

NANOSTRUCTURED DLC-Ag COMPOSITES FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

We have synthesized novel diamondlike carbon coatings with silver nanoparticles embedded into the DLC film. The size of silver nanoparticles that are confined into layered structures has been varied from 5 nm to 50 nm using an ingenious pulsed laser deposition technique. The size of nanoparticles was found to be remarkably uniform within 15%. We have characterized these samples using high-resolution cross-section TEM and STEM-Z contrast techniques, electron energy loss spectroscopy (EELS), Raman, nanohardness, adhesion, and biocompatibility measurements. In the STEM-Z, where the contrast is proportional to atomic number², we have obtained the details of the atomic structure of silver particles. We have correlated the microstructure with hardness and adhesion properties. The EELS was used in conjunction with STEM-Z to obtain sp³/sp² bonding ratio. This ratio was compared with Raman result to provide an average bulk value. The role of silver nanoparticles is surmised to provide a reservoir of electrons for antimicrobial activity on the surface, as revealed by our biocompatibility tests.

INTRODUCTION

The introduction of implantable medical devices into the body has been shown to greatly increase the risk of infection. The number of bacteria required to cause an infection reduced by the presence of a biomaterial; in addition, the persistence of bacteria is enhanced. Bioengineering of hybrid implant materials in order to achieve optimal performance and to prevent infection and inflammatory reactions is a field undergoing rapid development. The sustained delivery of antimicrobial drugs into the local micro-environment of implants systemic side-effects and exceeds usual systemic concentrations by several orders of magnitude. Silver antimicrobial coatings have been designed to slowly deliver antimicrobial drugs to reduce implant infections.

DLC describes hydrogen-free hard carbon solids with atomic number densities > 0.19 g-atom/cm³.¹ It is a cross-linked, non-crystalline network of sp²- and sp³- hybridized carbon. Film densities of these films have been reported to be as high as 3.1 g/cm³, and film friction and wear coefficient are among the lowest recorded to date. The mechanical properties and electronic properties can be tailored by the sp³/sp² ratio. Films demonstrate optical gap up to 3 eV, transparency to light from deep UV through visible to far infrared, high refractive index, and wide resistance to radiation. Finally, these films exhibit excellent thermal conductivity, and extremely low thermal expansion.

However, these films have internal stresses leading to poor adhesion and peel off. In this paper, we have designed a new architecture where silver, a compliant material, is incorporated as nanoparticles inside the DLC thin film matrix. It is based upon the theory that a more compliant entity in the hard carbon film may accommodate the large compressive stress and lower the stored strain energy. It is necessary to achieve these improvements without significantly altering the chemical and microstructural characteristics from those of undoped DLC.

The biocidal effect of silver, with its broad spectrum of activity including bacterial, fungal and viral agents, is particularly well known and the term "oligodynamic activity" was coined for this phenomenon.² Nanocrystalline silver has demonstrated unsurpassed antimicrobial spectrum and kill rates and are effective against 150 different pathogens including drug resistant forms of bacteria. In addition, nanocrystalline silver also provides the fastest and broadest-spectrum fungicidal action.³ These properties of nanocrystalline silver improve wound healing and improve biocompatibility around a medical implant. A silver- tetrahedral amorphous carbon nanocomposite would provide add features to the substrate. This infection resistant coating that is applied to polymers, metals, or ceramics of various geometries for medical applications. We have devised an innovative target configuration to incorporate foreign atoms in-situ into the DLC films during PLD. The DLC coatings were characterized by Raman spectroscopy, optical microscopy, nanohardness, and antimicrobial testing.

EXPERIMENTAL DETAILS

Silicon (100) (p-type) wafers were used as substrates. The Si wafers were cleaned in acetone and methanol ultrasonic baths. The substrates were subsequently dipped in HF to remove the native oxide layer before loading in the PLD chamber.

Incorporation of the foreign atoms was accomplished by covering a portion of the graphite target with a piece of desired element and ablating the target in a circular pattern. During pulsed laser deposition, the target was spinning and the focused laser beam impinged sequentially on graphite and dopant portions to ablate the target materials to form a composite film. The substrates were kept at room temperature during deposition.

The laser beam source used was the KrF pulsed excimer laser ($\tau(s)= 25$ ns) at a repetition rate of 10 Hz, with an energy density close to 3.0 J/cm^2 . All the depositions were conducted for 40 min at room temperature in a high vacuum exceeding 10^{-7} Torr.

Composition of the films can be controlled through changing (1) the scanning radius of the laser beam on the target surface and hence the fraction of the metal ablated, (2) the laser beam position, (3) the position of the circular target, (4) the size of the dopant piece on the target, (5) the energy density, or (6) optical reflectivity. The fraction of noncarbon atoms incorporated into the film is $\alpha \delta(1-R_d)/2 \pi \gamma(1-R_c)$, where α is the laser ablation ratio which is closest to unity, γ is the laser beam scanning radius, R_c is the reflectivity of carbon, R_d is the reflectivity of the dopant strip, and S is width of the strip.

DISCUSSION

Optical Microscopy

The presence of buckling patterns in undoped DLC films indicates the presence of very large internal compressive stress. On the other hand, DLC nanocomposite films prepared in high vacuum were atomically smooth. The absence of buckling in nanocomposite films suggests the moderation of compressive stress in these films. The result suggests that much thicker films can be grown using this nanocomposite design.

TEM

Transmission electron microscopy with an EELS attachment has been used to study the microstructure and bonding characteristics of DLC-foreign atom nanocomposites. Electron

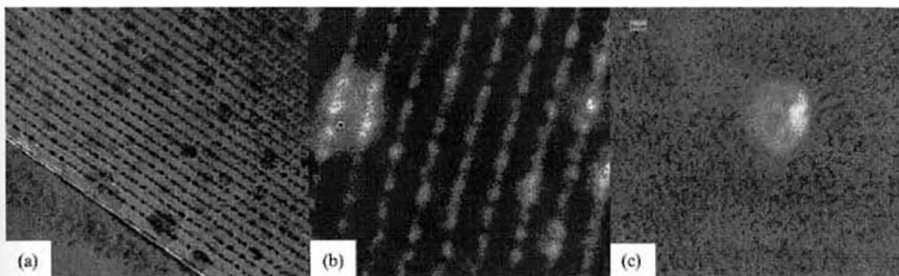


Figure 1. (a) Bright field image of DLC + silver.
 (b) 1,200,000x dark field Z-contrast image of DLC + silver.
 (c) 200,000x dark field Z-contrast image of DLC + silver.

diffraction patterns have been studied using radial distribution function (RDF) analysis to determine the atomic structure of DLC. Morphology and crystallinity of the films were determined by transmission electron microscopy (TEM) carried out in a Topcon 002B with point resolution of 0.19 nm at 200 kV, and scanning transmission electron microscopy (STEM) carried out in a VG HB501 UX with a point resolution of 0.13 nm at 100 kV.

DLC+silver composites demonstrate speckling. This speckling indicates the segregation of silver into a second phase. The selected area diffraction pattern in this composite demonstrates two haloes, which indicates that the films are amorphous. Using Cuomo's method, the sp^3/sp^2 ratio of DLC was determined to be near 70%.⁴

STEM was performed on these samples to understand the atomic microstructure of the films. In the VG HB501 UX dedicated STEM, the image is formed by scanning a 1.6 Å probe across the specimen. The integrated output from various imaging detectors is displayed on a TV screen scanning at the same rate. The Z-contrast signal is collected from a high angle annular detector where, by collecting the component of the electron signal scattered through large angles (typically 75 to 150 mrad) the resultant image is dominated by thermal diffuse scattering. In this technique, contrast is proportional to Z^2 , thus, the Ag:C contrast is over 60:1.

These figures reveal that the silver forms nanoparticle arrays. The DLC appears as uniform layers between these arrays. The large random particles that appear in these micrographs as artifacts of the ion milling used in sample preparation. There are atomically sharp boundaries between the metal particle and the hard carbon matrix.

The size of silver nanoparticles that are confined into layered structures has been varied from 5 nm to 50 nm. Nanodiffraction from STEM imaging of the above sample shows the metal particles are crystalline with an average crystal size varying from 3-5 nm. The silver layers above are separated by a distance of 7 nm. The low surface energy silver nucleates on the high surface energy DLC in the form of three-dimensional islands. This morphology allows these metals to act as electron reservoirs within hard carbon films.

Raman

As is common to all amorphous semiconductors, the distinct sharp peaks on seen in diamond film spectra are replaced by diffuse, broad peaks due to the relaxation of selection rules for optical transitions. All of the spectra show (1) a broad hump centered in the 1510-1557 cm^{-1} region, which is typical of DLC films, called a G- band, and (2) a small shoulder at 1350 cm^{-1}

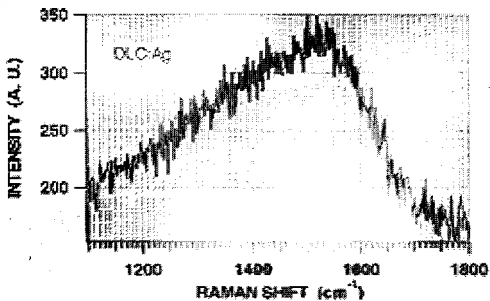


Figure 2. UV Raman spectra of DLC+Ag.

with disorder-allowed zone edge mode, called a D-band. High quality DLC films demonstrate the following: (1) a relatively symmetrical G-band in the visible Raman spectrum, (2) a smaller D-band, as this finding is associated with few graphite clusters in the coating.

We have performed a Raman comparative study on undoped and alloyed films using visible (314 nm) and UV Raman source techniques. Since UV Raman scattering efficiency is considerably higher than the visible Raman scattering efficiency, the Raman peak shift and sp^3/sp^2 ratios are more reliable. The undoped DLC and DLC+Ag results are qualitatively similar. The UV spectra confirm the presence of considerable tetrahedral bonding. In the case of Ag, since its d shell is fully occupied and it has been recognized that Ag has little chemical bonding with carbon, it might be expected that Ag would not contribute much to changing the short range environment of DLC either.

Hardness

The hardness of DLC nanocomposites was assessed by the Nanoindenter II instrument. The samples were indented with a conical diamond tip, with a radius of curvature of 20 μm . Indentations were performed using a trapezoidal loading curve. The nanohardness and Young's modulus were measured as a function of indentation depth.

The hardness of the undoped DLC is quite high. At lower contact depth the hardness is 25-30 GPa, which increases with increasing contact depth after which it remains constant at 37.0 GPa. This variation of properties with depth can be attributed to the indentation size effect. Near surface graphitic environmental residue may also play a role in this variation.

The hardness of Ag-doped DLC is lower than the undoped DLC. Since silver is a soft metal, the creation of a silver nanocomposite lowers the overall hardness of the film. The properties of these films are listed in the figure below. It is worth noting that most of the hard ceramic materials have hardness around or below 20 GPa. It can be seen that, in comparison to undoped DLC, both the Young's modulus and the hardness of the silver doped DLC film are slightly reduced. These nanocomposites exhibit a tradeoff between hardness and adherence. The most adherent films possess the lowest hardness, and the hardest films are the least adherent.

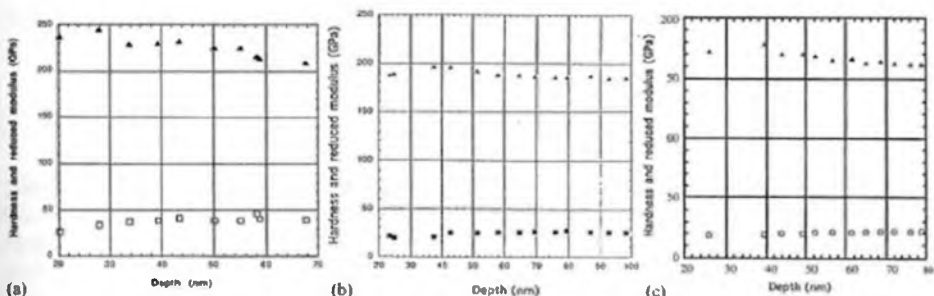


Figure 3. (a) Hardness (■) and Young's modulus (▲) as a function of depth for undoped DLC films created by pulsed laser deposition. $E_f=230$ GPa. $H_a=37$ GPa. (b) Hardness (■) and Young's modulus (▲) as a function of depth for silver-containing DLC films created by pulsed laser deposition. $Ag=2.0\%$. $E_f=190$ GPa. $H_a=25$ GPa. (c) Hardness (■) and Young's modulus (▲) as a function of depth for silver-containing DLC films created by pulsed laser deposition. $Ag=3.0\%$. $E_f=175$ GPa. $H_a=18$ GPa.

Antimicrobial susceptibility testing

The antimicrobial susceptibility testing performed on these coatings is a variant of the disk diffusion test. Diffusion of metal ions from DLC nanocomposites is relatively slow as compared with the diffusion rates seen with typical pharmacologic agents embedded in paper or in a resorbable polymer. Thus, assessment of the coated surface itself, as opposed to assessment of adjacent regions in the agar medium, is far more predictive of the true antimicrobial behavior of the coating. The antimicrobial testing on the coated surfaces were performed as follows. A tryptic soy agar plate was inoculated with *Staphylococcus aureus*. The coated material was placed on the inoculated surface, the coated surface face down in the agar medium. The agar plate was turned upside down to allow direct observation of the agar medium-coating interface. The incubation period was 24 hours incubation in ambient air at 35° C.

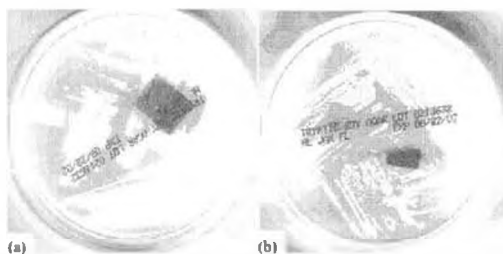


Figure 4. Antimicrobial susceptibility testing: (a) silicon (100) control surface, (b) silver-DLC nanocomposite surface.

The first result shown is that for the control surface, which is 1 cm x 1cm Si (100). *S. aureus* grows easily over the Si surface, as seen below. Figure 4a. demonstrates bacterial streaks on the Si surface of the same strength as those in the surrounding agar. The next result shown is

that for the silver-DLC nanocomposite surface. *S. aureus* does not grow over the Ag nanocomposite surface, as seen in Figure 4b. Thus, the DLC+Ag nanocomposite exhibits significant antimicrobial properties

CONCLUSIONS

DLC films that contain a small concentration of noncarbon atoms exhibit improved adhesion and wear. In the undoped DLC films, buckling is frequently observed. These buckling patterns exhibit sinusoidal shape, and imply the presence of large internal compressive stress. The DLC+Ag nanocomposites exhibit no buckling, indicating the reduction of internal compressive stress. This process can be understood by considering the atomic structure of DLC. The reduction of the internal compressive stress through the in situ introduction of dopants can then be explained on the basis of the effect of these dopants on the continuous rigid random network (CRN) model of DLC.⁵ Transition metals like silver are more compliant when compared with covalently bonded DLC. The substitution of metal dopants for carbon atoms in the CRN may be able to accommodate the strain by distortion of the electron density distribution since the outer shell electrons of the transition metals are loosely bound to the atom. The size of silver nanoparticles that are confined into layered structures has been varied from 5 nm to 50 nm using an ingenious pulsed laser deposition technique. The size of nanoparticles was found to be remarkably uniform within 15%. The role of silver nanoparticles is surmised to provide a reservoir of electrons for antimicrobial activity on the surface, as revealed by our biocompatibility tests.

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