Influence of the substrate bias on the stress in Ti-DLC films deposited by dc magnetron sputtering

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Abstract. Internal stress of titanium-diamond like carbon (Ti-DLC) films deposited by reactive sputter deposition from a titanium target in argon/acetylene atmosphere have been studied as a function of the substrate bias voltage from 0 to -80 V. The Ti-DLC films were deposited using a DC current of 150 mA and substrate temperature of as-deposited. The films were characterized by Raman spectroscopy, Auger electron spectroscopy (AES), scanning electron microscopy (SEM) and wafer curvature for stress determination. It has been observed that the compressive stress increases with increasing the substrate bias. From AES the titanium content increases with the substrate bias whereas the carbon content decreases. Raman spectroscopy indicates that line spectra and the ratios $I_D/I_G$ changes for bias voltages higher than -50 V. Based on the results, it is concluded that the variation in compressive stress is associated to changes in the chemistry and internal structure of the films.

Key Words: Ti-DLC, internal stress, magnetron sputtering.

1. Introduction

Metal-diamond like carbon (Me-DLC) films which are composed of metal particles and amorphous carbon matrix, have attracted scientific and industrial interest in large measure to the fact that Me-DLC films exhibit important properties like low friction coefficient, wear resistance and chemical inertness [1-12]. Me-DLC films is prepared by several deposition techniques including plasma assisted physical vapour deposition (PVD), an atomistic deposition process that take places at very low pressures and consist in the vaporization of metallic material from a solid target surface caused when energetic particles of positively charged ions bombard the target. Ti-DLC films are commonly deposited by reactive magnetron sputtering from titanium (Ti) target in an argon-hydrocarbon plasma under controlled experimental conditions. In order to understand the structure-property relationship of Ti-DLC films and ultimately be able to predict their physical properties, it is imperative to gather as much information on morphology, phase composition and microstructure as possible. In this sense, advanced deposition and characterization techniques for the study of Ti-DLC films are required to get a deeper understanding of the relationship between different sputter process conditions and the film properties.
During the last years, much work has been devoted to the study and understanding of the properties of Ti-DLC films, indicating that the microstructure, mechanical and tribological properties of these materials are largely dependent on the deposition conditions. Ding et al., using filtered cathodic vacuum arc technique, studied the composition, microstructure and mechanical properties of Ti-DLC deposited on silicon wafers, as a function of the negative bias voltage applied to the substrate [2]. They found that by increasing the negative bias voltage from 0 to 80 V, the internal stress and hardness increase, however, at higher negative bias voltage, the stress and hardness decrease. These results were associated to the variation of the \( sp^3 \) content in the Ti-DLC matrix. Cui et al., studied the mechanical and tribological properties of Ti-DLC films deposited on silicon substrates at room temperature using dc magnetron sputtering, as a function of the gas flow ratio of argon/methane [10]. They found that the titanium concentration in the Ti-DLC matrix depends on the argon/methane flow ratio, and for low titanium concentration, and the probability to find TiC phase is low. In this case, the hardness is high and the internal stress is low. However, when the argon/methane flow ratio is higher, the hardness decreases and the stress increases. This behaviour was attributed to the formation of the TiC phase in the Ti-DLC matrix. In the present paper we studies changes in the intrinsic stress of Ti-DLC films prepared on silicon substrate by dc reactive magnetron sputtering as a function of the negative substrate bias voltage. The correlations between these parameters with the chemistry and internal structure are discussed.

2. Experimental details
Ti-DLC films were produced in a home-made sputter deposition system. The samples were deposited by reactive dc magnetron sputtering of titanium target in an argon-acetylene plasma on a static (100) silicon wafer during 90 minutes. The substrate to target distance was 7 cm. Before deposition the chamber was pumped down to a base pressure of \(1 \times 10^{-5}\) mTorr. The argon gas flow was held constant at 6 sccm (standard cubic centimeters per minute) for the all the samples. The titanium target was sputter cleaned for 5 minutes in Ar plasma and with an applied current to the dc cathode of 150 mA. For the set of samples deposited using the bias voltage, the acetylene gas flow was held constant at 0.5 sccm. The applied DC current to the magnetron was 150 mA and the substrate temperature was of as-deposited. In order to study the effect of the substrate bias on the properties of Ti-DLC films, the negative voltage bias was varied from 0 to -80 V.

![Figure 1](image_url)

**Figure 1.** Schematic diagram showing the experimental set-up to measure the internal stress. \( d_0 \) and \( d \) are the distances between the two laser spots before and after deposition, respectively.
The surface morphology and fractured cross-sectional images of Ti-DLC films were characterized by scanning electron microscopy (SEM) using the FEI Quanta™ 250 system. The titanium and carbon contents in the Ti-DLC films were measured by Auger electron spectroscopy (AES). The Auger spectra were obtained in ultra-high vacuum (UHV) with a base pressure of $10^{-9}$ mbar, to get those conditions we use an ionic pump (Riber model 401150) with a titanium sublimation pump (Leybold-Heraeus NV12). The Ti-DLC sample was introduced to the vacuum chamber using a load lock chamber. Before the analysis, the sample was cleaning using an ion gun of argon with a current of $10^{-6}$ A and energy of 1500 eV. The energy of the primary electrons in the electron gun was 3 keV with a perpendicular incidence to the surface of the sample and a beam diameter of approximately 0.5 cm. Raman spectroscopy of Ti-DLC films was used to characterize the structural arrangement of C sites in the films. Raman spectra were obtained using a WITEC Alpha300 spectrometer. The double peak Raman spectra of the Ti-DLC films deposited at different experimental conditions were deconvoluted into D and G peaks commonly named as the disorder and graphite lines, respectively. The intensity ratio of D peak to G peak ($I_D/I_G$) was also calculated. The internal stress of the Ti-DLC films was calculated from the measured curvature of the substrate wafer before and after deposition by using the substrate curvature method, and by using the Stoney equation for stress measurements [13]. The thicknesses used in the Stoney equation to determine the internal stress, were measured using the cross sectional SEM micrographs of the Ti-DLC coatings. Figure 1 shows a schematic of the substrate curvature method for stress determination.

3. Results and Discussion

Figure 2 shows the titanium and carbon concentration in at.% determined by Auger spectroscopy in Ti-DLC coatings obtained at 0, -50 and -80 V of bias voltage. The peaks for carbon and titanium elements are also indicated. As is shown in figure 2, the titanium concentration increases from 22 at.% to 30 at.% with the increase of bias voltage, whereas the carbon concentration decreases from 78 at.% to 70 at.%. These variations of the elemental composition with the negative bias voltage are in agreement with other experimental results reported in the literature [4]. The authors related their results to the effect of re-sputtering of the carbon atoms during the deposition process, but other effects like the diffusivity of the coating elements and atomic desorption kinetics are also important to explain the experimental results.

![Figure 2](image-url)
Figure 3. Raman spectra of Ti-DLC coatings obtained at different bias voltage.

Figure 3 shows the Raman spectra for the Ti-DLC coatings deposited at 0, 50 and 80 V of negative voltage bias. The double peak Raman spectra of the Ti-DLC coatings were deconvoluted into D and G peaks. Raman spectroscopy shows a broad peak at 1576 cm$^{-1}$ and a shoulder peak centred at 1345 cm$^{-1}$, which represents the typical characteristic of hydrogenated amorphous DLC films [10]. The intensity ratios of D to G peaks (I_D/I_G) were also determined. Figure 3 (inset) shows the ratio I_D/I_G as a function of the negative bias voltage. The Raman spectra as a function of the bias voltage from 0 to -50 V do not shown a dramatic changes in the spectra line-shape, and their correspondent I_D/I_G ratio is approximately 1.3 as observed in figure 3. However, by increasing the negative bias voltage, the spectra line-shape changes increasing the I_D/I_G ratio up to 1.5. Experimental results observed in the literature, indicate that the position of the G peak and the I_D/I_G ratio are qualitatively related to the sp$^2$/sp$^3$ ratio in the DLC films [2].

Figure 4. Density of the Ti-DLC coatings as a function of the negative voltage bias. The solid line is a guide for the eye.
Figure 4 shows the density of the Ti-DLC coatings in function of the negative bias voltage from 0 to −80 V. The density of the Ti-DLC coatings was determined by dividing the deposited mass of the Ti-DLC coatings by their respective volume (the volume of the coating is obtained from the product of its thickness and the deposited area on the silicon substrate). By increasing the negative bias voltage from 0 to -50 V, the density remains almost constant at a value of 1.7 gr/cm³. However for negative bias voltage higher than -50 V, the density increases up to 3.2 gr/cm³. The decrease in the density with a bias voltage higher than -50 V is attributed to the compression in the thickness of the films as observed by cross-sectional SEM micrograph (not shown here). This effect is probably due to a high number of energetic argon ions striking the Ti-DLC film, decreasing, therefore, its thickness [4]. Figure 5 shows the dependence of the internal stress for the Ti-DLC coatings obtained at 0.5 sccm of acetylene flow as a function of the negative bias voltage. The compressive stress increases from −0.9 GPa to −2.7 GPa when raising the negative bias voltage from 0 to -80 V. By comparing with figure 3 (inset) and figure 4, the compressive stress shows a similar behaviour with both the I₀/Iₚ ratio and the density of the Ti-DLC coatings. As indicated before, the increase of compressive stress in Ti-DLC with substrate bias can be attributed to the fact that energetic ions strike the coating during deposition, promoting interstitials in a process known as ion-peening [14]. Dai e al., also associated the increases of the compressive stress to the increases of the carbide phase of the titanium (TiC) into the amorphous carbon matrix [8].

![Graph showing compressive stress in Ti-DLC deposited at 0.5 sccm of acetylene flow as a function of substrate voltage bias. The solid line is a guide for the eye.](image)

**Figure 5.** Compressive stress in Ti-DLC deposited at 0.5 sccm of acetylene flow, as a function of substrate voltage bias. The solid line is a guide for the eye.

4. Conclusions

Ti-DLC films produced by reactive dc magnetron sputtering were characterised for their chemistry and mechanical properties. The results showed that the intrinsic stress can be altered by the substrate bias, increasing it with the negative bias voltage. The Ti-DLC films exhibited a structure composed of titanium and carbon, increasing the Ti concentration with the negative bias voltage. The density increases with the voltage bias due in part to the decreasing of the thickness of the Ti-DLC films as observed by cross-sectional SEM micrographs. Finally, the results are useful in understanding of how process parameters affect the deposition of Ti-DLC films and consequently its properties.
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