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Industrial-scale deposition of highly adherent CN_x films on steel substrates

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ABSTRACT

Highly adherent carbon nitride (CN_x) films were deposited using a novel pretreatment with two high power impulse magnetron sputtering (HIPIMS) power supplies in a master–slave configuration: one to establish the discharge and one to produce a pulsed substrate bias. During the pretreatment, SKF3 (AISI 52100) steel substrates were pulse-biased in the environment of a HIPIMS Cr plasma in order to sputter clean the surface and to implant Cr metal ions. Subsequently, CN_x films were prepared at room temperature by DC unbalanced magnetron sputtering from a high purity graphite target in a N_2/Ar discharge at 3 mTorr. All processing was done in an industrial CemeCon CC800 system. A series of depositions were obtained with samples at different bias voltages (DC and pulsed) in the range of 0–800 V. Scanning transmission microscopy (STEM) and high resolution transmission electron microscopy (HRTEM) show the formation of an interface comprising a polycrystalline Cr layer of 100 nm and an amorphous transition layer of 5 nm. The adhesion of CN_x films evaluated by the Daimler-Benz Rockwell-C reach strength quality HF1, and the scratch tests gives critical loads of 84 N. Adhesion results are correlated to the formation of an optimal interfacial mixing layer of Cr and steel.

1. Introduction

The scope of the present study is to overcome the problem of insufficient adhesion of carbon-based coatings on metal substrates. As a model system, we have selected carbon nitride (CN_x), which is proposed as the best candidate to replace diamond-like carbon (DLC) films due to their superior wear resistance, high hardness, and low friction coefficient [1]. The first successful industrial application of this material has been the use of very thin (~2–5 nm) films for the protection of hard disks [2,3]. However, the scalability of CN_x coatings produced in laboratories to industrial engineering applications has been difficult as thicker films (1–5 μm) on steel substrates are required. The main reason is the development of high compressive intrinsic stresses during film growth which causes adhesion failures with delamination of films from the substrate surface [4].

The common practice to increase the adhesion of carbon-based coatings on steel substrates is to make a pretreatment of the substrates and the use of a metallurgical glue layer interposed between the surface substrate and the film. In this paper we study the deposition of highly adherent CN_x films on martensitic steel substrates using a novel high power impulse magnetron sputtering (HIPIMS) pretreatment where two HIPIMS power supplies are used in a master–slave configuration: one establish the discharge in the cathode and the second produces a pulsed substrate bias [5–7]. The plasma-processing methods used for improving adhesion of carbon-based coatings are reviewed from an historical point of view in Section 2. A description of our novel pretreatment and the experimental techniques are considered in Section 3. Section 4 presents the results and discussions, and Section 5 gives the conclusions.

2. Plasma-processing pretreatments

In-situ surface preparation is an essential step in vacuum coating processing and is critical to assure a good adhesion film-substrate. For instance, air-exposed stainless steel is covered by a native oxide layer (from 1 to 5 nm thick) composed of metal oxides and hydroxides [8]. Despite of pre-cleaning processes, other contaminants like organic and water molecules will also be present on the metal surface. Without the elimination of the oxide and contaminants, it is likely that any coating deposited on the surface will delaminate.

For many years, it has been known that cleaning of substrates using plasma techniques prior to physical vapor deposition processes can significantly improve coating adhesion. Such bombardment is expected not only to remove unwanted contaminant layers at the

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substrate surface, but also to create active dangling bonds, which may promote adhesion of the deposited film [9].

There are basically two different plasma processes that have been developed to *in-situ* clean substrates during PVD processing, namely: ion scrubbing and sputter cleaning [10,11].

2.1. Ion scrubbing

The first *in-situ* plasma cleaning technique was developed in 1935 by Strong [12] for the cleaning of glass surfaces used in astronomical telescopes, and it is nowadays included in many commercial coating machines. The equipment consists of a DC high voltage "glow bar" that allows the formation of plasma. The surfaces in contact with the plasma acquire a negative voltage (several volts) with respect to the plasma. This sheath potential accelerates positive ions to the surface. When an ion contacts the surface it combines with electrons and releases its energy of ionization (5–20 eV). This low-energy bombardment and heating desorbs adsorbed contaminants such as water vapor. The ion scrubbing can be done using argon or reactive gases like oxygen, chlorine, and hydrogen, the later are used to clean contaminants like hydrocarbons. In this technique, also known as "glow discharge cleaning" because of the light generated by the plasma, there is no bias voltage applied to the substrate [11].

2.2. Sputter cleaning

In this technique ions generated in a plasma discharge are accelerated toward the surface held at a negative voltage; the ions clean the surface by physical sputtering. In the beginning the technique was using gas ions accelerated by DC, RF, or pulsed–DC substrate biasing, but during the last decade, the development of new techniques like arc deposition and high power impulse magnetron sputtering (HIPIMS) allowed the simultaneous use of gas and metal ions [13].

2.2.1. Sputter cleaning by gas ions: DC biasing

One of the most successful techniques for adhesion enhancement has been the pretreatment of the substrate surface with a low-energy (500 eV) Ar^+ ions, *in-situ* before vacuum vapor deposition of the films [14]. The first report of this technique is back to 1955, when Farnsworth et al. [15] reported using sputter cleaning with Ar^+ ions to prepare ultra-clean surfaces for low-energy electron diffraction studies. Later, sputter cleaning was adopted by D. M. Mattox [16] to develop the "Ion-Plating" process. Mattox's process, with a filament used to evaporate a metal and a DC voltage used to accelerate the ions, evolved rapidly with the introduction of the DC magnetron sputtering technique for the deposition of thin films. Before deposition, the plasma cleaning is easily done by ions generated in the magnetrons, while the acceleration of the ions toward the substrate to be cleaned can be performed by a negative DC voltage applied to the substrate [17]. Fig. 1a shows a typical process where the ions are generated by a magnetron cathode with a Cr target and the bias is provided by a negative DC voltage: the magnetron generates mainly Ar^+ ions because the efficiency of Cr ion generation is very low. In industrial production, where it is common to have a large deposition area, Ar^+ ions are usually provided by external sources. Anders [18] has recently reviewed some of these ion sources, such as hollow cathode discharges, linear sources of end-Hall type, and capacitively or inductively coupled plasma sources.

There are two drawbacks of this method. The first is the substrate heating during ion bombardment that can change, per example, the properties of some temperature sensitive substrates like steels. Another disadvantage is the incorporation of the gas ions into the substrate. An inert gas like Ar can occupy interstitial sites and induce increased strains in the substrate lattice. These high strains can embrittle the substrate material by bringing it closer to its yield stress. Furthermore, when heated during pretreatment or under use, Ar could diffuse and agglomerate into bubbles, introducing porosity and weakening of the interface [19].

2.2.2. Sputter cleaning by gas ions: RF and pulsed–dc substrate biasing

Radio frequency (RF) biasing has been used since the 1970's to induce the energetic particle bombardment of insulating substrates. RF bias supplies, usually operating at 13.56 MHz, are connected to the substrates via a matching network [13].

The use of unipolar pulsed substrate biasing in cathodic arc evaporation was introduced in 1991 by Olbrich et al. [20] to reduce thermal input associated with ion bombardment. With the advent of pulsed–DC target sputtering, bias pulsing techniques with frequencies in the range 20–350 kHz become more popular in the late 1990's because it was then realized that it could provide improved control of substrate bombarding ion energy and flux, and be utilized to bias substrates during reactive deposition of insulating films [21]. Unipolar pulsed–DC substrate biasing is often carried out in combination with

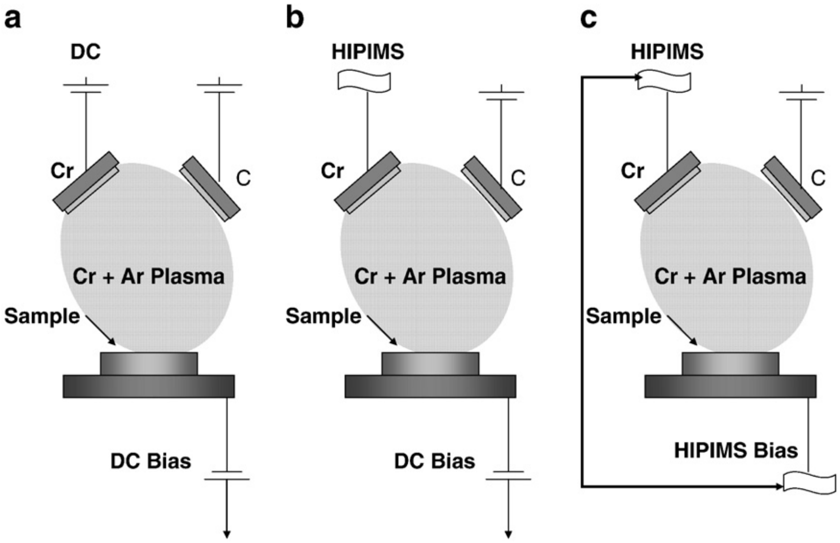

Fig. 1. Different methods to produce plasma cleaning of substrates. (a) Classic process where ions are generated by a magnetron cathode and the bias provided by a negative DC voltage. (b) HIPIMS process, where gas and metal ions are generated by an HIPIMS discharge in the cathode and the bias is provided by a negative DC voltage. (c) Novel process where two HIPIMS power supplies are used in a master–slave configuration whereby the first establishes the discharge in the cathode and the second produces a pulsed substrate bias.