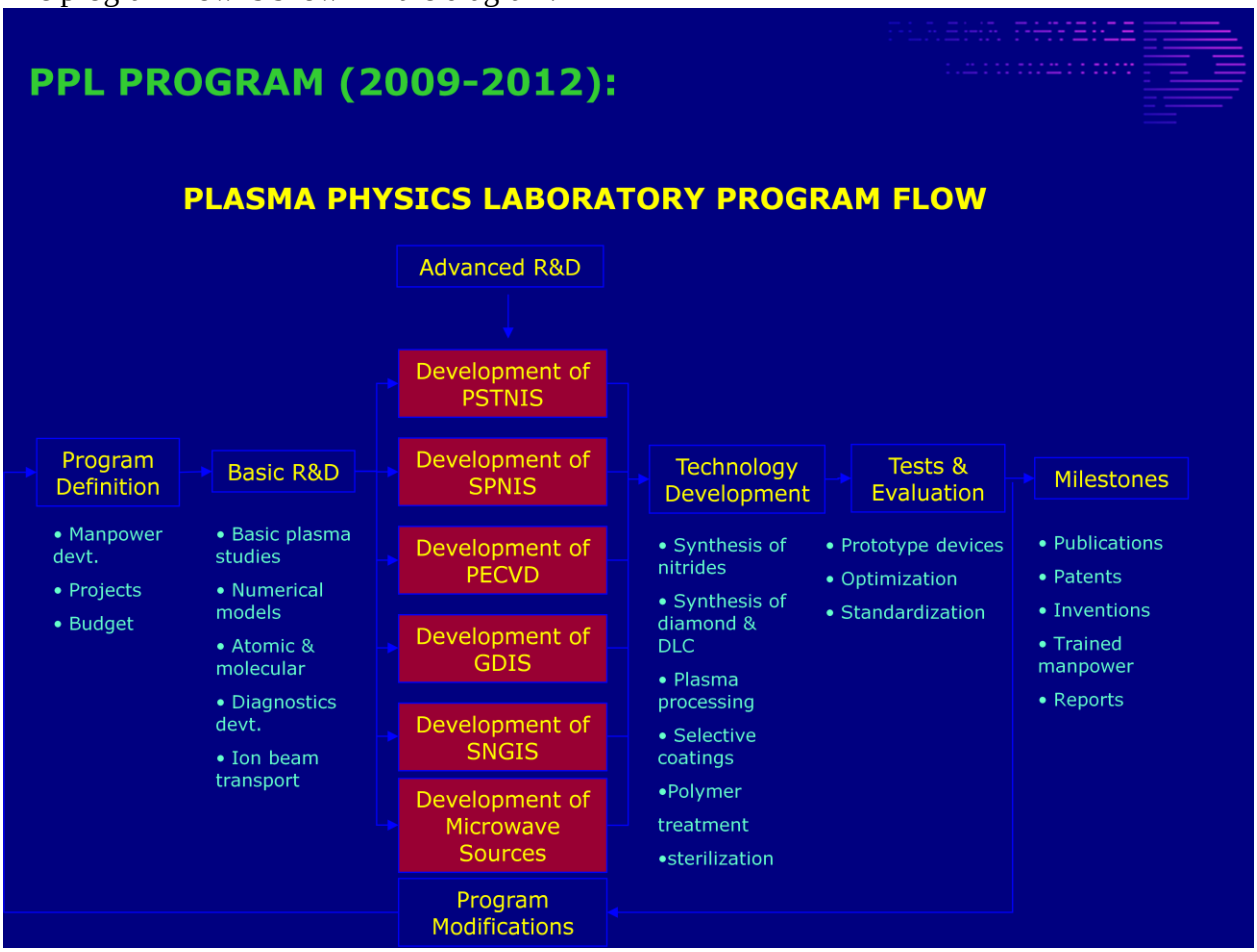
# PLASMA PHYSICS LABORATORY
## National Institute of Physics
## College of Science, University of the Philippines
## Diliman, Quezon City

**ANNUAL REPORT 2011**

## A. Introduction

The laboratory continued implementation of its program supported in part by the Department of Science and Technology (DOST) and other agencies in 2011. It has pursued the second year of implementation of projects on microwave systems, funded by DOST and donated equipment from IBF Electronic, GmbH, Germany. It has initiated Research Service Agreements on coating technology with three Philippines companies. It has also started the implementation of a DOST- Technicom grant towards commercialization of TiN coating developed in the laboratory. These programs and other projects are summarized in this report. They constitute the research and development program in plasma science and technology for the period 2009-2012. The program flow is shown in the diagram.



The acronyms stand for Plasma Sputter-type Negative Ion Source (PSTNIS), Sheet Plasma Negative Ion Source (SPNIS), Plasma Enhanced Chemical Vapor Deposition (PECVD), Gas Discharge Ion Source (GDIS), and Streaming Neutral Gas Injection System (SNGIS). A description of the R&D activities on each device follows.

**IA. Project Title: Research Service Agreements on Coating Technology**

**Funding Source: Various Philippine Companies**
**Amount of Funding : 10% of cost of uncoated tools**
**Duration: January 2011- December 2011**

**IB. Project Title: Market testing and process optimization of industrial prototype plasma enhanced chemical vapor titanium nitride coating technology**
**Total Funds:** P 9,797,092.00
**Source: DOST-TECHNICOM**
**Duration: November 16, 2011 – November 15, 2012**

The Sheet Plasma Negative Ion Source (SPNIS) was developed from previous DOST-funded projects purposely for the production, extraction and enhancement of negative hydrogen ions ($H^-$) using a mixture of hydrogen, argon and magnesium plasma. The $H^-$ ions extracted using a modified Wien filter was used in the synthesis of silicon hydride. Selective solar (IR) coatings of tin-bismuth on various metal substrates were also deposited using the facility. The facility was subsequently configured for TiN coating of metal tools used by various industries (tool and dye, etc.) operating in the Philippines.

In the first project component (IA), the facility is used for the synthesis of titanium nitride (TiN), for specific type of cutting, engraving, milling, and punching tools used by industries in the Philippines. Under a Research Service Agreement (RSA) between the company and the university, sample tools used by industry are solicited for actual coating and lifetime tests. The coated samples are then tested in coordination with the various industries in actual performance tests. These tests serve as demonstrations and proof of principle of the capability of the developed coating technology. The documented tests from the various industries serve as baseline data on lifetime enhancement and actual performance of these TiN-coated samples.

A similar machine is being developed (for project IB) starting November 16, 2011 under a DOST-TECHNICOM project titled "Market testing and process optimization of industrial prototype plasma enhanced chemical vapor titanium nitride coating technology". Costing PhP 9,797,092.00, the one year project builds an industrial prototype of the magnetized sheet plasma source for coating of TiN to service the manufacturing needs of industry. The prototype machine will be based at the DOST-Metals Industry Research and Development Center (MIRDC). Once developed, it will be operated under a research and licensing memorandum of agreement with the Asian Semiconductor Electronics Technologies (ASET) Corporation and the university.

**II. Project Title. Plasma Etching Using Low Energy Ions from a Gas Discharge Source**

**Funding Source: NIP MOOE Allotment**

**Amount of Funding : PhP 100,000.00**
**Duration: January 2011- December 2011**

A Gas Discharge Ion Source (GDIS) was developed as an example of a low energy ion beam source. Ion beams of carbon tetrafluoride ($CF_4$) plasma are used for surface modification applications such as ion etching on silicon samples. The ion treatment that the sample surfaces undergo changes their physicochemical properties. The modification is of great significance in the moisture absorption of the material improving its characteristic features like contact angle and other physical characteristics. Results can be extended to applications on other substrates like polymers, metals and other composite materials, e.g. SiC..

**III. Project Title. Beam Transport in a Sputter-type Ion Source**

**Funding Source: NIP MOOE Allotment**
**Amount of Funding : PhP 100,000.00**
**Duration: January 2011- December 2011**

In this study, Zirconium (Zr), Copper (Cu), Silver (Ag), Niobium (Nb), Aluminum (Al), Titanium (Ti) and Gold (Au) are used as metal targets to produce negative metal ions. The metal ions are fully characterized in terms of ion beam energies and ion currents using a retarding-type electrostatic energy analyzer. The behavior of ion energies and ion currents towards increasing target voltages and differences in beam characteristics between each metal used are studied. The effect of the chamber pressure to the ion beam characteristics is also studied.

Produced ions like that of copper are impregnated onto a porous ceramic material capable of filtering wastewater. The embedded copper acts as inhibitor of bacterial and fungal contamination of the treated water.

A single pass tandem accelerator and focusing techniques using an Einzel lens are employed in the extraction of metal ions produced in a sputter-type ion source. Enhancement of ion yield is tried with noble gases like argon. The extracted and highly focused beam is studied in terms of its transport properties specifically on techniques of increasing acceleration voltage. Acceleration voltages in the order of a few keV and a few hundred microamperes of ion current are essential in ion beam implantation and etching applications. Ion beam etching is necessary in the preparation of materials for various investigations such as thinning of samples for transmission electron microscopy or for texturing surfaces in the semiconductor industry. High-energy particles (ions or neutral particles) bombard the specimen in the physical process. Ion beam etching has merits over conventional metallographic etching methods specially when etching composite materials or material compounds. The production of highly energetic ions in this study is the first step towards comprehensive etching tests and parameter studies to be done on various materials.

**IV. Project Title: Treatment of Wood via Plasma Technology for a) Flame Retardation and b) Enhanced Adhesion Properties**

**Funding Source: Philippine Council for Advanced Science and Technology Research and**

**Development, Department of Science and Technology**
**Amount of Funding : PhP 1,369,696.00 for project a; separate fund for project b coursed through UPLB**
**Duration: August 1, 2009-March 31, 2011 for project a; November 1, 2010 – October 31, 2011 for project b.**

The developed Plasma Enhanced Chemical Vapor Deposition (PECVD) machine used previously for sterilization applications is upgraded to a Dielectric Barrier Discharge (DBD) machine for the plasma treatment of wood. For project a, the efficacy of chemical and plasma treatments with phosphate and boric compounds, and nitrogen as flame retardants on wood are compared. The chemical treatment involves the conventional method of spraying the solution over the wood surface at atmospheric condition and chemical vapor deposition in a vacuum chamber. The plasma treatment utilizes the DBD configuration ionizing and decomposing the flame retardants into innocuous simple compounds. Wood samples are immersed in either phosphoric acid, boric acid, hydrogen or nitrogen plasmas or a plasma admixture of two or three compounds at various concentrations and impregnated by the ionized chemical reactants. Chemical changes on the wood samples are analyzed by Fourier transform infrared spectroscopy (FTIR) while the thermal changes through thermo gravimetric analysis (TGA). Plasma treated samples are compared with untreated, vacuum-treated and spray-painted samples in terms of thermal stability and fire retardant properties based on the highest onset temperatures, temperatures of maximum pyrolysis, highest residual char percentages and comparably low total percentage loss.

For project b, plasma surface modification to improve adhesion property of *S. contorta*, *G. arborea* and *A. mangium* wood specimens is performed using the same dielectric barrier discharge (DBD).

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**V. Project Title: Studies on Microwave Plasma Systems**

**Project A: Adhesion enhancements of metal and plastic surfaces with adhesives using microwave-induced atmospheric plasma jets**
**Total Funds: P6,850,713.50 (cost of equipment donation)**
**Source: IBF Electronic GmbH & Co. KG, Ober-Ramstadt, Germany**
**Duration: August 2010 – July 2012**

The R&D aims to develop an atmospheric plasma jet from a 2.45 GHz microwave source and use it for adhesion enhancements of epoxy on industrial materials. The R&D preliminary targets are the studies on the stability of the plasma jet in terms of ignition, minimum reflection, and heating using high-ripple 2 kW and low ripple 6 kW magnetrons. An initial experiment on a low pressure microwave plasma source shows that the treatment of stainless steel surfaces have enhanced its adhesion with an epoxy adhesive. Based on tensile test results, the adhesion strength of epoxy-bonded $O_2$/Ar plasma treated surfaces was increased to 3816.0 N from 3038.3 N for the epoxy-bonded untreated surfaces. These results would be replicated in the atmospheric microwave plasma jet.

**Project B: Development of microwave-induced plasma jets**
**Total Funds: P1,966,423.00**
**Source: DOST-PCIEERD**
**Duration: September 2010 – August 2011 and December 2011 – November 2012**

Continuing R&D is pursued on an atmospheric plasma jet developed from an existing microwave waveguide system (MWS) and equipment donated by IBF Electronic, GmbH & Co. KG, Germany. The plasma chamber and vacuum systems of the MWS are replaced with customized tapered waveguide and gas nozzle system, specifically designed for enhanced stability of the plasma jet. The atmospheric microwave plasma jet is developed to enhance the paintability of various industrial materials such as stainless steel, glass, plastics, etc. Plasma treatment can quickly enhance the surface paintability of industrial materials to ordinary paints without the need for primers. From initial results, it has been shown that the plasma jet treatment of stainless steel can achieve superhydrophilic surfaces using argon and argon-nitrogen plasmas.

B. R&D Highlights

**Sheet Plasma Negative Ion Source (SPNIS) Projects**

The developed process technology titled "Titanium nitride thin film formation on metal substrate by chemical vapor deposition in a magnetized sheet plasma", was awarded European Patent No. EP 1 485 516 B1 issued on August 24, 2011, in addition to patents earlier awarded for the same process technology from Taiwan, Singapore, Japan, People's Republic of China, United States of America and the Philippines.

The Asian Semiconductor Electronics Technologies (ASET) Corporation has agreed to provide financial and other support for conducting research and development under the DOST-Technicom project and to license the patented technology.

In conjunction with the project, RSAs were entered into with the following companies to coat their specific tools provided with TiN: 1) Bangko Sentral ng Pilipinas; 2) San Miguel Yamamura Packaging Corporation; and 3) SIDCOR Industrial Systems.

Continuing studies on the sheet plasma specifically on high dynamic range imaging resulted in the paper published in C1a.1

**Plasma Enhanced Chemical Vapor Deposition (PECVD) Projects**

Flame endurance of wood samples was increased using chemical and plasma treatment. The chemical treatment involved the conventional method of spraying the solution over the wood surface at atmospheric condition and chemical vapor deposition in a vacuum chamber. In the plasma treatment, wood samples were immersed in reactive plasmas comprised of various ratios of flame retardant solutions and/or reactive gases. Based on the thermo-gravimetric analysis (TGA) results, chemical treatment by exposure to vapor was found to be more effective compared to the direct application. However, comparing the chemical treatment and plasma

treatment, the 25 mA phosphoric acid plasma treatment was found to yield superior thermal stability and flame retardant properties; in terms of the highest onset temperature and temperature of maximum pyrolysis, highest residual char% and comparably low total weight%. These results are detailed in the papers C.b1.1, C.b3.3, C.b4.1, C.b7.5 and C. b7.7 and in the theses D.1.2 and D.2.4.

Plasma surface modification to improve adhesion properties of *S. contorta*, *G. arborea* and *A. mangium* wood specimens were done dwith the DBD machine. Results are publishe din the paper

**Microwave Projects**

The atmospheric microwave plasma jet operates at 2.45 GHz up to an input power of around 3 kW and gas flow rates of more than 1 lpm. The ignited atmospheric plasmas are contained in a cylindrical dielectric tube with a diameter up to 2 cm. Microwave energy is concentrated ín the middle of the dielectric tube with the aid of a tapered waveguide. Plasma filaments (Figure 1) and plasma flume (Figure 2) have been observed at different discharge conditions. The plasma jet facility aims to make plasma processing of industrial materials more easier and faster to implement due to vacuum-free operations. It has been already demonstrated that stainless steel becomes superhydrophilic with plasma jet treatment of just a few seconds. An image of the typical atmospheric jet produced is shown.

Figure 1. An actual image of the atmospheric microwave plasma jet at an argon gas flow rate of 6 lpm and microwave forward power of 600 W. The plasma filaments are contained in an alumina tube.

Figure 2. An actual image of the atmospheric microwave plasma jet at an argon gas flow rate of 6 lpm and microwave forward power of 2000 W. The plasma flame is contained in a quartz

tube.

**Other Highlights**

Publications of the laboratory in SCI-indexed international journals, proceedings of international and local conferences and papers presented in various other conferences are summarized in Section C of this report.

Three Ph.D. students were sent on on-the–job (OJT) training and one went on scholarship overseas towards completion of their requirements for their Ph.D. Henry Lee, Jr,, Leo Mendel Rosario, and Julie Anne Ting were sent on OJT at IBF Electronic, GmbH & Co. KG, Ober-Ramstadt, Germany for six months; Henry Lee starting May, 2011, Leo Mendel Rosario and Julie Anne Ting starting November 2011. Hernando Salapare, III left for Nice University in France under a one-year EMMA scholarship for his Ph D.

**C. 2011 Publications and Papers Presented** (*italicized authors are collaborators, otherwise affiliated with the laboratory*)

**a1. SCI –indexed international journal**

1. L. M. D. Rosario, J. A. S. Ting, R. P. B. Viloan, B. A. T. Suarez, M. M. S. Villamayor, R. B. Tumlos, *M. N. Soriano*, and H. J. Ramos, 'High dynamic range imaging of magnetized sheet plasma', IEEE Trans. Plasma Sci. **39** (11) (2011) 2492-2493.

2. H. V. Lee, Jr., *M. E. Arciaga*, L. M. D. Rosario, J. A. Ting, A. Ulano, R. B. Tumlos, and H. J. Ramos, 'A 2.45 GHz microwave air plasma under a double-hexapole maagnetic field', IEEE Trans. Plasma Sci. **39** (11) (2011) 2590-2591.

3. K. G. Pabelina, C. O. Lumban, and H. J. Ramos, 'Plasma impregnation of wood with fire retardants', Nucl. Instrum. Meth. Phys. Res. B **272** (2012) 365-368.

4. *L. Jirkovsky*, L. Ma Bo-ot, *A. Muriel*, and H. Ramos, 'Time development of two and three-dimensional self-gravitating system using initial Dirac delta function distribution' Physica A **391** (2012) 1128-1132.

5. *M. N. Acda, E. E. Devera, R. J. Cabangon*, and H. J. Ramos, 'Effects of plasma modification on adhesion properties of wood', Int. J. Adhesion Adhesives **32** (2012) 72-75.

6. *D. B. Putungan*, H. J. Ramos, *F. C. Chuang* and *M. A. Albao*, 'Modeling of co-deposition of indium and tin on silicon (100) : a kinetic Monte Carlo study', Int. J. Modern Phys. B. **25** (14) (2011) 1889-1898.

7. R. Tumlos, J. Ting, E. Osorio, L. Rosario, H. Ramos, A. Ulano, H. Lee, G. Regalado, 'Results of the study of chemical-, vacuum drying- and plasma-pretreatment of coconut (*Cocos nucifera)* lumber sawdust for the adsorption of methyl red in water solution', Surface and Coatings Technol. **205** (2011) 5425-5429.

**a2. International conference proceedings (20th International Toki Conference)**

1. M. M. S. Villamayor, *T. Nakajima*, H. J. Ramos, and *M. Wada*, 'Optical emission signatures of dual planar magnetron plasmas for $TiO_2$ deposition', Plasma and Fusion Research **6** (2011) 2406045-1-4.

2. H. S. Salapare III, G. Q. Blantocas, *W. L. Rivera, V. A. Ong, R. S. Hipolito*, and H. J. Ramos, 'Anti-bacterial property of hydrogen-ion and oxygen-ion treated polytetrafluoroethylene (PTFE) materials', Plasma and Fusion Research **6** (2011) 2406043-1-4.

**b1. Paper presented at the 14th International Conference on Ion Sources (ICIS11), September 12-16, 2011, Giardini Naxos, Taormina, Italy**

1. M. Poral, G. Malapit, C. L. Mahinay, and H. Ramos, "Electrostatic energy analyzer measurements of low energy zirconium beam parameters in plasma sputter-type negative ion source"

**b2. Paper presented at the International Conference on Materials for Advanced Technologies (ICMAT 2011), Suntec, Singapore, June 26 – July 1, 2011**

1. *L. Reyes*, J. A. Ting, H. J. Ramos, R. B.Tumlos, and *R. Sarmago*, "$O_2$ plasma treatment of electrospun chitosan–pcl/hydroxyapatite bioscaffold for bone tissue engineering"

**b3. Paper presented at the 31st Annual Meeting and Symposium of the Philippine-American Academy of Science and Engineering, National Institute of Physics, College of Science, National Science Complex, University of the Philippines, Diliman, Quezon City, June 25-28, 2011**

1. J. A. S. Ting, M. C. C. Lacdan, L. M. D. Rosario, H. J. Ramos, and R. B. Tumlos, "Enhanced adhesion of epoxy on a stainless steel surface treated with $O_2$/Ar microwave plasma".

**b4. Paper presented at the Philippine Association of Microscopists Inc. Conference (MACROSPHIC), De la Salle University, Manila, April 28-29, 2011**

1 *J. G. Chan, S. C. Bombita, J. C. M. Flores*, H. J. Ramos, and *A. V. Amorsolo, Jr*., "Ssurface morphology variation of treated low density polyethylene (LDPE) films characterized by atomic force microscopy".

**b5. Papers presented at the 21st International Toki Conference (ITC21): Integration of Fusion Science and Technology for Steady State Operation, Ceratopia, Toki, Gifu, Japan, November 28 - December 1, 2011.**

1. A.R.B. Gines, J.M. Salamania, B.M. Villanueva, H.S. Salapare III, H.J. Ramos, "Fabrication of SiC nanopillars on SiC substrate by direct $CF_4$ etching using a gas discharge ion source"

2. E. Tuballa, M.C. Lacdan, J.K. Soriano, J.A. Ting, H. Lee, Jr., **L.M. Rosario**, H. Ramos, and R. Tumlos, "Optical emission characteristics of atmospheric pressure $Ar/N_2$ microwave plasma jet in relation to superhydrophilic surface treatment of stainless steel"

3. K.G. Pabelina, C.P. Romero, J.Y. Daseco , H.J. Ramos, "Wettability and bacterial retention property of plasma-treated polyethylene terephthalate"

4. J.R.M. Guhit, K.G. Pabelina, H.J. Ramos," Effects of argon and water plasma treatments on Philippine coconut fibers"

**b6. Paper presented at the 33rd Annual Scientific Meeting of the National Academy of Science and Technology, Manila Hotel, Manila, 13-14 July 2011.**

1. M.C. Lacdan, T. Tuballa, J.A. Ting, H.V. Lee, Jr., L.M.D. Rosario, R. Tumlos, and H. Ramos, "Initial studies of a microwave-induced plasma jet"

**b7. Paper presented at the 161st Meeting of the Acoustical Society of America, Seattle, USA, May 2011.**

1. L. Ma. Bo-ot, H. Lee, H. Ramos and C-M Chiang, "Four-chamber cochlea box model: establishing acoustic comfort, illustrating injury and towards therapy'

**b8. Proceedings of the 29$^{th}$ SPP Physics Congress, National Institute of Physics, National Science Complex, College of Science, University of the Philippines. Diliman, Quezon City October 24-26, 2011, ISSN 1656-2666, Vol. 8.**

1. J.A.S. Ting, *J.C. de Vero*, L.M.D. Rosario, H.J. Ramos, and R.B. Tumlos, "Optical emission spectroscopic studies of an $O_2$/Ar microwave plasma in correlation to surface wettability"

2. J.K.T. Soriano, L.M.D. Rosario, M.C. Lacdan, H.V. Lee, Jr., J.A.S Ting, H.J. Ramos, and R.B. Tumlos, "Reflected power measurements for microwave plasma jet contained in different dielectric tubes"

3. T.E. Tuballa, M.C. Lacdan, J.K. Soriano, J.A. Ting, H. Lee, Jr., L.M. Rosario, H. Ramos, and R. Tumlos, "Superhydrophilic stainless steel via fast treatment with atmospheric-pressure $Ar/N_2$ microwave plasma jet"

4. E.J.C. Tinacba, J.A.S. Ting, L.M.D. Rosario, H. Ramos, and R. Tumlos, "Enhancement of paint adhesion on stainless steel by an atmospheric plasma jet"

5. M.C. Lacdan, L.M.D. Rosario, H.V. Lee, Jr., J.A.S. Ting, H. Ramos, and R. Tumlos, "Temperature profiles of quartz discharge tubes containing microwave plasma jets of argon"

6. A. Aquino, and L. M. Bo-ot, “Eigenvalues, eigenvectors and the two-level system”

7. A. P. J. Pacho, E. Pares, *J. M. Presto, J. Ibanez*, A. M. Ulano, and H. J. Ramos, “Electron temperature measurement of argon discharge in a streaming neutral gas injection hollow cathode using optical emission spectroscopy”

8. C. L. S. Mahinay, G. M. Malapit, A. M. Ulano, M. D. Poral, V. F. Mascarinas, and H. J. Ramos, “ Ion currents of $Cu^-$ ion beams in a plasma sputter-type negative ion source and its correlation with sputtering and negative ion formation”

**D. Manpower trained**

D.1 Bachelor of Science (BS) Physics/Applied Physics

1. Mary Ann G. Tenorio, “Comparative studies of the streaming neutral gas injection (SNGI) facility operating in two modes”, BS Applied Physics Thesis, University of the Philippines Diliman, April 2011.

D.2 Master of Science (MS) Physics/Materials Science

1. Michelle Marie S. Villamayor, “Photoreactive properties of $TiO_2$ synthesized by dual planar magnetron”, MS Physics Thesis, University of the Philippines Diliman, April 2011.

2. Julie Anne S. Ting, “Enhancement of the adhesion between two AISI 304 stainless steels using $O_2$/Ar microwave-induced plasma treatment”. MS Materials Science Thesis, University of the Philippines Diliman, April 2011.

PREPARED BY:

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Coordinator, January 12, 2012