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Study of the discharge gas trapping during thin film growth

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Abstract

Discharge gas trapping in thin films produced by sputtering is known to be due to high energy neutrals bouncing back from the cathode. Qualitatively, the phenomenon is enhanced by raising the discharge voltage and is strongly dependent on the atomic masses of the discharge gas and of the cathode material. In addition to these known effects it is shown that, for a given gas, the trapped amount decreases with increasing the melting temperature of the deposited material. The results obtained both by sample melting and laser ablation are presented and discussed.

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1. INTRODUCTION

Incorporated sputter gas is often the main impurity found in thin metallic films deposited by sputtering under UHV conditions. Sputtering ions may be neutralised on arriving at the target and be backscattered from it, with an energy which depends mainly on their incident energy and on the target-to-gas atomic mass ratio [1, 2]. This phenomenon results both in mechanical bombardment of the growing film, which influences its crystallographic properties and its adhesion to the substrate, and in gas incorporation. Gas incorporation influences in turn most of the mechanical and electrical characteristics of the film, and controlling its amount allows to fine-tune the film properties, as it has been done for example in the case of superconducting niobium films [3]. Extensive Monte-Carlo calculations are available in literature to estimate the reflection probability and the energy of the reflected atoms for any gas-target combination, as well as the "burial probability" of the gas atoms [4, 5]. These data alone are however not sufficient for an easy calculation of the quantity of gas incorporated into a film in a specific coating process. In particular, the precise geometry of the sputtering apparatus, the mean free path of the gas atoms and the nature and the temperature of the substrate on which the film is grown play a determinant role which has to be accounted for separately. Direct measurement of the gas content of films is necessary for estimating these contributions.

In this paper, first results of a study of the influence of coating parameters on the gas content of films made with transition metals belonging to the 4a, 5a, 6a columns of the periodic table are presented. The variables explored are the sputtering voltage, the type of sputter gas and its pressure, and the temperature of the films, in planar and in cylindrical magnetron sputtering systems. Preliminary data on the gas contents of films made of ternary alloys of these transition metals are also presented.

2. EXPERIMENTAL PROCEDURE

Most of the samples discussed in this paper have been produced using a bakeable, UHV planar magnetron system, with a target 150 mm in diameter and a target-to-substrate distance of 65 mm. The samples, 10 mm x 10 mm in size, have been positioned on the sample holder along a circumference having a diameter of 100 mm, corresponding to the diameter of the magnets in the magnetron. Uniform and reproducible thickness and gas content are thus obtained for the several samples coated together in a single run. The sample holder is heated at about 200 °C by the discharge power, which is always kept at about 200 W in order to have comparable temperatures in different runs. To span the desired voltage range from 280 V to 400 V, it has been necessary to vary the gas pressure between 6×10^{-3} Torr and 6×10^{-4} Torr. Samples have also been coated in a second bakeable UHV system of cylindrical magnetron configuration with a cathode made of three inter-twisted wires of 1 mm diameter and a target-to-substrate distance of 20 mm. The temperature of the four samples can in this system be controlled and is normally kept at 100 °C. The magnetic field is produced with an adjustable solenoid, and the voltage can thus be varied independently from the pressure. The voltages spanned vary from 360 V up to 650 V, with a gas pressure generally at 3×10^{-2} Torr. Argon has been used as sputter gas in both systems, except for a few samples coated using krypton.

Films of Ti, V; Zr, Nb, Mo; Hf, Ta and W of thickness between 1 μm and 2 μm have been deposited both on glass and on copper substrates, the latter chemically polished and passivated in air. These substrates are known not to induce any epitaxy in the films, which grow along the most energetically favourable crystallographic plane. Changes in texture due to epitaxy modify the quantity of trapped gas, for identical coating conditions, and should thus be avoided [6].

The gas content is measured using laser ablation to vaporise the film, coupled to a calibrated gas analyser to measure the pressure of the gas released. Its layout is illustrated in Fig. 1, and is similar to an analogous device developed in the 60's [7,8]. Eight samples are mounted on a rotatable sample holder fitted on a UHV system, which is evacuated and baked at 150 °C. The vaporisation of the film is performed in static vacuum conditions maintained with a NEG pump, which does not pump the rare gases. A XeCl excimer laser of 308 nm wavelength is used to irradiate the samples through a quartz window. A few hundreds of pulses of about 120 mJ each are shot at a frequency of 1 Hz over an area smaller than 1 mm^2, and are usually sufficient to completely vaporise films up to 2 μm in thickness. The pressure of the released gas is recorded during the sequence of pulses, and shows a monotonical growth followed by a plateau from which the total quantity of gas released can be calculated. The irradiated area is subsequently measured in an optical microscope by image analysis techniques, as illustrated in Fig. 2. The irradiated region presents damaged boundaries of an area much smaller than the vaporised area, and a possible gas release from them does not introduce significant errors in the measurement. The measurement of the thickness of the films is performed by X-ray fluorescence on copper substrates and by stylus profilometry on glass substrates. The uncertainty in the calculation of the gas content is estimated at ± 12%, to which a systematic error of ± 20% for the calibration of the gas analyser should be added in calculating the absolute concentrations. It has been directly verified that the nature of the substrate, either glass or passivated copper, does not influence the gas content.

Gas content has also been measured on a few niobium films by thermal extraction using eutectic melting, a method already described elsewhere [9]. An UHV vacuum furnace where the released gas is accumulated in a closed volume has been used to melt the samples. The results obtained with this technique are comparable to those obtained by laser ablation.

Figures 3a and 3b illustrate the gas content of Hf, Ta, and W films (third row of the periodic table) and of Zr, Nb, Mo films (second row of the periodic table) deposited in the planar magnetron system using argon as sputter gas. Films of Ti and V (first row of the periodic table) have also been deposited but their Ar content was lower than the detection limit. The latter coatings have been repeated with the cylindrical magnetron system, and the Ar content measurements are illustrated in Fig. 4. Cr coatings have not been attempted.

The Ar content of Ti coatings performed at various temperatures and sputter gas pressures with the cylindrical magnetron system is reported in Fig. 5. Zr has been deposited at identical voltage in the two coating systems to provide a correlation point.

3. DISCUSSION

It is commonly understood that the quantity of gas implanted in a sputtered film depends on the energy of the gas atoms backscattered from the target, and thus in first approximation on the applied plasma voltage. This trend is very well followed by all the data reported in Fig. 3 and Fig. 4. The huge difference in the scale of gas content between Fig. 3a and 3b is due to the higher atomic mass ratio between the elements of the third row of the periodic table and argon, compared to those of the second row. A consequence of a higher atomic mass ratio is a higher energy of the atoms backscattered from the target for an equal incident energy. Not all backscattered atoms are implanted in the growing film as some may be reflected, but the reflection probability decreases monotonically with increasing energy [4]. However, the reflection probability depends also on the mass ratio, and increases with increasing mass ratio. These two counteracting effects of an increased mass ratio together with an increased backscattering probability at the target produce indeed a higher implantation rate in the film. A theoretical estimation can be carried out only when considering strict normal incidences. In a magnetron coating system, the trajectories of the energetic atoms have wide angular distributions, perturbed

by scattering on the thermalised gas present in the system, and simple calculations do not allow a quantitative prediction.

The importance of the geometry of the coating system, and thus of the angular distribution of the backscattered atoms is underlined by Fig. 4. The Ar content of Ti and V films produced with the cylindrical magnetron system is much higher than for films produced with the planar magnetron, where the gas content is below the detection limit of the measuring apparatus. A confirmation is obtained from a Zr coating performed at 360 V, voltage that is also within the range applied to the planar magnetron, which has an Ar content of 960 ppm ± 120 ppm. The gas atoms backscattered from the target may be reflected from the growing film, but in a cylindrical geometry the new trajectory will most likely be directed towards another region of the film and not towards the cathode, which has a small cross section. This process increases the gas content of the film. Furthermore, as discussed in [10], in a cylindrical magnetron the gas atoms can be backscattered tangentially to the target and still be directed towards the film, contrary to a planar geometry. Their energy will then be higher than in perpendicular backscattering, resulting in higher implantation rates.

The argon content of Ti and V films deposited at 1.5 kV with the cylindrical magnetron system (6200 ppm ± 800 ppm and 1540 ppm ± 190 ppm respectively) maintains the same proportion than in films deposited at lower discharge voltage. The proportionality is not preserved when comparing Ti with Zr, since a Zr film deposited at 1.5 kV contains only 9900 ppm ± 130 ppm of Ar. The greatly different mass ratio can result in a different shape of the energy dependence of the reflection probability, thus justifying in part this result.

The energy and the angular distribution of the backscattered atoms are also modified by collision with gas atoms at thermal energies. This has been verified in the cylindrical magnetron where the standard coating pressure results in a mean free path of the order of a few mm, much shorter than in the planar magnetron. The results plotted in Fig. 5 confirm that lower pressures result in higher gas trapping in the film due to the higher energy of the backscattered atoms.

The coating temperature is also known to influence the quantity of gas trapped in a film [11]. The temperature acts on weakly bound gas atoms at the surface of the growing film, which are released by thermal activation before being buried by the incoming metal atoms. A few preliminary tests have been performed, by depositing Ti films in the cylindrical magnetron system at four different temperatures, and the results are also plotted in Fig. 5, where a decrease in gas content with increasing temperature is clearly evident.

Although the difference in atomic mass ratio between the target and the gas can grossly explain the difference in argon content between films made of materials belonging to different rows of the periodic table, it cannot explain the wide spread existing between materials in the same row and only a few atomic mass units apart. The substitutional implantation of a gas atom depends on the energy needed for displacing the lattice atoms from their rest position to interstitial sites [5]. This quantity is related in first approximation to macroscopic quantities such as the density of the material or its melting point. Both these quantities increase going from the 4a materials to those in 6a, meaning that the displacement of lattice atoms is more difficult and thus the implantation of gas reduced. These considerations are in qualitative agreement with the experimental data. A possible second-order effect of the hexagonal structure of the 4a materials compared to the bcc structure of the 5a and 6a materials cannot however be excluded.

The same reasoning can be applied to qualitatively explain the data of Hf and Ta coatings performed using Kr as sputter gas, which are reported in Fig. 3b. From the point of view of the atomic mass ratio alone the combinations Zr/Ar and Hf/Kr and the combinations Nb/Ar and Ta/Kr should behave in an identical way. However the higher density and melting point of Hf and Ta compared to Zr and Nb could well explain a lower gas content.

Preliminary results on nano-crystalline TiZrV alloy films deposited in a cylindrical magnetron with an inter-twisted composite cathode indicate that the gas content can be as high

as 3500 ppm. A reduction in gas content at a level of a few tens of ppm is obtained when Kr is used as sputter gas. Experiments performed in a three-target planar magnetron system indicate that the gas content is correlated to the quantity of Zr present in the alloy.

4.   CONCLUSION

The discharge gas content of sputter-deposited thin films has been measured by laser ablation and sample melting, with consistent results. Besides the known dependence on the applied discharge voltage, discharge gas-to-target atomic mass ratio, discharge pressure and substrate temperature during coating, a new dependence on film material density and melting temperature has been observed. It is interpreted as a consequence of the energy required to displace a film atom from its lattice position to interstitial sites. First results on alloys suggest that this effect can even be dominating.

## Acknowledgement

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Figures

Figure 1 - Schematics of the laser ablation apparatus for the measurement of rare gas content in films produced by sputtering.
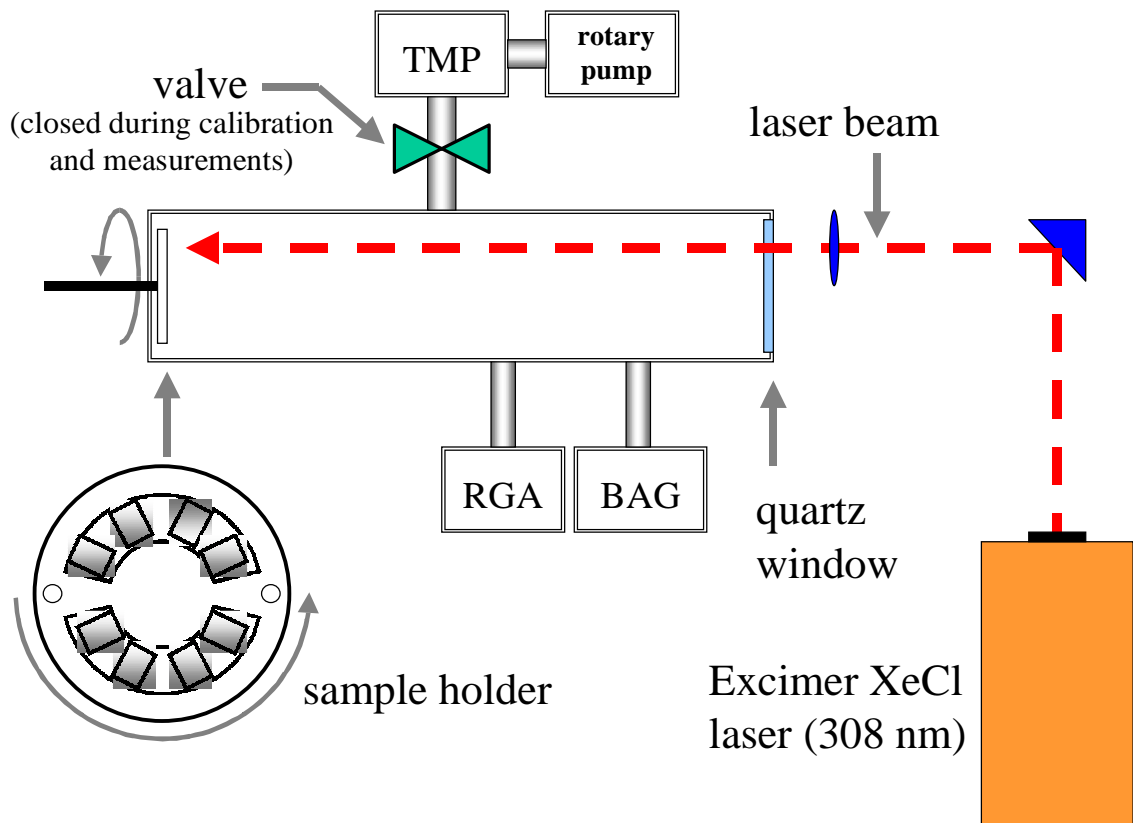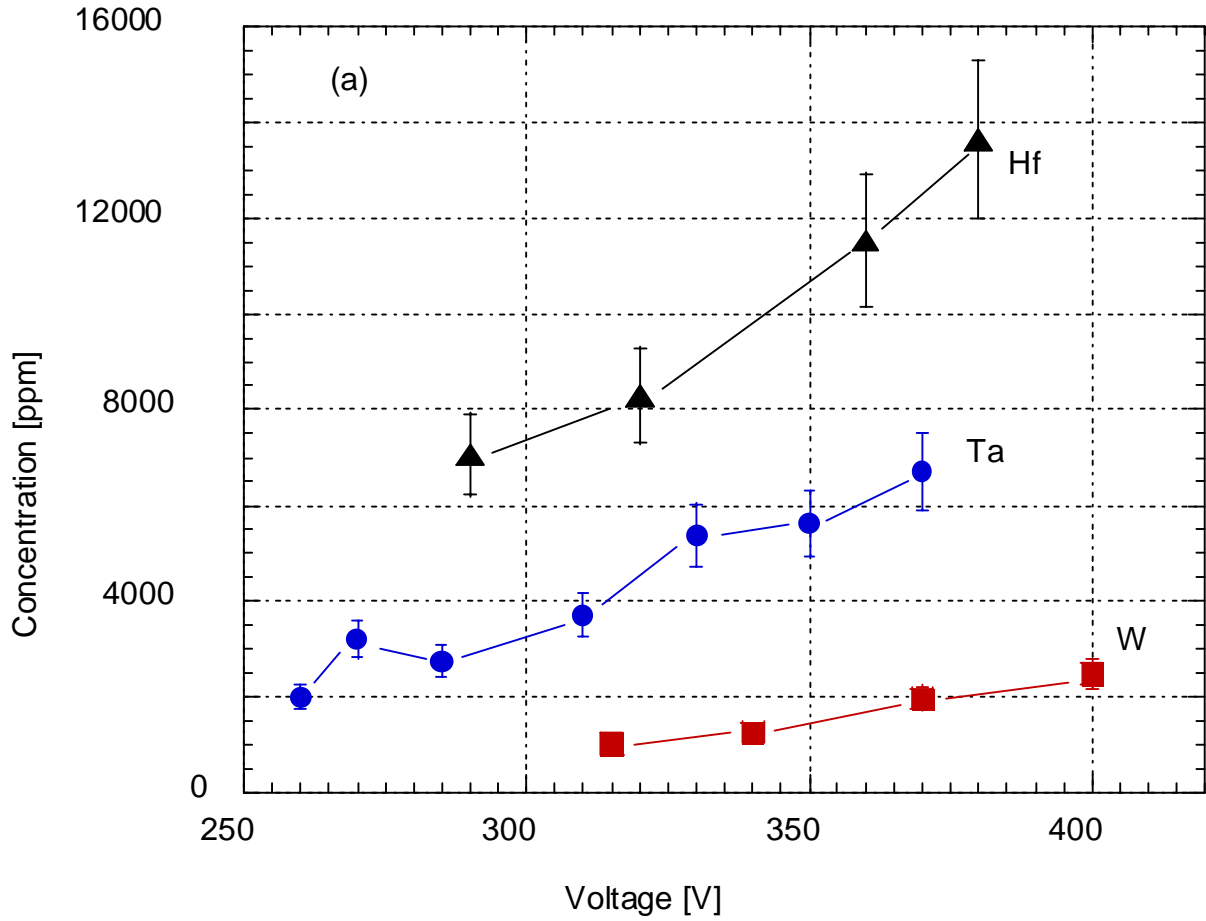
**Figure 2 -** SEM image of the crater produced in a film by the laser ablation**.**
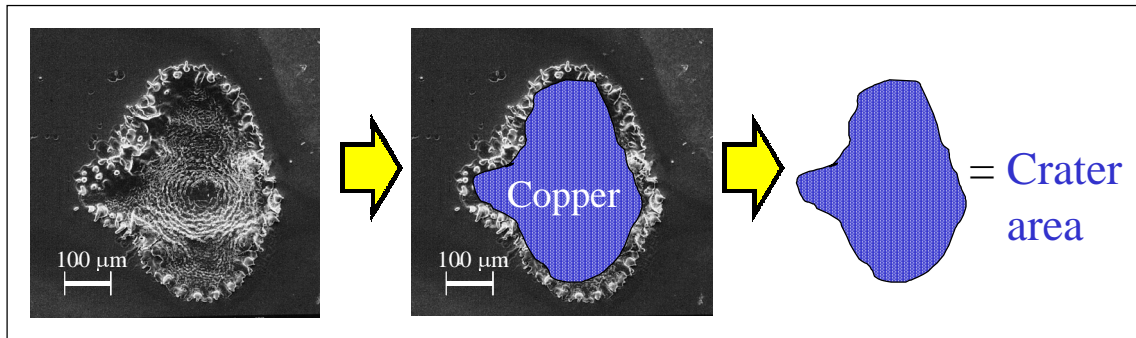
Figure 3 – Argon content

(a) Argon content in Hf (triangles), Ta (circles), W (squares) films produced with the planar magnetron system. The error bars correspond to the uncertainty described in the text.

(b) Argon content in Zr (triangles), Nb (circles), Mo (squares) films produced in similar conditions as the films above. Also reported here is the krypton content of one Hf (cross) and a few Ta (diamonds) films. The lines in both plots are intended only as a guide for the eye.
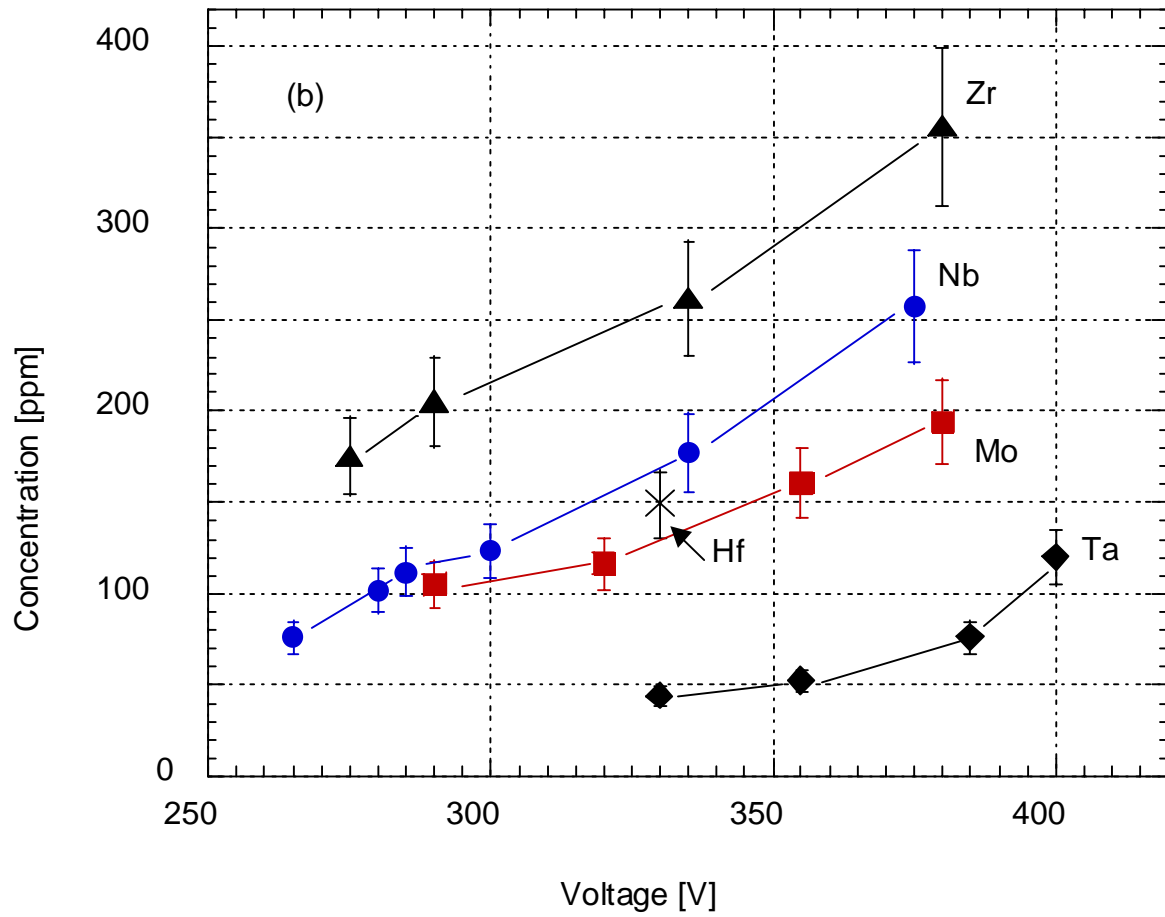
Figure 4 - Argon content in Ti (triangles) and V (circles) films produced with the cylindrical magnetron system. The error bars correspond to the minimum and maximum value obtained within a series of four samples. All the coatings have been performed at an Ar pressure of 3×10^{-2} Torr.
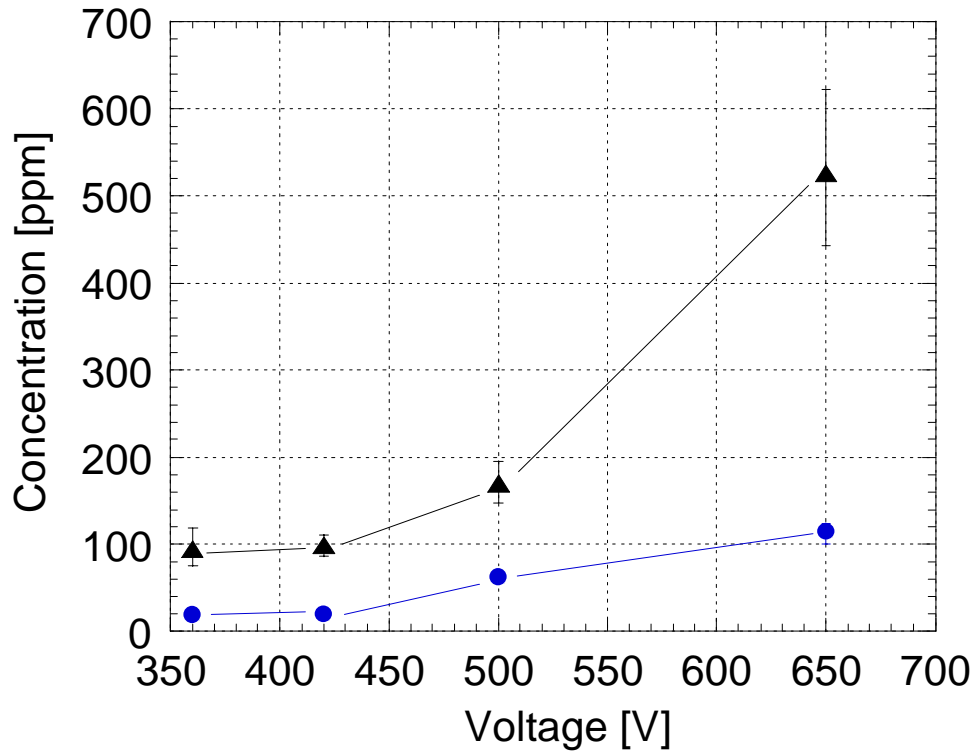
Figure 5 -   Argon content in Ti films produced at the fixed pressure of 3 x 10^{-2} Torr and different temperatures (circles), and at the fixed temperature of 100 ºC and different pressures (triangles). All coatings have been performed at 500 V.