# Influence of deposition parameters on the properties of Ag-C films deposited by rf magnetron sputtering

B.R. Pujada [1] †, J.L. Ampuero [1], N.Z. Calderon [1], S. Ponce [1],P. Valenzuela [2] and W. Gacitúa [2]
[1] *Faculty of Science, National University of Engineering, Av. Túpac Amaru 210, Lima, Perú.*
[2]*Faculty of Engineering, University of Bio-Bio, Av. Collao 1202, Concepción, Chile.*
† *bpujadab@uni.edu.pe*

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Surface morphology, chemical composition and hardness of silver-carbon (Ag-C) films, rich in silver, deposited by reactive sputter deposition from a silver (Ag) target onto silicon (100) substrate in an argon/acetylene plasma, have been studied as a function of acetylene flow, cathode power and substrate bias. Ag-C films were obtained at acetylene flow rates from 0 to 10 scc, and cathode powers of 120 and 150 W. Ag-C films were characterized by x-ray diffraction, Raman spectroscopy, atomic force microscopy, scanning electron microscopy and nanoindentation. It has been observed the increase of graphite-like bonds in the Ag-C films with the acetylene flow. The AFM revealed that the acetylene gas promotes changes on the surface morphology. Also, the density and hardness decrease with the acetylene flow rate. In particular, for Ag-C films deposited at acetylene flow rates from 2 to 8 sccm, the hardness decreases from 1,8 GPa to 0,40 GPa. These changes on the surface morphology and hardness are discussed in terms of atoms diffusion on the surface and the chemical composition of the Ag-C films.

**Keywords:** Thin Films, Sputtering, Hardness.

## 1 Introduction

Ag-C (silver-carbon) and Ag-DLC (silver-diamond like carbon) films which are composed of silver and amorphous carbon, have attracted increasing scientific and industrial interest in large measure to the fact that such films exhibit interesting properties like low friction coefficient, chemical inertness and antibacterial properties, constituting an multifunctional bio-film, attractive to the biomedical industry [1-16].

Depending on the carbon content and the ratio $sp^3/sp^2$, Ag-C films can also derivate in a silver-doped diamond-like-carbon (Ag-DLC) film, which shows high wear resistance and high hardness in comparison to Ag-C films.

Ag-C and also Ag-DLC films can be prepared by several deposition techniques including plasma assisted physical vapour deposition (PVD). PVD magnetron sputtering is an atomistic deposition process that occurs at very low pressures and consists in the vaporization of material from a solid target surface caused when energetic particles of positively charged ions bombard the surface. The target surface is negatively biased to make it the cathode of the discharge and an inert gas is ionized by an electric discharge to form plasma [17]. Ag-C and Ag-DLC films are commonly deposited by reactive magnetron sputtering from silver (Ag) target in an argon-hydrocarbon plasma.

In order to understand the structure-property relationship of Ag-C and Ag-DLC films and ultimately be able to predict their physical behavior, 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 Ag-C and Ag-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 Ag-C and Ag-DLC films. These works have shown that the microstructure, mechanical and antibacterial properties of these materials are largely dependent on the deposition conditions. Choi et al., using a hybrid ion beam deposition system, studied the composition, microstructure and mechanical properties of Ag-C films deposited onto Si (100), as a function of the argon fraction in the argon/hydrocarbon reaction gas [1]. They found that by increasing the argon fraction in the plasma, the silver concentration increases. Also, the hardness and compressive stress of the Ag-DLC films decrease with the silver content. The authors related their results to the variation of the chemical composition in the film and to the $sp^2/sp^3$ bonding ratio. Wang at al., studied the microstructure and mechanical properties of Ag-C films deposited by PVD magnetron sputtering on silicon substrate, as a function of silver content [5]. They found that the intrinsic compressive stress decreases with silver content into the DLC matrix whereas the hardness present a maximum value at silver content of around 10%. These results were associated to the content and size of the silver nanograins into the Ag-DLC films. Garcia-Zarco et al., studied the influence of the magnetron power supply and target-substrate distance on the structure and composition of nanocomposite a-C:Ag films deposited by PVD magnetron sputtering [7]. They found a nanostructure of silver crystalline clusters uniformly distributed in the amorphous carbon matrix at a cathode power of 40 W and a target-distance of 28 mm.

In the present paper we report and analyse surface morphology, chemical composition and hardness of a series of Ag-C films rich in silver, prepared on silicon substrate by reactive RF magnetron sputtering at various acetylene flows and rf cathode power. The correlations between the acetylene flow and rf cathode power with the hardness, chemistry and microstructure are discussed.

## 2 Experimental details

Ag-C films were produced in a home-made sputter deposition system. The samples were deposited by reactive rf magnetron sputtering of Ag target in an argon-acetylene plasma on a rotating (100) silicon wafer substrate during 10 minutes. The diameter of the target is 5.04 cm and the substrate to target distance 6 cm. Before deposition the chamber was pumped down to a base pressure of $6 \times 10^{-4}$ Pa and the substrate heated at 210 °C. The argon gas flow was held constant at 30 sccm for the complete series of samples. Before deposition, the silicon substrate was sputter etched for 5 minutes in Ar plasma with a negative substrate bias power of 30 W at pressure of 2,6 Pa. In order to obtain a silver-rich composition, a short substrate-to-target distance and high cathode power were used. A first set of Ag-C films was deposited at rf cathode power of 120 W and acetylene gas flows between 0 and 10 sccm. Also, one sample of Ag-C film was deposited at 5 sccm of acetylene flow but a rf cathode power of 150 W. In order to study the effect of the substrate bias on the hardness, we deposited a series of Ag-C films at 120 W of cathode power and 5 sccm of acetylene flow, and substrate bias of 10, 20 and 40 W.

The structure of the Ag-C films was determined by x-ray diffraction (XRD) using a Bruker D8 Advance diffractometer. The surface morphology and fractured cross-sectional images of Ag-C films were characterized using atomic force microscopy (WITec Mercury 100 AFM) and scanning electron microscopy (FEI QuantaTM 250). Ag and C contents in Ag-C films were determined by using energy dispersive spectrometer (EDS) attached on the scanning electron microscopy. Raman spectroscopy of Ag-C films was used to characterize the structural arrangement of C sites in the films. Raman spectra were obtained using a WITEC Alpha300 spectrometer. Nanoindentation tests were carried out at room temperature in order to determinate the hardness of Ag-C films. For these measurements we used a Hysitron TI-900 TriboIndenter system with a Berkovich diamond indenter tip. Hardness was determined from the load-displacement curves and calculated by the Oliver and Pharr method [18].

## 3 Results

XRD patterns of Ag-C films deposited at rf cathode power of 120 W and acetylene flows of 2 and 5 sccm are indicated in figure1-(a) and -(b), respectively. Figure 1-(c) shows the XRD pattern for Ag-C film deposited at 5 sccm of acetylene flow and rf cathode power of 150 W.

From cross sectional SEM micrographs we measured the thickness of the Ag-C films. The densities of the Ag-C films were determined by dividing the deposited mass of the films on the substrate by their volume (the volume of the films is obtained from the product of its thickness and the deposited area on the silicon substrate). The density for pure silver is 10,5 gr/cm$^3$. For Ag-C films deposited at cathode power of 120 W and acetylene flows of 2 and 5 sccm, the densities were calculated in 7,92 gr/cm$^3$ and 7,01 gr/cm$^3$, respectively. EDS results show that the silver content decreases approximately from 90 to 77 (in at%) when increasing the acetylene flow from 2 to 5 sccm, respectively. Figure 2 shows the Raman spectra for Ag-C films at different acetylene flows and cathode power. The double peak Raman spectra of the Ag-C films 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 (ID/IG) was also determined. At cathode power of 120 W, the Raman spectra for Ag-C films deposited at 2 sccm of acetylene shows the D and G peaks at 1347,55 cm$^{-1}$ and 1584,49 cm$^{-1}$, respectively, and an ID/IG ratio of 1,43 (figure 3-a). For Ag-C films deposited to 5 sccm of acetylene, the Raman spectra exhibits the D and G peaks at 1352,69 cm$^{-1}$ and 1579,47 cm$^{-1}$, respectively, and an ID/IG ratio of 1,28 (figure 3-b). Also, Raman measurement was performed for a Ag-C film deposited at acetylene flow of 5 sccm, and cathode power of 150 W (figure 3-c). For this sample, the Raman spectra exhibits the D and G peaks at 1341,62 cm$^{-1}$ and 1578,31 cm$^{-1}$, respectively, and an ID/IG ratio of 1,50.

Figure 3-a and 3-b, shows AFM images of the surface of the Ag-C films deposited at rf cathode power of 120 W and acetylene flows of 2 and 10 sccm, respectively. It can be seen from figure 2 that the surface morphology changes during growth with the acetylene flow rates. The surface of Ag-C deposited at 2 sccm of acetylene consists of many granular structures with similar sizes whereas the film deposited at 10 sccm of acetylene is principally composed of islands with different sizes distributed irregularly on the surface. At 150W of rf cathode power, the surface morphology of the Ag-C film was not significantly affected.

Figure 4 shows the dependence of the hardness of Ag-C films obtained by nanoindentation, on the acetylene flow rate. The obtained hardness for pure Ag film was 0,4 GPa. For Ag-C film deposited at 2 sccm of acetylene flow, the hardness increases up to 1,8 GPa, but for higher acetylene flows the hardness start to decreases monotonically in the studied range of acetylene. Figure 5 (inset) also shows the effect of applying bias to the substrate.

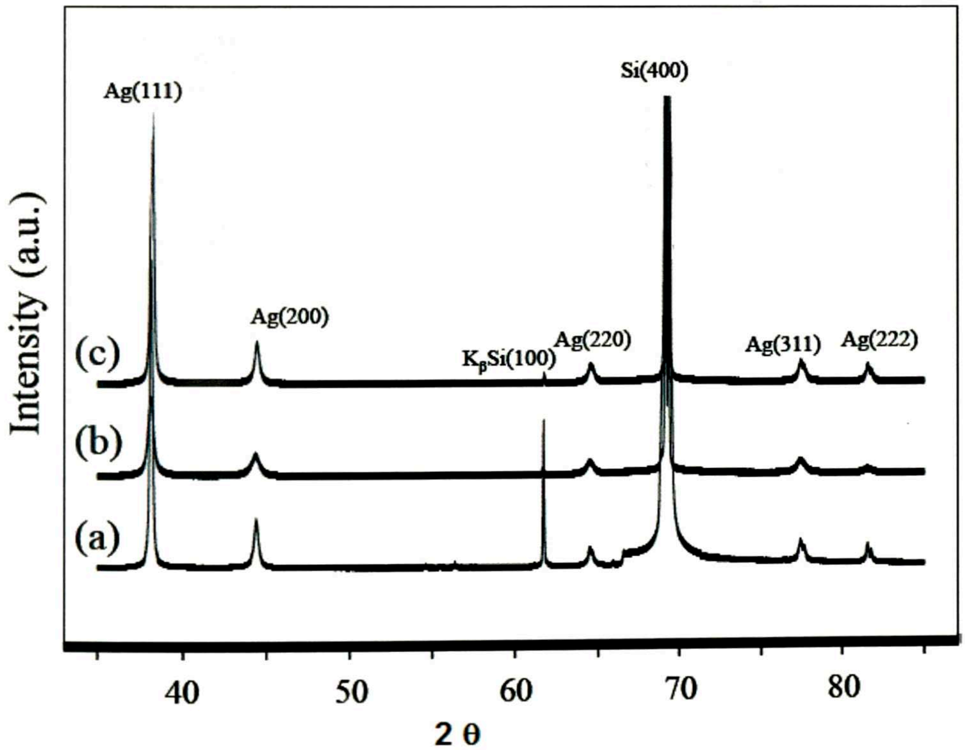


**Figure 1.** *X-ray diffraction pattern for Ag-C film, (a) at 2 sccm of scetylene flow and 120 W , (b) at 5 sccm of scetylene flow and 120 W and (c) at 5 sccm of scetylene flow and 150 W.*

An increase in substrate bias up to 20 W (for samples deposited at 5 sccm of acetylene and 120 W of cathode power), leads to the increase of hardness, however, further increase of bias power leads a slight hardness decrease.

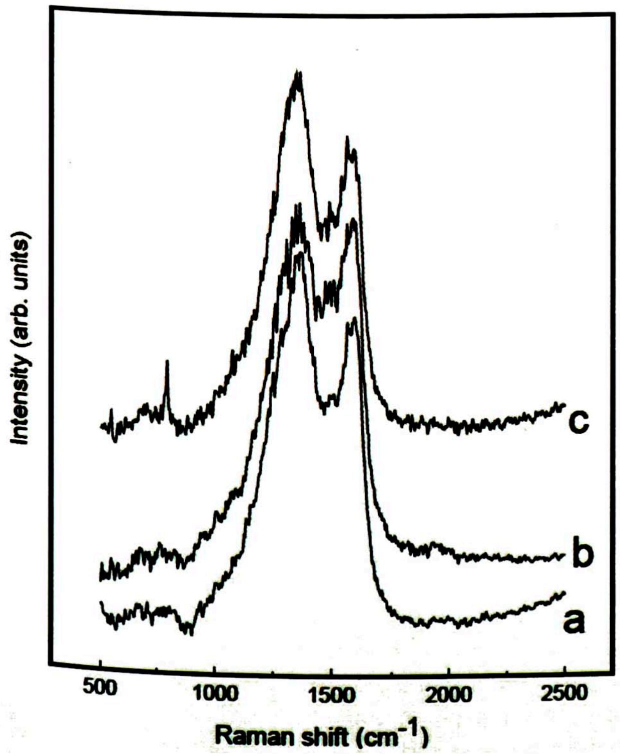


**Figure 2.** *Raman spectra of Ag-C films at different acetylene flows.*

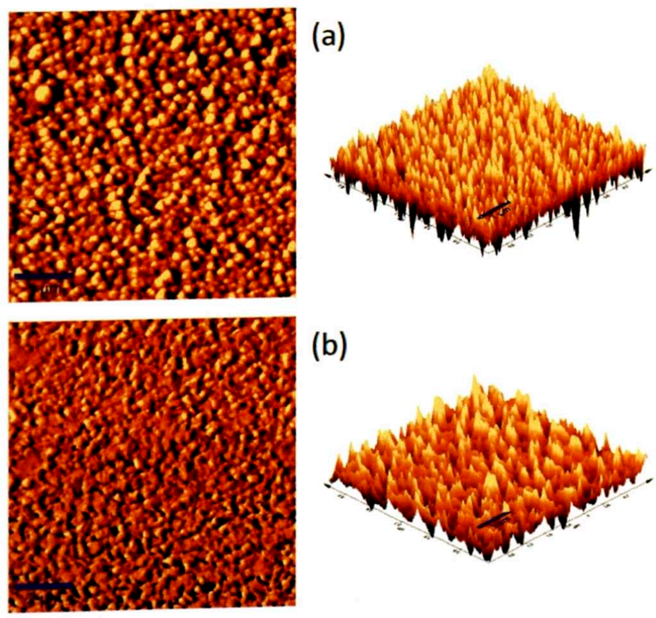


**Figure 3.** *AFM images of the surface of Ag-C films.*

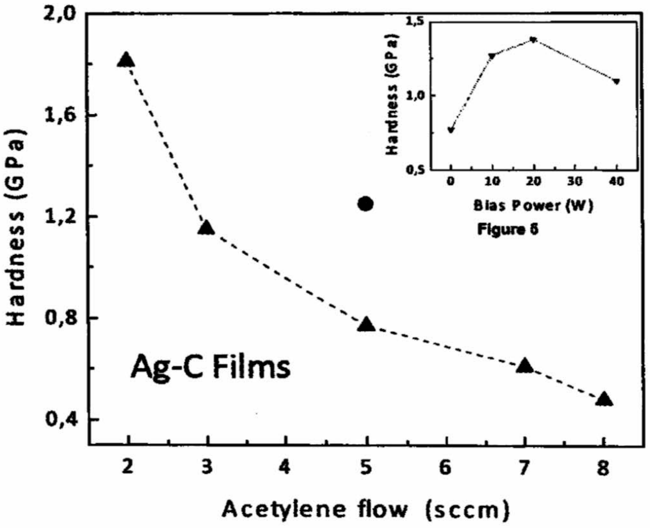


**Figure 4.** *Dependence of the hardness of Ag-C films obtained by nanoindentation, on the acetylene flow rate.*

## 4 Discussion

The high rate deposition in Ag-C films is consequence of the short substrate-to-target distance and high rf cathode power, producing silver-rich predominant composition films in agree with the XRD patterns. The density for Ag-C films diminishes with the acetylene flow rate. This effect is expected and can be attributed to the increase of the carbon content in the Ag-C films due to the acetylene dissociation during discharge [19].

The XRD patterns for Ag-C films indicate a slight dependence on the parameters deposition. From figure 1, it is clear the presence of peaks arising out from the (111), (200), (220) and (331) planes of Ag crystalline phase. Ionescu et al., in their studies of silver containing carbon amorphous nanocomposite films deposited by termionic vacuum arc technique, observed similar results in their XRD pattern, confirming the existence of Ag nanocrystalline phases in their films [8]. Chen et al., also observed similar results in their studies of phase transformation of DLC/silver composite films deposited by magnetron sputtering [20]. A slight broadening of the peaks of the Ag-C films with the acetylene flow (not shown here) was also observed, this effect could be caused by the structural disorder in silver grains due to the increase of carbon content in the film as observed from EDS results.

From Raman measurements for Ag-C films we found that by varying the acetylene flow from 2 to 5 sccm the ID/IG ratio decreases. From EDS results, the Ag content decreases with the acetylene. Also, at higher cathode power the ID/IG ratio increases with the cathode power. Choi et al., in their studies of Ag-incorporated DLC films deposited by a hybrid ion beam system, found the same dependence of the ID/IG ratio with the incorporation of Ag [1], indicating therefore the increase of $sp^2$-bonded clusters in the Ag-C film with acetylene flow.

The morphology changes revealed that adding acetylene gas into the argon plasma, its promote changes on the surface morphology. Due to the physics of the sputtering process, these changes are closely related with changes in the atoms diffusion on the surface, producing an atomic rearrangement of the silver and carbon atoms in the structure and consequently on the surface morphology of the Ag-C films. At low acetylene flow, the characteristic of AFM is the island structure with a small diameter, whereas at high acetylene flow, the average grain sizes increase but separated by deep trenches. By increasing the substrate bias, the surface morphology changes to a bigger and closely compacted islands (not shown here).

Compared with Ag-DLC films, the hardness values decrease tremendously in Ag-C films rich in silver.

Due to the acetylene dissociation, the observed hardening in Ag-C films is triggered by incorporation of carbon into the film. By increasing the acetylene flow, the changes in morphology of the Ag-C films suggest that the hardness decreases with increasing the grain size. At cathode power of 150 W (figure 4, black circle), the hardness increases in approximately 50%. The observed changes with the cathode power can be attributed to the variations in the $sp^2$ fraction in agree with Raman results. The increases of Ag-C film hardness with bias power can be associated to the energy of argon ions that penetrate through the film, removing away carbon atoms and increasing its density. However, by increasing the substrate bias from 0 to 20 W, the grain size increases and the hardness also increases. This discrepancy may be due to the formation of denser islands product of the differences in the relaxation mechanisms that dominate the morphology evolution of the Ag-C films. At higher rf bias power, the argon ions have enough energy to penetrate into the subsurface, decreasing its hardness.

## 5 Conclusions

Ag-C films produced by reactive RF magnetron sputtering were characterised for their chemistry, surface morphology and mechanical properties. The results showed that the surface morphology, chemical composition and hardness of the Ag-C films can be altered by changing the acetylene flow rate, rf cathode power and substrate bias. The Ag-C films exhibited a structure composed of silver-rich predominant composition and carbon. The XRD patterns indicated that the addition of acetylene does not change substantially the crystallographic structure of the samples. By increasing the acetylene flow rate, the hardness and density decrease whereas the carbon content and $sp^2$ bonds increase. At 150W of rf cathode power, the surface morphology of the Ag-C film was not affected but its hardness showed a higher value which was associated to the variation of the $sp^2$ bonds. The increases of the hardness of the Ag-C films with the substrate bias have been attributed to the formation of denser islan
Finally, the results are useful in understanding of

process parameters affect the deposition of Ag-C films and consequently its properties.


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