual design of the companies first ion beam enhanced deposition machine. From 1971-1982, Dr. Hirvonen was a technical staff member at the Naval Research Laboratory where he headed a seven member technical group (1976-1982) conducting basic and applied R&D on the application of ion implantation for beneficially modifying chemical and mechanical surface sensitive properties of materials.

He has (co)written over fifty papers in this area and has edited two books on ion implantation. He organized topical symposia and taught several short courses on this topic as well as speaking at numerous national and international conferences.

9. FACILITIES/EQUIPMENT

To support its position as a leader in surface modification technologies, Spire maintains extensive laboratory facilities dedicated to the production and characterization of novel thin films and thin film techniques.

9.1 ION BEAM ENHANCED DEPOSITION FACILITY

Drawing upon its extensive background in surface modification technology, Spire has designed a powerful, highly versatile IBED system. The facility consists of a modified EATON NV 10-160 high current (10mA) implanter mated to a Spire designed high volume end station, along with a customized ion beam control system resulting in a highly versatile unit capable of forming nearly any simple compound. The customized end station houses an Airco 4-pocket electron beam turret source (8kW capacity) and an Inficon deposition rate controller. Evaporation deposition rates range from 3-300 A/sec. The end station with its 27 cubic ft volume can accommodate virtually any part less than 3 feet long, yet can still attain a background pressure of 10-7 torr. Ion beams of up to 10 mA intensity from 10-16OKeV energy can be generated for a variety of elements and provide versatility in the choice of IBED parameters. Handling of all parts to be coated is done in a Class 10,000 clean area, ensuring cleanliness and quality control (see Figure 6). Temperature control and feedback are implemented via a Williamson 8200 dual wavelength IR pyrometer.

9.2 THIN FILM DEPOSITION FACILITIES

In addition to the IBED facility, Spire operates a variety of thin film deposition equipment. Boron nitride has previously been deposited via Spire's MRC Model 8620J RF Sputter facility. In addition, Spire has designed plasma and ion beam deposition systems for in house and service work. For simple evaporated films, Spire has three Sloan electron beam evaporators and one Edwards thermal evaporator. Spire also operates an ion beam sputter deposition facility designed around the needs of its surface modification service area. For additional support, Spire presently operates 6 ion implanters dedicated to a variety of applications primarily in the metals implantation areas. Finally Spire offers services and equipment sales for application of coating via chemical vapor deposition (CVD, MOCVD, LPCVD).

9.3 MATERIALS CHARACTERIZATION

Spire is well equipped to handle material characterization by photometry, ellipsometry and optical analysis, with elemental and crystallographic analysis being provided by local services and universities.

The Spire tribology laboratory is equipped to characterize the mechanical properties of the hard coatings. For hardness measurements, either Tukon microhardness tester or Mhos scratch tests can be used. To measure wear resistance and mechanical integrity, several pin-on-disc testers are available. A Dectak surface profile plotter is available to analyze resultant wear and decohesion areas.

The services of Cornell University will be used to provide Rutherford Backscattering analysis and the services of SUNY/at Stony Brook will be used to provide SEM, TEM and x-ray measurements.

10. CONSULTANTS

No consultants are presently foreseen for the Phase I program. If a need should arise, Spire has several well known consultants available from the facilities of M.I.T., Harvard, Boston University and other local universities.

11. PRIOR, CURRENT OR PENDING SUPPORT

Spire has no prior, current or pending support for a similar proposal.

12. COST PROPOSAL

See attached.

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