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Surface Modification of Optoelectronic and Biomedical Materials Using Plasma-Based and Related Technologies

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Abstract

Plasma-based surface treatment techniques such as plasma immersion ion implantation and deposition (PIII&D) is a very useful technique in the fabrication of silicon-on-insulator and high-k dielectrics and is commercially used to produce shallow junctions in deep-submicrometer integrated circuits. The applications of PIII are in fact much broader covering many other areas such as metallurgy and particularly biomedical engineering and optoelectronics. Many of the innovations and protocols developed for PIII&D in semiconductor applications have been translated to the processing of biomedical components. In this invited talk, our recent work pertaining to surface treatment of optoelectronic and biomedical materials is reviewed.

Results and Discussion

Many biological reactions occur in a physiological medium containing various ions and liquids. For surgically implanted biomaterials, the important reactions occur at the interface between the materials and tissues / body fluids, and so the surface properties of biomaterials determine their suitability. Properties of relevance include physiochemical, topographical, and mechanical characteristics, biocompatibility, as well as bio-functionalities. Most bulk materials are not natural biomaterials. That is to say, they may possess excellent mechanical properties, but they may not interface well with biological tissues and fluids *in vivo*. Hence, surface modification plays a very important role because selected surface properties such as cytocompatibility and antimicrobial characteristics can be enhanced while the relevant bulk materials attributes like mechanical strength, robustness, and inertness can be preserved.

Magnesium and its alloys possess many unique properties such as low density, high specific strength, good electromagnetic shielding, and so on. They are therefore attractive to many applications in transportation, aerospace, and electronics. Moreover, because magnesium and magnesium alloys can degrade naturally in a physiological environment, they are potentially useful to biodegradable implants. However, the corrosion resistance of Mg in the physiological environment is typically inadequate and some form of surface treatment is thus necessary. In this respect, oxygen, hydrogen, and nitrogen have been implanted into magnesium alloys. Our results reveal enhanced corrosion potentials after nitrogen PIII and the implantation voltage and fluence are observed to impact the corrosion resistance. Dense oxide layers have also been fabricated on magnesium by oxygen ion implantation and water PIII. Our recent work on metal PIII into magnesium alloys will also be presented.

Metal elements have been implanted into magnesium alloys to achieve surface alloying and enhanced surface mechanical and anticorrosion properties. In traditional alloying processes, the contents of the alloying elements depend on the solid solubility, but in PIII, the amounts of alloying elements are not limited by solid solubility and so more dramatic changes in the surface properties can be attained. In this respect, Al, Ti, Zr, Ag, Ta, and other metallic elements have been studied. For instance, the incorporation of Al not only enhances the mechanical properties but also better corrosion resistance, but stress corrosion increases with higher Al concentrations. As shown by the electrochemical impedance spectroscopy, the total impedance value of the Al implanted sample is about ten times higher than that of the untreated sample.

Titanium-based implants such as joint prostheses, fracture fixation devices, and dental implants are commonly used in surgeries, but ensuing bacterial infection constitutes one of the biggest complications and implant failure. Bacteria can form a biofilm on the implant surface subsequently leading to bacterial infection and related deleterious effects. Therefore, it is crucial to prevent initial bacteria adhesion onto the implant surface by rendering the biomaterials antibacterial. Silver is a biocide that is known to kill a broad spectrum of bacterial and fungal species including antibiotic resistant strains. In this respect, silver nanoparticles (Ag NPs) have been shown to be more reactive than the bulk counterpart because of the larger active surface area.

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As an important material in bioMEMS, the biocompatibility of single-crystal silicon must be improved. Our experiments indicate the osteo-compatibility of crystalline silicon can be improved by hydrogen plasma immersion ion implantation. The ability to grow apatite (bone) on silicon stems from the hydroxyl bonds on the silicon surface after hydrogen PIII and the amorphous surface created by ion bombardment. The concept has been expanded to hip joints with a plasma-sprayed titania and improved surface biocompatibility can indeed be attained by hydrogen PIII, nano-powder plasma spraying, and irradiation with ultra-violet light.

A couple of new innovations in this area such as plasma treated polymers and medical devices used to automatically correct spinal problems such as scoliosis will be presented in this invited talk. The latter has in fact gone into clinical trials with a number of patients having been implanted with the correction devices surgically.

With regard to applications to optoelectronic materials, several cases will be described. For instance, the discovery of efficient sources of terahertz radiation has been exploited in imaging applications, and a nanoscale terahertz source could lead to additional applications. High-frequency mechanical vibrations of charged nanostructures can lead to radiative emission, and vibrations at frequencies of hundreds of kHz have been observed from a ZnO nanobelt under the influence of an alternating electric field. We have observed mechanical resonance and radiative emission at ~0.36 THz from surface-modified core-shell ZnO mesocrystal microspheres excited by a continuous green-wavelength laser. We find that ~0.016% of the incident power is converted into terahertz radiation, which corresponds to a quantum efficiency of ~33%, making the ZnO microspheres competitive with existing terahertz-emitting materials. The mechanical resonance and radiation stem from the coherent photo-induced vibration of hexagonal ZnO nanoplates which make up the microsphere shells. The ZnO microspheres are formed by a nonclassical, self-organized crystallization process, and represent a straightforward route to terahertz radiation at the nanoscale

A good understanding of the reaction mechanism in the electrochemical reduction of water to hydrogen is crucial to renewable energy technologies. Although previous studies have revealed that the surface properties of materials affect the catalytic reactivity, the effects of a catalytic surface on the hydrogen evolution reaction (HER) on the molecular level are still not well understood. Contrary to general belief, water molecules do not adsorb onto the surfaces of 3C-SiC nanocrystals (NCs), but rather spontaneously dissociate *via* a surface autocatalytic process forming a complex consisting of –H and –OH fragments. We show that ultra-thin 3C-SiC NCs on a glassy carbon substrate possess superior electrocatalytic activity in the HER. This arises from the large reduction in the activation barrier on the NC surface enabling efficient dissociation of H_2O molecules. Furthermore, the ultra-thin 3C-SiC NCs show enhanced HER activity in photoelectrochemical cells and are very promising to the water splitting based on the synergistic electrocatalytic and photoelectrochemical actions. This study provides a molecular-level understanding of the HER mechanism and reveals that NCs with surface autocatalytic effects can be used to split water with high efficiency thereby enabling renewable and economical production of hydrogen.

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