Three different types of plasma deposition systems were constructed for film syntheses. 1) A laser absorption wave deposition (LAWD) was constructed to deposit diamond and diamond-like films and nitride based films on steel, aluminum and other substrates from flowing methane/hydrogen mixtures. A pulsed infrared YAG laser was used to create simultaneously two plasmas—from the flowing gas mixture and from the substrate onto which the film was to be deposited. 2) An electron cyclotron resonance microwave plasma enhanced chemical vapor deposition system was designed and used to grow diamond and diamond-like films on structural materials such as Fe-based alloys (316 stainless steel). Films were grown at low temperatures (400°C and below) from methane/hydrogen mixtures, without use of diamond seeding and without use of a template layer between the Fe-based substrate and the diamond-like film. 3) A pulsed UV krypton-ion laser deposition system was constructed for growth of structured oxide films. ZnO films were grown on various substrates. A method for p-type doping of ZnO films was developed for use in creating p-n junctions for electronic device applications.
Statement of the Problem to be Studied
The overall theme of the proposed effort was to generate new protective thin films for structural materials using novel deposition techniques. Three different types of plasma deposition systems were constructed for thin film syntheses and each was used to deposit films on various substrates.

Summary of Most Important Results
A laser absorption wave deposition (LAWD) was constructed to deposit diamond and diamond-like films and nitride based films on steel, aluminum and other substrates from flowing methane/hydrogen mixtures. A pulsed infrared YAG laser was used to create simultaneously two plasmas—from the flowing gas mixture and from the substrate onto which the film was to be deposited. These plasmas have ion densities of approximately $10^{19}$ /cm$^3$, exceeding those of CVD by a factor of $10^8$ or more. The high energy of the ions, in the range $10 - 100$ eV, can be used to transport ionic species across several mm distances at atmospheric pressures. As such, films can be deposited in an “open air” environment using flowing mixtures near a substrate to be coated with thin film material. Diamond and diamond-like films were grown using methane/hydrogen mixtures. Film growth rates were tens of microns per hour and greater. Solid aluminum nitride films were investigated using aluminum as the substrate material (and as a source for aluminum) and flowing nitrogen gas. Films were characterized by phonon lines using Raman and micro-Raman spectroscopy. Atomic force microscopy and SEM were used to observe surface morphology. Crystalline aspects were measured by x-ray diffraction.

An electron cyclotron resonance microwave plasma enhanced chemical vapor deposition system was designed and used to grow diamond and diamond-like films on structural materials such as Fe-based alloys (316 stainless steel). A microwave source designed and manufactured by Wavemat, Inc. produced ions and species with orbit trajectories parallel to the growing film surface. This geometry reduced surface damage from energized electrons and film precursor species, allowing the substrate to be placed in regions of the plasma with higher ion densities. Film growth was increased, and films could be grown at lower temperatures. Films were grown under various conditions. Powers were between 200 and 700 W. Films were grown at low temperatures (400 C and below) from methane/hydrogen mixtures ranging from 0.5 to 20%, at flow rates of 270 sccm at pressures below 3 torr were used. Growth was made with a variety of conditions—with and without mechanical polishing, and with and without the use of diamond seeding and scratching, and on several substrate materials other than Fe-based alloys (including Ni, Si, and aluminum oxide). Of special significance, diamond and diamond-like films could be grown without use of diamond seeding and without use of a template layer between the Fe-based substrate and the diamond-like film. Film growth rates were approximately 0.2 microns/hour.

A pulsed UV krypton-ion laser deposition system was constructed for growth of structured oxide films. ZnO films were grown on various substrates. Early growth concentrated on ZnSe to develop the method since laboratory personnel had experience with this material. Following this effort, attention was directed to ZnO, which has greater hardness. In the process of growing ZnO a method for p-type doping of ZnO films was discovered. P-type doped ZnO has potential use in creating p-n junctions for electronic device applications. In particular, ZnO based light emitting diodes (LEDs) and lasers would emit in the blue region of the spectrum, and would have important uses for the Army and other DoD agencies for light emission, sensors such as solar blind detectors, and high frequency electronic applications.
Papers Published in Peer-Review Journals


Papers Published in Conference Proceedings


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Report of Inventions

U.S Patent Application Serial No. 09128,516, entitled, “Zinc Oxide Films Containing P-Type Dopant and Process for Preparing Same,” by Henry W. White, Shen Zhu and Yungryel Ryu, assigned to The Curators of the University of Missouri.