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13. ABSTRACT (Maximum 200 words) The goal of this project is to investigate the Plasma Source Ion Implantation (PSII) process as an environmentally clean surface modification technique for defense related applications. Through this grant, considerable progress has been made in the understanding of the science and technology of the PSII process. A co-axial geometry technique has been developed and patented to deposit coatings on the inside surface of hollow cylinders and may have applications in gun barrels and recoil mechanisms. A perforated, staggered cathode configuration has been devised to deposit complex nitride coatings with properties superior to mono-nitrides. Erosion-resistant chrome-oxide coatings have been deposited and an optical emission spectroscopy diagnostic has been successfully used as a diagnostic for plasma chemistry. Enhancement of adhesion of titanium-nitride coatings to steel has been achieved by the use of titanium interlayers. Research has been conducted on wear-resistant diamond-like carbon coatings in collaboration with Army Research Lab. Computer models have been developed to predict plasma-workpiece interaction for different target shapes. The grant has provided the opportunity to establish interactions between the University of Wisconsin and personnel at Rock Island Arsenal, Corpus Christi Army Depot, Army Research Lab, and the Watervliet Arsenal.				
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SUMMARY OF SIGNIFICANT ACCOMPLISHMENTS

Co-axial System to Deposit Wear-Resistant Coatings on Inside Surfaces of Hollow Cylinders Developed and Patented

A process has been developed to deposit adherent, wear resistant coatings on the inside surfaces of hollow cylinders in the Plasma Source Ion Implantation (PSII) process system. The process utilizes a rod electrode which is placed co-axially in the cylinder whose inner surface is to be coated. For the deposition of compound coatings, a reactive gas is introduced. For example, if a titanium-nitride coating is to be deposited, a titanium rod would be used co-axially and nitrogen gas would be introduced. When the electrode rod is biased to a high negative voltage, a uniform radial electric field normal to the inner surface of the cylinder is generated. For the deposition of DLC, a methane plasma is used. Using this technique, titanium-nitride and diamond-like carbon (DLC) coatings were deposited on the inside surface of a steel cylinder 3.5" in diameter and 18" in length. The idea was envisaged during the collaboration with Rock Island Arsenal, IL. The process has profound implications for coating on the insides of gun barrels and recoil mechanisms. Moreover, many of these applications presently use wet-bath electroplating and the environmental cleanliness of plasma techniques is a significant advantage.

References:

"Development of an Energetic Ion Assisted Mixing and Deposition Process for TiNx and Diamond-like Carbon Films using a Co-axial Geometry in Plasma Source Ion Implantation", S.M. Malik, R.P. Fetherston, and J.R. Conrad, J. Vac. Sci. Technol., A15(6), 1997, pp. 2875-2879. (attached)

"Method for Plasma Source Ion Implantation & Deposition for Cylindrical Surfaces", R.P. Fetherston, S.M. Malik, and J.R. Conrad, U.S. Patent No. 5,693,376, December 1997.

Deposition of Hard Chrome-Oxide Coatings for Abrasion Resistance

Chromium-oxide has a high hardness (~29Gpa) and provides very high erosion and abrasion resistance. Chrome-oxide coatings have been successfully synthesized using a chrome sputter cathode and an oxygen plasma. Adjustment of oxygen gas flow is crucial for achieving the right stoichiometry (Cr_2O_3) as chromium forms a number of stoichiometric oxides. Another issue that was investigated was cathode poisoning. This refers to the formation of a film of chrome-oxide on the sputter cathode rendering it unsuitable for further sputtering. Cathode poisoning is a ubiquitous problem in reactive sputter deposition systems. Chrome-oxide coatings have wide ranging applicability in defense applications especially in areas where sand erosion is a problem.

Reference: "Process Development for Deposition of Chromium-Oxide Using Plasma Source Ion Implantation", S.M. Malik, presented at the 50th Gaseous Electronics Conf., Madison, Oct. 1997.

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Development of Optical Emission Spectroscopy Diagnostic for Monitoring Plasma Chemistry

In order to tailor the right coating chemistry to achieve the desired properties, it is important to have a knowledge of various ion species in the plasma. Such diagnostics is particularly difficult due to the high vacuum and voltages used in the PSII process. Optical emission spectroscopy was employed effectively to determine the concentration of various ion species in the plasma for the deposition of chrome-oxide coatings. The technique is applicable for the diagnostics of plasma chemistry in PSII for the synthesis of a wide range of coatings.

Deposition of Complex Nitride Coatings using Perforated Cathode Geometry

Complex nitride coatings generally have properties superior to mono-nitride coatings. Adjustment of ratios of the metals that comprise the complex nitride is difficult due to different sputtering rates of the metals. To overcome this problem, a perforated cathode geometry has been developed. Here, one of the metal sheets is perforated, providing the ability to adjust the relative areas of the of the two metals. In this way the desired ratios of the two metals can be achieved. Using this procedure, Ti-Al-N coatings with various Ti:Al ratios were successfully deposited.

Reference: Design of a Sputter Cathode for Binary Alloy Deposition in Plasma Source Ion Implantation", S.M. Malik, R. Breun, P. Fetherston, K. Sridharan, and J.R. Conrad, 49th Gaseous Electronics Conference, Chicago, IL.
(attached)

Adhesion of Titanium-Nitride PSII-IBED Films

The adhesion of PSII-coated TiN films to the steel substrates has been enhanced by the use of a titanium interlayer. The thickness of titanium-nitride films were in the range of 2800Å to 3500Å, while the thickness of the titanium interlayers studied were in the range of 150Å to 2400Å. Hardness of the titanium-nitride films as measured with a low load microhardness tester was about 2700 (Hk). Adhesion of the film to the substrate as a function of titanium interlayer thickness was measured using an in-house scratch tester. Optimal adhesion occurred when the interlayer thickness was 750Å. Auger mapping of the scratched surface showed that the delamination always occurred at the steel-titanium interface. TAMIX computer simulations were used to simulate the deposition process in order to determine deposition parameters which could most likely improve the stitching of the titanium interlayer to steel.

Reference: Ph.D. Thesis, James Firmiss, University of Wisconsin-Madison, anticipated completion 1999.

Determination of Stresses in PSII-IBED Coatings

As the coating thickness increases, the build-up of stresses can lead to cracking. It is therefore important to quantify the level of stress in the films. Using the equipment in the Physical Sciences Laboratory in Stoughton, WI, the film stresses were determined by a technique that utilizes change in curvature of a silicon wafer after film deposition. Here, a laser is employed to amplify the curvature of the wafer over a distance of 20 feet. The measurements showed the films to be under compressive stresses with magnitude in the range of 250 to 400 ksi.

Reference: Ph.D. Thesis, James Firmiss, University of Wisconsin-Madison, anticipated completion 1999.

Investigation of High Dose Rate Effects in Plasma Source Ion Implantation

PSII provides the unique capability to operate in the high current, low energy regime. In this regime unique amorphous structures can be synthesized. Experiments have been initiated to implant argon and nitrogen into silicon wafers to study high dose rate effects. In addition to providing insight into many fundamental materials science issues, the results of these high dose rate studies are expected to have a profound impact on semi-conductor fabrication processing.

Reference: Ph.D. Thesis, Moon Chun, University of Wisconsin-Madison, anticipated completion 1999.

Modeling Efforts to Gain Predictive Capability in PSII

Computer modeling of various aspects of the PSII process have been ongoing since the inception of the PSII program at University of Wisconsin in the late 1980s. These efforts have spanned a period covered by the preceding ARO grant, the no cost extension period, and through the present grant. Some of the findings of these modeling efforts under these grant periods are summarized below:

Two-dimensional Fluid Simulations of Expanding Plasma Sheaths around a Cylindrical Bore Target

The high voltage pulses in PSII result in an expanding sheath, the boundary of which represents the demarcation between ion-rich and ion-replenished regions in the plasma. The extent and the rate of propagation of the sheath edge is important to dose uniformity in PSII. Two-dimensional fluid simulations have been conducted for expanding plasma sheaths in a cylindrical bore target with finite depth. Sheath propagation characteristics have been modeled for various sheath thickness-to-bore size ratios and for the prediction of incident dose on the inner walls and

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the outside corners of the bore. The results of these modeling efforts are useful for the development of plasma surface modification processes for inside surfaces of hollow cylinders.

Two-dimensional Fluid Simulations of Expanding Plasma Sheaths at Sharp Corners

A two-dimensional fluid flow model has been developed to numerically simulate the evolution of transient sheath around a cross-shaped target at both the convex and concave corners. The angular distribution of the ions impinging on the target surface and the incident ion dose have been calculated. The anomalous dip at the convex corner has been investigated in detail. Such a study is very useful for PSII treatment of sharp corners and die crevices.

Reference: "Two-dimensional simulation of expanding plasma sheaths", M.P. Hong and G.A. Emmert, J.App. Phys., 78 (12), 1995, pp. 6967-6973.
(attached)

Comprehensive Model for Plasma Source Ion Implantation

A comprehensive model for plasma source ion implantation has been developed, that ties together modules for chamber, pulse modulator, ion-material interaction effects including diffusion and implantation, and material hardness. Such a comprehensive model facilitates the industrial applicability of the PSII process.

Reference: "Comprehensive Modeling of Plasma Source Ion Implantation"; M.W. Kissick, J.P. Blanchard, J.D. Callen, J.R. Conrad, S.M. Malik, and K. Sridharan, proc. 27th International SAMPE Technical Conference, Albuquerque, NM, October, 1995, p.11.

(attached)

TAMIX-PC Code

A user friendly TAMIX-PC code to predict ion-material interactions has been developed and is available as a public resource to the scientific community.

Sagamore Workshop on Gun Barrel Wear and Erosion (sponsored by U.S. Army Research Laboratory)

Dr. Robert Breun and Dr. Shamim Malik (University of Wisconsin) attended the Sagamore Workshop held in July 1996 in Wilmington, Delaware. The workshop focused on gun barrel erosion. Dr. Malik presented a talk on coatings that have been generated by Plasma Source Ion Implantation techniques that are directly applicable to gun barrel erosion technologies. The presentation also included a scheme to effectively coat the inside of cylindrical tubes. The workshop included presentations on the present state of gun barrel technology and efforts to improve the lifetime of gun barrels especially for high velocity, high repetition rate projectile

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delivery systems. Dr. Breun co-chaired the summary discussion session. During this visit Dr. Breun and Dr. Malik also visited the Army Materials Research Laboratory in Watertown, MA.

Reference attached

Visit to Benet Laboratories in Watervliet New York for Potential Collaborations in the Area of Gun Barrel Coatings

Dr. Robert Breun (University of Wisconsin) visited Benet Laboratories in Watervliet, New York in August 1996. He gave a one hour seminar on PSII coating technology and developments to 15 Benet Laboratory personnel and then had extensive discussions with key personnel on specific Benet Laboratory concerns. Among other things, Benet Laboratory is interested in developing gun barrel coatings that can improve and supplant the current chrome electroplating techniques. Dr. Breun visited the sputter deposition system that was being developed on site to test-coat the inside of gun barrels and to increase the scientific understanding of this application of that technology. The system utilized vacuum magnetron sputter techniques originally developed by a small high technology company.

Participation in Workshop on Hot Gas Erosion and Wear of Materials sponsored by the U.S. Army Research Office

Dr. John Conrad and Dr. Kumar Sridharan (University of Wisconsin) participated in a workshop on "Hot Gas Erosion and Wear of Materials" held in Ann Arbor, MI, September 1996. The workshop which was sponsored jointly by the Army Research Office and the University of Michigan brought together researchers from a number of Army laboratories and universities. Discussions focused on theoretical and applied research related to coatings development, high temperature materials, and problems of erosion and wear in defense applications. Dr. Sridharan presented a poster entitled "Ion-Assisted Coatings for Wear and Corrosion Resistance". Dr. Conrad chaired a panel on near-term research goals of the Army Research Office in the area of wear and erosion of materials.

Participation in Environmental Quality Basic Research Program, Ft. Belvoir, VA

Dr. Kumar Sridharan and Dr. Robert Breun (University of Wisconsin) attended a meeting on "Environmental Quality Basic Research Program" at Ft. Belvoir, VA, in May 1996. The meeting consisted of a number of presentations by personnel from Army laboratories and universities and focused on improving environmental cleanliness in defense manufacturing processes.

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Reduction/elimination of cadmium and chromium electroplating processes were addressed by a number of speakers. Dr. Sridharan presented a talk entitled "Investigation of Plasma-Aided Coatings as an Environmentally Acceptable Alternative to Wet Bath Electroplating Procedures". One recommendation from the review panel was that the University of Wisconsin collaborate with the Watervliet Arsenal, NY for the development of coatings on the inner surface of gun barrels which are presently coated using the electroplating process.

Participation in two North American Technology and Industrial Base Organization (NATIBO)-Ion Beam Processing Workshops

Dr. Kumar Sridharan (University of Wisconsin) participated in the North American Technology and Industrial Base Organization (NATIBO) - Ion Beam Processing Workshop held in Corpus Christi, TX, May 1996 and May 1998, respectively. The workshop was organized by the Office of the Director of Defense Research and Engineering and provided a forum for discussions on the future of ion-assisted techniques in defense applications. Representatives from defense laboratories, universities, private companies participated in the workshop. Dr. Sridharan gave presentations on the PSII process research at University of Wisconsin and with the goal of identifying defense related applications for this technology.

Collaboration with Army Research Laboratory (Phase I)

Dr. James Hirvonen of the US Army Research Laboratory visited University of Wisconsin September 1996. Discussions were conducted to identify future collaborations between the UW and ARL. Some potential areas included a comparison of IBED coatings produced at the two laboratories and materials characterization.

Collaboration with Army Research Laboratory (Phase II)

Captain Brian M. Stout has joined the PSII group as a graduate student to work on his M.S. degree in Nuclear Engineering. Captain Stout is an Army Communications Officer with a Functional Area in Nuclear Weapons/Operations Research. He is attending school through the Army's fully funded Advanced Civil Schooling Program prior to his assignment as Associate Professor at the U.S. Military Academy. Captain Stout visited ARL for ten days in July 1998 to conduct research on DLC coatings for his thesis. There he characterized DLC coatings deposited by the UW-PSII process using techniques available at the ARL and is presently comparing the properties of UW-PSII DLC coatings with those of Si-DLC coatings produced at ARL.

Reference: M.S. Thesis, Brian Stout, University of Wisconsin-Madison, anticipated completion 1999.

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Other Publications/Presentations

"Plasma Source Ion Implantation - Science and Technology"; K. Sridharan, J.R. Conrad, F.J. Worzala, A. Chen, M.M. Shamim, R.P. Fetherston, J.P. Blanchard, R.J. Matyi, D.L. Chapek, and R.A. Dodd, proc. Surface Modification Technologies IX-ASM-TMS Conference, Cleveland, OH, October, 1995, p.401. (attached)

"Plasma-Assisted Deposition of Tribological Coatings"; K. Sridharan, S.M. Malik, J.R. Conrad, R.A. Breun, R.P. Fetherston, and A. Chen, Advances in Coatings Technology, TMS Conference, Orlando, FL February, 1997 (conference organizer - J.K. Hirvonen, Army Research Lab, Aberdeen).

Scientific Personnel

Undergraduate Students: Nathaniel Horswill (BS), John Hockers, Roger Bloom (B.S. '98), and Ethan Treptow (BS '99)

Graduate Students: David Chapek (Ph.D. '96), M.P. Hong (Ph.D. '96), Robert Ulfing (M.S. '97), James Firmiss (Ph.D. '99), Brian Stout (M.S. '99), and Moon Chun (Ph.D. '99)

Faculty and Staff: John Conrad, Jake Blanchard, An Chen, Robert Breun, Kumar Sridharan, Shamim Malik, and Paul Fetherston

Related Successes

1. Along with Los Alamos National Lab, General Motors, and Empire Hard Chrome, the PSII research group at the University of Wisconsin received the R&D 100 award in 1997.
2. During the period of the ARO grant the University of Wisconsin PSII research group was a part of a ATP consortium involving 14 U.S. companies and Los Alamos National Laboratory. As a result of this collaboration, installation of three commercial PSII systems is underway. Nitrogen PSII into hard chrome, an idea originally conceived at the University of Wisconsin, was shown to improve the wear life of industrial tools and dies by factors ranging from 2x to 10x.
3. An international effort is underway to publish a Handbook of Plasma Immersion Ion Implantation & Deposition by a leading publisher of scientific literature, John Wiley & Sons; three members of the University of Wisconsin PSII research group have been selected to contribute to this handbook.