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Title: DIAMOND-LIKE CARBON PRODUCED BY PLASMA SOURCE ION IMPLANTATION AS A CORROSION BARRIER

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Diamond-Like Carbon Produced by Plasma Source Ion Implantation as a Corrosion Barrier

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Introduction

There currently exists a broad range of applications for which the ability to produce an adherent, hard, wear and, corrosion-resistant coating plays a vital role. These applications include engine components, orthopedic devices, textile manufacturing components, hard disk media, optical coatings, and cutting and machining tools (e.g., punches, taps, scoring dies, and extrusion dies). Ion beam processing can play an important role in all of these technologies.

Plasma source ion implantation (PSII) is an emerging technology which has the potential to overcome the limitations of conventional ion implantation by: (1) reducing the time and expense for implanting onto complex shapes and large areas and (2) extending the thickness of the modification zone through ion beam enhanced plasma growth of surface coatings. In PSII, targets are placed directly in a plasma source and then pulse biased to produce a non-line-of-sight process for complex-shaped targets without complex fixturing. If the pulse bias is a relatively high negative potential (20 to 100 kV) ion implantation will result. If however, a low voltage (50 - 1200 eV) high duty cycle pulse bias is applied, film deposition from the chamber gas will result, thereby increasing the extent of the surface modification into the 1–10 micron regime.

To evaluate the potential for DLC to be used as a corrosion barrier, Electrochemical Impedance Spectroscopy (EIS) and traditional electrochemistry techniques were used to investigate the breakdown mechanism in chloride and nonchloride containing environments(1). The effect of surface preparation on coating breakdown was also evaluated.

Experimental

High purity CVD Ni was made from the thermal decomposition of nickel carbonyl $(Ni(CO)_4)$. The resultant CVD Ni samples were polished to a 0.30 μm finish. These samples were then placed in an ion implantation chamber where the native oxide was removed by sputter etching with argon (Ar) for one hour. This sputter cleaning was immediately followed by carbon (C) implantation from methane at 30 kV. Carbon implantation prior to coating with DLC improves the adhesion properties of the DLC. After implantation, the surface was sputter cleaned for approximately 15 minutes. DLC was then deposited onto this surface from an RF plasma of acetylene to a thickness of approximately 4-5 microns(2).

The DLC coating produced by PSII had a density of 1.9 g/cm^3 and consisted of approximately 70 at% C and 30 at% hydrogen (H). The C:H ratio was found to greatly effect coating properties with lower hydrogen content yielding coatings with the highest hardness values. The C:H ratio also effected coating resistivity and adhesion. The hardness of the DLC coatings examined was found to be to directly proportional to sp3 bonding content which varied between 55% and 20%. Hardness values between 6 and 12 GPa(3).

Results and Discussion

Characterization of DLC in Chloride Solution and EIS Model The EIS data of samples exposed to deaerated 0.25M NaCl solution (pH 7), are presented in Figures 1 as a function of immersion time. As seen in Figure 1, three separate break point frequencies are observed in the Bode magnitude and phase data. While the low frequency data remain relatively unchanged during the 28 hr immersion period, dramatic changes were measured in the frequency range >10 Hz. Upon removal from solution, large corrosion pits in the DLC could be easily seen. The EIS response in Figure 1 is best modeled by the equivalent circuit (EC) shown in Figure 2b. In this figure, the intrinsic electrical properties of the carbon implanted layer are represented by the elements C_{IL}^{i} and R_{IL}^{i}, where the superscript 'i' represents "intrinsic" and are in units of farads/cm^2 in ohm cm^2 respectively. This layer acts in series with the DLC coating represented by the

elements $C_{DLC}{}^i$ and $R_{DLC}{}^i$ which model the capacitance and charge transfer resistance of the DLC. The elements representing the carbon implanted layer and DLC act in parallel with the elements representing small "pinholes" in the DLC. These pinholes (less than 20μm in diameter) expose either the carbon implanted layer, a very thin DLC layer or, a combination of both. The fraction of surface covered by these pinholes is defined by Θ and the fraction of surface covered by DLC is defined by 1-Θ. The parameters from the CNLS fitting of the DLC data are presented in Table 1. As seen in this table, large changes in $R_{corr}{}^o$ (polarization resistance in ohms) were observed.

Properties of the C-implanted Layer Anodic polarization experiments for carbon implanted CVD Ni (without the DLC coating) in deaerated 0.25M NaCl found active dissolution of the specimen at all potentials more positive than the OCP. Further, a positive hysteresis was observed upon reversal of the anodic potential scan indicating surface damage. While the unexposed surface was charcoal gray, the exposed surface was deep black. Scanning electron microscopy revealed that this exposed surface contained an extremely fine porosity not found in the unexposed surface.

X-ray photoelectron measurements of the unexposed and exposed surfaces revealed two very different concentrations of Ni as a function of depth (Figure 3a). For the unexposed sample the initial surface C concentration is more than 80 at.% while that of Ni is less than 5 at%. Between approximately 6 and 12 minutes of sputtering, the concentrations of both C and Ni level off near 50 at%. The C KLL Auger transition lineshape (Figure 3b) over this sputtering range does not vary and, indicated a strong Ni-carbide component(3). In contrast, during the first 16 minutes of sputtering in the exposed sample (Figure 4a) the concentrations of both C and Ni remained close to their initial values. The C KLL Auger lineshape for the sample (Figure 4b) in this sputtering interval resembled that for graphitic or amorphous carbon(4,5).

Collectively these results indicate that in Cl⁻ environment, the preferential dissolution of Ni from the implanted layer occurs at the OCP as well as at more anodic potentials. This process leaves behind a porous carbon rich layer with a graphitic amorphous bonding configuration. At the OCP this preferential dissolution likely owes to the galvanic interaction between Ni-rich and C-rich deposits in the implanted layer *inside the defect*. Because of restricted mass transport oxygen is depleted from the defect and separation of the anodic reactions in the defect and cathodic reaction on the boldly exposed DLC occurs. A galvanic couple is then established between the boldly exposed DLC and the C implanted Ni layer at the base of a defect. In the absence of OH⁻ production, Cl⁻ migrates into the defect to maintain charge neutrality. This rise in Cl⁻ concentration decreases the pitting potential of the Ni below the couple potential and allows the process to become autocatalytic once only Ni is exposed at the base of the defect.

References

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Table 1 Select parameters from CNLS fitting of EIS data for DLC Ni in 0.25M NaCl as a function of immersion time. Also presented is the % area of the surface covered by defects (Θ).

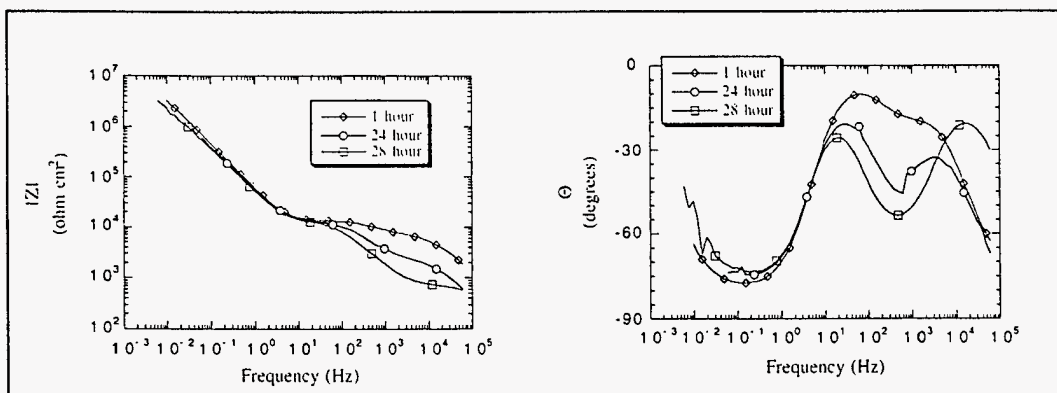| Immersion Time (hrs)	$R_{corr}{}^o$ (ohms)	$C_{dl}{}^o$ (Farads)	$R_{IL}{}^o$ (ohms)	$R_{DLC}{}^o$ (ohms)	$\Theta \times 100$ % defect	$(1-\Theta) \times 100$ % DLC
1	1.14×10^4	1.58×10^{-8}	1.13×10^4	5.89×10^6	0.003	99.997
24	2.51×10^3	6.63×10^{-8}	1.13×10^4	1.44×10^6	0.02	99.98
28	489	1.26×10^{-7}	1.07×10^4	2.91×10^6	0.08	99.92

Figure 1 Bode a) magnitude and b) Bode phase plots for DLC coated CVD Ni in deaerated 0.25M NaCl solution after 1 hr, 24 hrs, and 28 hrs of immersion.
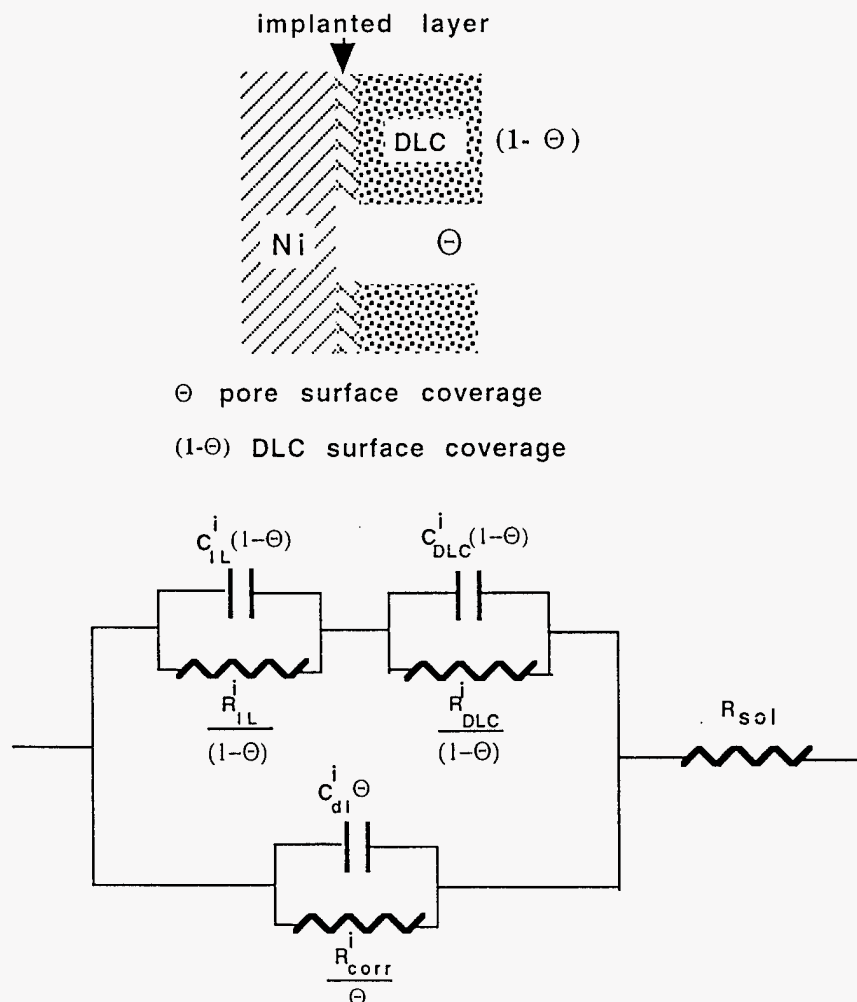

Figure 2 a) Schematic diagram representing the layers in DLC coating and a defect native to the coating b) electrical equivalent circuit model representing the breakdown of DLC coated CVD Ni in NaCl solution
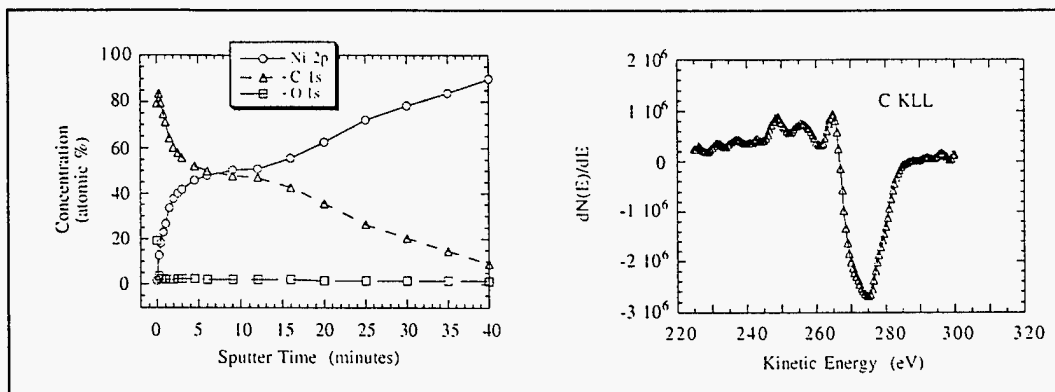
Figure 3   a) XPS sputter profile of carbon implanted CVD Ni prior to immersion in test solution. **b)** Auger line shape for C KLL on the same pre-immersion surface after 12 minutes of sputtering.
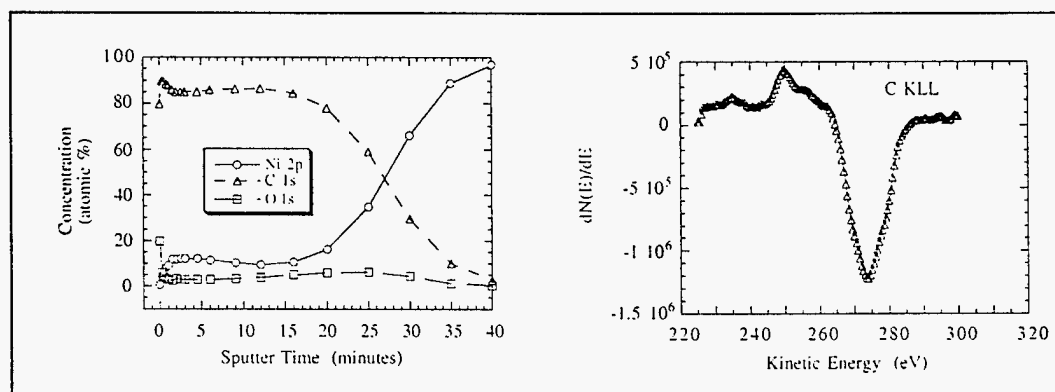

Figure 4   a) XPS sputter profile of carbon implanted CVD Ni after immersion and polarization in test solution. **b)** Auger line shape for C KLLon the same post-immersion surface after 12 minutes of sputtering.

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