## PHYSICAL AND CHEMICAL REGULARITIES OF THE STRUCTURE AND PROPERTIES OF DOPED CARBON FILMS DEPOSITED FROM THE PLASMA OF PULSED CATHODE-ARC DISCHARGE

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a-C films gain ever-growing popularity in scientific and industrial communities on the dependence of the excellent properties like high hardness, low friction coefficient, high wear resistance, better chemical inertness, biocompatibility and optical transparency in IR region [1]. Various deposition techniques have been used to fabricate a-C films, such as plasma enhanced chemical vapor deposition (PECVD) [2], magnetron sputtering [3], pulsed laser deposition (PLD) [4], and cathode arc evaporation (CAE) [5]. Compared with other methods, CAE is a low temperature deposition method with a better ion ratio and higher ion energy. By CAE method, films with strong  $sp^3$ are easily produced. During deposition, bonding ion bombardment on the substrates improves adhesion between the film and the substrate. Preparation of a-C films using CAE technique, the power supply is operated in direct-current or pulsed mode. Bias voltage is an important parameter for directcurrent cathode arc evaporation technique. Pulse frequency is crucial influencing factors for pulsed cathodic arc method. In recent years, the incorporation of metallic elements into the a-C films provides an effective way to improve the properties of the films, such as Ti doping, Cu doping, W doping, Cr doping and etc. [6]. Incorporating metals in a-C films considerably influence their microstructure and lead to significant changes in

electrical conductivity, biocompatibility, mechanical, optical and tribological properties. Compared with Ti-doped a-C (a-C:Ti) films containing TiC nanometer grains, copper atoms are not chemically bound with carbon in Copper-doped a-C films (a-C:Ti) [7]. In addition, some researchers also proposed a mechanism for the effect of incorporating metal on the tribological properties of the a-C films, including the relationship between variation of metals-doping and the graphitization of films [8]. It signifies that doping metal (Ti or Cu) is a promising technology improving the structure and mechanical properties of a-C films [9]. a-C films are composed of a sp<sup>2</sup> hybrid graphite phase and a sp<sup>3</sup> hybrid diamond phase. The graphite phase exists in the highly crosslinked network structure of diamond phase, which improves the a-C film by higher hardness, resistivity, thermal conductivity and chemical inertness. Recent data indicate that a-C films show high transparency in a wide wavelength range starting from ultraviolet up to infrared revealing, in turn, high resistivity, low permittivity and high refractive index. Therefore, the studied a-C films can be used as infrared antireflection films, which requires that the film thickness, its structure and optical properties (the refractive index, the extinction coefficient, the optical band gap) are precisely controlled by improved deposition technology. a-C films doped with metals such as W, Au, Pt etc. reveal excellent performance regarding to adhesion, corrosion resistance and residual stress. When choosing an ultimate element, Cu can be regarded as an ideal alternative for Pt and Au, due to its low cost, high stability and excellent electrical conductivity. However, Cu in a-C films cannot form carbide, but only a weak chemical bond between carbon and copper, which, in turn, affects the relative content of the graphite phase and the diamond phase. As it is known, the relative content of the phases influences the film properties, therefore, special methods of using Cu can be applied to get the necessary performance of a film. It is worthwhile to mention that one important feature for a-C films is its facile manipulation of their physical properties, ranging from the mechanical properties

to the photoconductivity, by simply controlling the relative ratio of the  $sp^3$  to  $sp^2$  carbons in films. However, the shortcomings of a-C films, involving the large internal stress, low adhesion and thermal stability have hindered their practical applications in engineering. For example, conventional a-C films exhibit limited adhesion to many metallic substrates and high internal compressive stress (up to 10 GPa), as a result, leading to peeling-off of the films from the substrate when the film thickness is more than 1µm. Consequently the development of a-C films with improved adhesive to metallic substrate has become one major topic in engine applications. To reduce internal stress, wear and friction, and to improve adhesion between film and substrate, one of the most efficient methods is metal doped a-C film deposited by introducing metal elements into the system. Unfortunately, the effects of metals implanted on the structure and further on the properties of a-C films are very complex, as the functions of each metal element varies. For example, some metals (e.g. Ag, Cu, etc.) do not chemically bond with carbon and only arranged in the form of nanoparticles within the diamond-like carbon matrices. The other species (e.g. Ti, W, etc.) can be chemically bonded with carbon atoms which results in the formation of the composite film with metal carbide phases. Although the introduction of metallic species can reduce the internal stress of a-C films, which on the other hand will unavoidably change the films' hardness. To our knowledge, no report has been given on the effects of binary metal doped a-C composite films on the structures and properties of a-C films with the aim to improve its surface properties. Consequently, the development of a-C films with simultaneous improved adhesion to substrate, low stress and high hardness has become one major topic in engineering applications. Recently, many stress-demoting strategies have been investigated for a-C films, such as incorporating a small percentage of metal or nonmetal ions in the films, and producing functional films in the form of interlayer or buffer layer between the substrate and a-C films. However, there are still presenting

the challenges in the deposition of carbon films with good integrated performance for engineering application. To address these shortcomings, different technological methods are used such as doping different elements or introducing interlayer in the a-C films.

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