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Adherent amorphous hydrogenated carbon films on metals deposited by plasma enhanced chemical vapor deposition

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Abstract

This paper reports the findings of a study of the structural, mechanical, and tribological properties of amorphous hydrogenated carbon (a-C:H) coatings for industrial applications. These thin films have proven quite advantageous in many tribological applications, but for others, thicker films are required. In this study, in order to overcome the high residual stress and low adherence of a-C:H films on metal substrates, a thin amorphous silicon interlayer was deposited as an interface. Amorphous silicon and a-C:H films were grown by using a radio frequency plasma enhanced chemical vapor deposition system at 13.56 MHz in silane and methane atmospheres, respectively. The X-ray photoelectron spectroscopy technique was employed to analyze the chemical bonding within the interfaces. The chemical composition and atomic density of the a-C:H films were determined by ion beam analysis. The film microstructure was studied by means of Raman scattering spectroscopy. The total stress was determined through the measurement of the substrate curvature, using a profilometer, while micro-indentation experiments helped determine the films' hardness. The friction coefficient and critical load were evaluated by using a tribometer. The results showed that the use of the amorphous silicon interlayer improved the a-C:H film deposition onto metal substrates, producing good adhesion, low compressive stress, and a high degree of hardness. SiC was observed in the interface between the amorphous silicon and a-C:H films. The composition, the microstructure, the mechanical and tribological properties of the films were strongly dependent on the self-bias voltages. The tests confirmed the importance of the intensity of ion bombardment during film growth on the mechanical and tribological properties of the films.

Keywords: Amorphous hydrogenated carbon; Plasma enhanced chemical vapor deposition; Silicon interlayer; Adhesion; X-ray photoelectron spectra; Mechanical properties

1. Introduction

Diamond-like carbon (DLC) coatings have attracted significant attention recently due to their low friction, high degree of hardness, chemical inertness, and high wear resistance [1]. Currently DLC film deposition can be accomplished economically at low temperature, utilizing various chemical vapor deposition techniques, sputtering methods, arc-discharge, pulsed laser deposition and ion beam assisted deposition techniques [1]. Plasma synthesis of coatings is a powerful, versatile way to obtain such materials. Among DLC films, the amorphous hydrogenated carbon (a-C:H) coatings stand out due to their attractive tribological properties which may be by specific settings to meet the plasma conditions and deposition technique [2].

Amorphous hydrogenated carbon films are mostly obtained by plasma decomposition of a hydrocarbon-rich atmosphere. It is usually accepted that surface chemisorption of carbon carrying neutral radicals is the main channel for the film growth [3]. In a-C:H films deposited by methane decomposition, the structure is composed of sp^2 hybridized clusters interconnected by sp^3 hybridized carbon atoms. Furthermore, the mechanical properties (e.g. hardness, Young's modulus, adhesion to the substrate, internal stresses) as well as important electronic

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properties (e.g. optical gap, photoluminescence, conduction behavior) may be pre-determined to certain extent by varying the sp^3/sp^2 bonding ratio [1].

The major disadvantage of hard a-C:H film deposition and, therefore, their technical applications is that there is often a relatively low adhesion of these films on metallic substrates caused by very high total compressive stress on these coatings. To overcome the low adhesion problems of these films on metallic substrates, different coating concepts have been proposed by many research groups, such as: deposition of a thin metal interlayer (Si, Cr, Ti, Ta, W, etc.) [4–18]; surface implantation (B, N, C, Cu, Zr, Ni, Al, F, etc.) [19–23]; chemical interlayer gradients or a multilayer coating (SiC, TiC, TiN, TiCN, CrN, etc.) [24–28]; variation of the self-bias voltage in the beginning of the deposition [29–31]; and the use of surface thermal treatments [32,33]. The interlayers, especially the multilayers, cause a continual change in the thermal expansion coefficient and help to reduce stress in a-C:H films.

The plasma enhanced chemical vapor deposition (PECVD) technique, using different silicon precursors, was applied to deposit a thin silicon interlayer between metallic substrates and a-C:H films in order to increase the coatings' adherence. $C_6H_{18}Si_2O$ (hexamethyldisiloxane) [5], $Si(CH_3)_4$ (tetramethylsilane) [6,13,34,35], and SiH_4 (silane) [4,7,36] have used as precursor gases to deposit the silicon interlayer.

In this study, a thin amorphous silicon interlayer was used to improve the a-C:H films' adhesion on Ti6Al4V and stainless steel substrates. The silicon interlayer and a-C:H films were deposited via radio frequency (rf) PECVD (rf-PECVD), using silane and methane atmospheres, respectively. The a-C:H films were analyzed according to their microstructure, mechanical, and tribological properties as a function of self-bias voltage.

2. Experimental details

Amorphous silicon interlayers and a-C:H films were deposited using the rf-PECVD technique with silane and methane as precursor gases, employing an asymmetrical capacitively-coupled deposition system. The polished Ti6Al4V alloy and 304 stainless steel substrates were mounted on a water-cooled 6 cm diameter cathode fed by a 13.56 MHz rf power supply. The substrates were cleaned ultrasonically in an acetone bath followed by HF+HNO3 dip for titanium alloy substrates and HCl dip for stainless steel substrates to remove the native oxide layer before loading into the vacuum chamber. The substrates were additionally sputter cleaned in an argon atmosphere for 30 min prior to deposition. In addition, Si(100) substrates were used in order to measure the total stress of the a-C:H films. Thin amorphous silicon interlayers (100–300 nm) were deposited to improve the film's adhesion. The a-C:H films were deposited with a total gas pressure of 10.5 Pa up to a thickness of approximately 2 μm. The self-bias voltage (V_b) was varied from −100 up to −500 V by adjusting the rf power input for a-C:H films, while V_b was fixed at −100 V for silicon interlayer depositions.

X-ray photoelectron spectroscopy (XPS) was employed to study the chemical bondings within the interfaces, using a surface Kratos XSAM HS instrument with a monochromatic Al Kα line of an X-ray source with energy of 1486.6 eV and 168 W of power. The measurements were taken in an ultra-high vacuum environment. Binding energy positions were verified using the C 1s peak at 284.8 eV, which was associated to C–C and/or C–H bindings. The peaks were adjusted using Gaussian curves and the background was determinated by the Shirley method.

The chemical composition was determined by ion beam analysis (IBA), using Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA), using a 1.6-MV Pelletron 5SDH electrostatic accelerator from the National Electrostatic Corporation. For the RBS measurements, a 2.2-MeV He^+ beam was used with the particle detector positioned at 170° with respect to the incident beam. ERDA measurements determined the hydrogen content using a 2.2-MeV He^+ beam with the detector positioned at 20°, while the sample was tilted by 75° with respect to the incident beam. The atomic density was inferred by combining the atomic density of the area provided by IBA and the film thickness obtained by stylus profilometry.

The film's atomic arrangements were analyzed by Raman scattering spectroscopy. The spectroscopy was performed with a Renishaw 2000 system using an Ar^+-ion laser (λ=514 nm) in backscattering geometry. The laser power on the sample was approximately 0.6 mW and the laser spot had a 2.5 μm diameter. The Raman shift was calibrated in relation to the diamond peak at 1332 cm^{-1}. All measurements were carried out in air at room temperature.

Total stress was determined by measuring the film curvature by means of stylus profilometry and by applying Stoney's equation, as described in detail in the literature [37,38]. The hardness of the films was measured by employing a Fisherscope micro indenter, applying a load of 20 mN. The values presented in this study correspond to the average of 13 indentations carried out in different spots for penetration depths that were shallower than 10% of the thickness of the films.

Friction coefficient and critical load were determined using a CETR pin-on-disk tribometer under ambient conditions (20 °C, 55% RH). In the pin-on-disk tribometer, a pin is mounted on a stiff lever and pressed onto the test sample (in the form of a disk) with a precisely known weight. As the sample is rotated, the resulting frictional force acting between the pin and the sample is measured from the small lateral deflection of the lever. The continuous friction force recording not only provides numerical values of the friction coefficient, but also monitors the change in sliding behavior. According to standard methodology, the load at which the coating is stripped from the substrate is deemed the critical load. The present study, used a 20 mm high stainless steel pin with a 6 mm diameter and the 3 mm thickness Ti6Al4V and stainless steel disks with a 51.4 mm diameter and machined finishing (Ra=0.3 μm). The a-C:H films were deposited on metal disks, using amorphous silicon interlayer, with a thickness of approximately 2 μm. Friction coefficient measurements were carried out keeping the load constant at 5 N, while for the critical load measurements the load was varied from 2 to 15 N.