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# **Microstructure and composition evolution of He charged solid-gas nanocomposite films of different matrix elements during thermal annealing in vacuum**

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1 analyses are presented from ion beam analysis (IBA) and scanning and transmission  
2 electron microscopies (SEM and TEM). Helium desorption was investigated by IBA in a  
3 dedicated chamber for “in situ” thermal evolution in vacuum. The simultaneous recording  
4 of the helium and matrix-element signals shows different behaviors of the different matrix  
5 elements (i.e. Co, Si and Zr) and deposition conditions (i.e, DC or RF discharge modes  
6 and dynamic or quasistatic vacuum). Effusion, blistering, delamination and flaking have  
7 been observed for the different samples leading to the formation of nano-  
8 porous/nanostructured thin films. The methodology is being envisaged as a process for  
9 nanostructured thin-films fabrication with potential applications.

10

## 11 **Introduction**

12 The predominant characteristic of noble gas atoms implanted in most solids through ion  
13 beam irradiation, across a wide energy spectrum (500 keV-100 eV), is their high heat of  
14 solution. This results in nearly zero solubility and the precipitation of gas atoms, forming  
15 small 'bubbles' [1-5]. Helium, in particular, has been extensively studied due to its  
16 technological importance in examining damage in nuclear reactor materials [6-7]. Helium  
17 plasma irradiation of metal surfaces was reported to produce fuzzy nanostructures  
18 together with He bubbles formation [8-10]. Also the growth process of aluminum thin  
19 films by MS, using different Ar/He plasma mixtures, showed that in the He rich plasma  
20 regime the film nanostructure can be controlled from He bubbles formation (closed pores)  
21 to a highly porous fiber-form nanostructure [11]. At the ICMS laboratory in Seville  
22 special attention was paid to the investigation of helium incorporation and He filled pores  
23 formation during magnetron sputtering (MS) deposition of thin films of silicon [12-13]  
24 and cobalt [14]. Also, other authors have reported He incorporation in Ti [15-16] and C  
25 [17] during MS deposition using He as process gas. The development of what we named

1 “solid-gas” nanocomposite films allowed to propose these films as solid-targets of noble  
2 gases for nuclear reactions [18-21] and spectroscopic studies [22]. This avoids the use of  
3 cryogenic or high-pressure cells facilitating usage, reducing energy straggling effects and  
4 simplifying geometry for calculations. In addition, due to their intrinsic nanoporosity  
5 (filled with gas), the silicon films fabricated by MS in pure He show a reduced refractive  
6 index [12] and have been used for the fabrication of optical devices [23]. In another  
7 previous work we have demonstrated improved activity for the catalytic combustion of  
8 hydrogen in Pt-Cu porous films prepared by MS deposition in helium followed by  
9 dealloying. The effect has been attributed to enhanced lattice strain effects associated to  
10 the nanoporosity of the as prepared films [24].

11 Building on the above-described state of the art, we present in this article the study of  
12 Helium release by heating in vacuum the He-charged films fabricated by magnetron  
13 sputtering in helium plasma. Different matrix elements and different deposition  
14 conditions were investigated. In two previous works first results were presented for the  
15 case of Si:He films [25-26]. The simultaneous recording by IBA analysis of the helium  
16 and the matrix-element signals during “in situ” annealing experiments are presented here  
17 for the first time. Also, the microstructure of the films before and after annealing was  
18 analyzed by electron microscopy (SEM and TEM). The article aims to presents the  
19 different mechanism of He release for three investigated matrix elements (Co, Si and Zr)  
20 evolving from He filled nanocomposite to different nanoporous structures. The work also  
21 aims to show the fabrication of porous structures out of the different He-charged films.  
22 This contributing to the actual growing knowledge on the fabrication and applications of  
23 films and coatings obtained by magnetron sputtering using Helium as process gas.

24

25

# 1 **Results**

## 2 **Solid-gas nanocomposite films: preparation and characterization (by IBA).**

3 Table 1 summarizes the nomenclature of the investigated samples along with their MS  
4 deposition parameters: substrate onto which the film was growth, deposition time, gas  
5 pressure, discharge power and evaluated deposition rates. Table 2 shows the absolute  
6 determination of He and “matrix element (M)” area densities, given in  $10^{15}$  atom/cm<sup>2</sup>  
7 (TFU units), for the total film thickness of the as prepared samples. Atomic ratios of He  
8 to matrix elements have been also included in the table. The solid-gas nanocomposite  
9 nature of the “as prepared” films is therefore demonstrated by the IBA analysis results.  
10 Considering the matrix element total areal densities in at/cm<sup>2</sup> and the film thicknesses,  
11 the density of the films, in number of atoms per cm<sup>3</sup>, were evaluated. These values were  
12 compared to reported densities for amorphous-Si, Co and Zr. The reduction in density is  
13 therefore used to quantify the % of porosity and the results are included in Table 2. Film  
14 thicknesses have been determined from “cross-sectional” SEM images showed in the  
15 following section.

16 In our previous work for Si films in Ref. 25, we found that oxygen incorporation during  
17 film growth promotes He diffusivity and therefore reduces He accumulation. In this study  
18 we worked under optimum conditions to minimize possible impurities bellow 5 at% for  
19 these films. For the case of Zr the oxygen incorporation is relevant and needs to be  
20 considered more in detail. It can be estimated from RBS results and it is of the order of  
21 15 at% in sample 5 and 45 at% in sample 6, which is the most porous. Actually, the  
22 incorporation of oxygen can take place during the growth, and is promoted when the  
23 deposition rate is low, which is the case in 100% He (sample 6). However, it may also  
24 occur after the growth due to air exposure when porosity is high and included closed  
25 nanopores but also open porosity. In this last case, the role of oxygen incorporation on

1 the growth process itself would be less relevant for sample 6. For additional information  
2 we refer to Ref. 11 where the growth of Aluminum films, in pure He and different He+Ar  
3 mixtures were investigated. In this article it was also shown that the plasma drastically  
4 changed, turning from 95% He to 100% He compositions [11].

5 **Thermal annealing of solid-gas nanocomposite films: “*In situ*” IBA analyses coupled**  
6 **to microstructural characterization before and after annealing.**

7 For each of five investigated samples the IBA signals of helium and the corresponding  
8 matrix element were simultaneously recorded during annealing in the dedicated  
9 DIADHEM chamber. In order to facilitate the visualization and quantification of the  
10 matrix element signals, Co and Zr films were grown on silicon wafer substrates while  
11 glassy carbon substrates were used for the Si films. SEM (top and cross views) and TEM  
12 images were also recorded for the samples before and after annealing.

13 **Fig. 1** shows the results for the cobalt film (sample 1). Even at the lower resolution  
14 achieved with the SEM microscope, top and cross images of the as prepared film show  
15 strong porosity and nano-structuration. Thermal annealing in vacuum produces the He  
16 release without modification of the cobalt IBA signal (Fig. 1a). A noticeable He release  
17 starts at 673 K. The nanoporous structure is maintained, both in the “top” and “cross-  
18 sectional” images although an increase in pores size was clearly observed. These results  
19 can be described as a helium effusion mechanism associated to a matrix modification due  
20 to ductility of the cobalt nanoporous structure under He release pressure at the reached  
21 temperatures of up-to 873 K [27]. Complementary results (before and after annealing) are  
22 presented in **Fig. 2** from TEM images of the Co films at low (top) and high (bottom)  
23 magnifications. The strong porosity and the increase in pore sizes after annealing is also  
24 clearly visualized at the higher resolution achievable by TEM. In addition, the higher  
25 magnification TEM images allow to visualize the characteristic contrast associated to

1 nanobubbles/(He-filled nano-pores) [13]. Arrows are used in the high magnification  
2 images to indicate some of these nano-pores. Some larger ones appeared in the annealed  
3 sample and are clearly faceted. This effect is associated to the crystalline character of the  
4 Co film (see Fig. 1s (a) in the supporting information file). Smaller and round  
5 nanobubbles are also clearly observed both in the “as prepared” and ”annealed” samples.  
6 **Fig. 3** shows the results for the Si film grown in DC mode (sample 2). In comparison to  
7 cobalt, at the resolution achieved by SEM, the “cross-sectional” images for this sample  
8 does not show pores. For the visualization of nanopores TEM resolution is needed due to  
9 the smaller pore sizes in this sample. First relevant observation in Fig. 3 is a moderate  
10 blistering in the top view low magnification SEM image for the as prepared film (sample  
11 2) that become stronger after annealing. Also after annealing both smaller and bigger  
12 blisters are observed. An image of one blister can be seen in the high magnification inset  
13 in the SEM “cross-sectional” image after annealing. For sample 2 blistering produces the  
14 local detachment of the Si film coupled to He release. This leads to the simultaneous  
15 decrease of the Si and Helium IBA signals observed in Fig. 3a under annealing from ca.  
16 515 to 573 K. For further heating helium release occurs continuously without  
17 modification of the silicon signal. Blistering appears to be a consequence of the higher  
18 stress reported for the Si films fabricated in DC conditions [25]. Fig. 2s in supporting  
19 information shows two enlarged “cross-sectional” SEM images of representative areas  
20 showing different sizes of blisters for sample 2 after annealing. Complementary results  
21 (before and after annealing) are presented in **Fig. 4** from TEM images of sample 2. The  
22 characteristic structure associated to numerous nanobubbles/nano-pores [12-13] is clearly  
23 observed. The pores for the Si matrix are not faceted due to the amorphous character of  
24 the Si films. See Fig 1s (b) in supporting information showing the absence of

1 characteristic diffraction peaks for Si. In spite of the blistering effect, the pore size and  
2 shape distribution are similar in the remaining Si film before and after He release.

3 **Fig. 5** shows the results for the Si film grown in RF mode (sample 3). As compared to the  
4 sample fabricated in DC mode, the absence of blistering in this sample is obvious from  
5 the top view images after annealing. This correlates with the observation, during the  
6 thermal annealing in vacuum, of He release (starting at 625 K) without modification of  
7 the silicon IBA signal (Fig. 5a). An effusion mechanism is therefore proposed without  
8 producing significant changes in the nano-porous structure of the Si matrix. For the  
9 visualization of nanopores, TEM resolution is needed. **Fig. 6** shows representative TEM  
10 images of sample 3 showing the characteristic structure associated to nanobubbles/nano-  
11 pores. Similar pore size and shape distributions are observed before and after He release.  
12 The pores are not faceted in agreement with the amorphous character of the Si films.

13 **Fig. 7** shows the results for the Si film grown using the  $^3\text{He}$  isotope as the process gas  
14 (sample 4). Note that in the rest of the samples  $^4\text{He}$  was always used. The “top-view” and  
15 “cross-sectional” SEM images clearly show a delamination effect during the thermal  
16 annealing in vacuum. This effect also explains the observed simultaneous decrease of the  
17 He and Si signals during the in-situ IBA analysis (Fig. 7a). The behavior is attributed to  
18 the particular case of the use of  $^3\text{He}$  as process gas. During fabrication of  $^4\text{He}$  charged  
19 films by MS deposition, we work in a dynamic operation mode [12, 14]. In this mode the  
20 He pressure in the chamber is established by introducing a given gas flow and controlling  
21 the aperture of a throttle valve that is connected to a continuous pumping system [12, 14].  
22 For the case of the  $^3\text{He}$  isotope a quasi-static method is used to strongly reduce the  
23 consumption of the costly  $^3\text{He}$  [19-20]. In this method the throttle bulb is almost closed  
24 and the helium working pressure is established with a needle valve employing a very low  
25 gas flux. We tentatively attribute this delamination effect to a different temperature

1 regulation during film growth. Thermal conductivity of Helium is high and the minimum  
2 He flux used in quasi-static mode leads to a higher temperature at the substrate (486K for  
3 sample 4 as compared to 393K for sample 3). The resulting delamination effect in this  
4 work is however relevant in the context of the fabrication of exfoliated silicon films [28,  
5 29]. Complementary results (before and after annealing) are presented in **Fig. 8** from  
6 TEM images of sample 4. The characteristic structure associated to numerous  
7 nanobubbles/nano-pores is observed. The pores are again not faceted due to the  
8 amorphous character of the Si films. A delamination border is also shown for the  
9 annealed sample in the higher resolution TEM image.

10 **Fig. 9** shows the results for the Zr film grown in 95%He+5%Ar mixture and in DC mode  
11 (sample 5). The “top-view” and “cross-sectional” SEM images evidence a columnar “as-  
12 prepared” film. After annealing, a notorious flaking effect is evidenced. Large (several to  
13 10  $\mu\text{m}$ ) almost spherical interconnected zones are visible. They exhibit a rough surface  
14 state, whereas unaffected surface state is found in areas where the film is still present.  
15 The extended damages caused to the film by the release of both He and part of the Zr are  
16 clearly observed on the “cross-sectional” SEM images. This flaking effect correlates with  
17 the simultaneous sharp decrease of the Zr and He signals as measured by *in-situ* IBA  
18 analyses (Fig. 9a). The Zr films are stable up to temperatures as high as 773 K when the  
19 helium release starts accompanied by flaking of the film. Due to the micrometer scale of  
20 the blisters forms by annealing on Zr films, TEM images are only provided in **Fig. 10** for  
21 the as-prepared He-charged zirconium films synthesized in pure He plasma. Nano-  
22 bubbles from 5 nm to 25 nm (marked by arrows) are clearly observed almost  
23 homogeneously spread over the thickness in this sample. Additional images obtained by  
24 SEM-EDS measurements have been included in Fig. 3s of the supporting information file  
25 for the Zr:He+Ar-DC sample after annealing. The EDS spectra couple to elemental

1 mapping of Si (as substrate) and Zr from the film, confirm the strong flaking for this  
2 sample under thermal annealing.

3

#### 4 **Discussion**

5 In this work we used the MS deposition methodology in helium plasmas for the  
6 fabrication of solid-gas nanocomposite films of Co, Si and Zr. Helium incorporation  
7 reached high values in the range of  $1 \times 10^{18}$  to  $3 \times 10^{18}$  contents (in number of atoms per  
8  $\text{cm}^2$  units). In terms of atomic percentages, He contents achieved a maximum of 42 at%  
9 value for sample 3 (Si:He-RF). The fabrication of solid-gas nanocomposite films is  
10 therefore clearly demonstrated. The helium content is measured by the IBA technique in  
11 a macroscopic area covering matrix and pores. However, from the previous results using  
12 EELS (Electron Energy Loss Spectroscopy) in a TEM microscope [30], we know that  
13 helium is located inside the pores as also reported for Helium implanted samples [30].  
14 Helium in the matrix if any is not relevant. In addition, the smaller pores stabilize the  
15 higher densities and pressures of trapped He (nanobubbles) [30], therefore a direct  
16 correlation of porosity with the measured total He content is not straight forward. The  
17 microstructural characterization in SEM, and at higher magnifications in TEM, allows to  
18 identify contrast details which correspond to He bubbles as described in the previous He  
19 implantation works [1-5]. Alternatively, we describe the He bubbles in these films as He  
20 filled nanopores formed during the MS deposition procedure [30]. For the case of the  
21 cobalt matrix, we may first notice that pores are larger, and the amount of trapped Helium  
22 is smaller, as compared to values found for the silicon matrix. It is interesting to note that  
23 the microstructures of Co and Zr He-charged films are very different, even at similar He  
24 content (E49 and G2). This indicates that the different deposition conditions play a major  
25 role in the trapping and releasing processes of He in magneton sputter deposition.

1 Starting from this description of the solid-gas nanocomposite films we also present in this  
2 paper the study of the He release elucidating the evolution of the microstructure. For the  
3 different matrix elements, different nanostructures are formed after helium desorption. It  
4 is worth to emphasize the simultaneous recording of the helium and matrix-element IBA  
5 signals in a dedicated chamber for “in situ” thermal evolution in vacuum. Different  
6 behaviors are described for the different matrix elements. One of the main results obtained  
7 in this work is that blistering (flaking), only evidenced in DC sputtered films (Zr and Si),  
8 appears as a consequence of higher stress for the films fabricated in such conditions [25].  
9 It is well known that the energy distribution functions of film forming species (depositing  
10 atoms and neutralized backscattered He ions) are different in RF and DC discharges.  
11 Therefore, for the silicon films the effect of the microstructure in the as-prepared sample  
12 **2** (Si:He-DC), incorporating both pores and blistering (Fig. 3), is likely affecting its  
13 lowest temperature when He release starts (515 K). For sample **3** (Si:He-RF), although  
14 with similar He/M ratio, the reduced blistering lead to stable films up to 625 K. For the  
15 case of sample **4** (Si:3He-RF), with the lowest He/M ratio, He release coupled to  
16 delamination starts in the range 673 to 723 K. For the case of a cobalt matrix, it is worth  
17 to mention the strong deformation of the matrix during He release under thermal  
18 annealing.

19 In conclusion, the here investigated thermal annealing procedure is leading to the  
20 fabrication of nano-porous and nano-structured films opening the scope for applications.  
21 In perspective the materials investigated in this work are expanding applications. An  
22 example are the recent reports of the use of porous amorphous Silicon [31] and  
23 Germanium [32] films as anodes for all-solid-state lithium batteries. The nanostructured  
24 films (fabricated by He assisted MS) can relieve deformation-induced stress and therefore  
25 enhance cycling performance.

1

## 2 **Methods**

### 3 **Films fabrication by magnetron sputtering in He plasma:**

4 **Co and Si films charged with Helium:** These films were prepared in a magnetron  
5 sputtering (MS) deposition chamber (residual vacuum in the range  $1 \times 10^{-4}$  Pa), operated  
6 with magnetron heads for 2 inches cathodes placed on top of the sample holder. For the  
7 preparation of the Co film, a magnetron from de AJA (USA) company was used with the  
8 adequate magnets configuration to work with magnetic targets. For the Si films we used  
9 a magnetron ION'X from the TFC (Germany) company. For operation power supplies  
10 from CesarRF-Dressler and Advance Energy-Pinnacle Plus were respectively used in RF  
11 and DC mode with constant power. The sample holder is at floating potential and was not  
12 cooled during the process. To estimate and monitor the substrate temperature during film  
13 growth, a thermocouple is placed in a lateral zone of the sample holder a few millimeters  
14 above the surface. The Si and Co targets were supplied from Neyco respectively with  
15 99,999 % and 99,95 % purity. The distance from target to substrate was 8 cm for Cobalt  
16 and 10 cm for Silicon. As process gas we used He (and Ar for targets cleaning) supplied  
17 by Air Liquid with 99,999 % purity. The  $^3\text{He}$  was supplied by Chemgas ( $\geq 99.9\%$  purity).  
18 Table 1 summarizes the nomenclature of investigated samples along with their deposition  
19 parameters (gas pressures, power and time).

20 **Zr films charged with Helium:** films were deposited onto (100) oriented p-doped Si  
21 wafers by sputtering a 4-inch. Zr target (99.999% purity from Neyco). The substrates  
22 were pasted on a rotating substrate holder, and the distance between the substrate and the  
23 target was fixed at 12 cm. The system was kept under vacuum, reaching a base pressure  
24 of about  $6 \times 10^{-6}$  mb. The total pressure in the chamber was settled to 1 Pa using a gate  
25 valve before turning on the discharge. The Ar and He gas flow rates were adjusted using

1 two Bronkhorst EL-FLOW mass flow controllers. The discharge current was regulated  
2 and set at 1 A using a DC power supply (Pinnacle plus from Advanced Energy). When  
3 the plasma is initiated in pure He, the resulting power was 300 W. In such working  
4 conditions, because of the discharge characteristics and of the very low sputtering yield,  
5 the deposition rate is very limited (about 2 nm/min as reported in table 1). To study films  
6 of comparable thickness we decided to synthesize a second Zr sample, using a gas mixture  
7 containing 95% of He and 5% of Ar. As reported in reference for Al [11], with such a gas  
8 ratio, the deposition rate is significantly increased, while He is still incorporated inside  
9 the film, even at higher percentages than in pure He plasma.

10 Co and Zr films were grown on 100 Si wafer substrates (0.5 mm thick) provided from  
11 Neyco. Si films were grown on the same Si substrates and on glassy carbon substrates  
12 (0.5 mm thick) also provided by Neyco.

13

#### 14 **Films characterization by IBA analyses:**

15 For the as prepared samples the elemental analyses were done in two laboratories: **(i) At**  
16 **the National Centre for Accelerators (CNA, Seville, Spain)** for the helium charged Co  
17 and Si films. Proton elastic back scattering (p-EBS) was employed using a 2.0 MeV  
18 proton beam and a passivated implanted planar-silicon (PIPS) detector set at 165° for  
19 sensitivity to <sup>4</sup>He and the matrix elements Si and Co. For the particular case of sample  
20 (Si:<sup>3</sup>He-RF) the p-EBS was carried out with the planar-silicon (PIPS) detector set at 159°  
21 for sensitivity to <sup>3</sup>He. **(ii) At the Pelletron accelerator of CEHMTI laboratory**  
22 **(Orléans, France)** for the helium charged Zr films. Rutherford back scattering (RBS)  
23 and p-EBS were carried out using respectively: an  $\alpha$ -beam at 2 MeV, 75° incidence angle  
24 and 166° scattering angle for sensitivity to zirconium and a proton-beam of 2400 keV, 0°

1 incidence angle and  $178^\circ$  scattering angle for sensitivity to  $^4\text{He}$ . Data analyses were  
2 performed by simulations with the SIMNRA code [33].

### 3 **“*In situ*” IBA analyses during annealing in vacuum:**

4 Thermal annealing experiments were done for all samples included in Table 1 in the  
5 dedicated DIADDHEM chamber [34] at the Pelletron accelerator of CEHMTI laboratory.  
6 p-EBS spectra were *in-situ* recorded each 1.5 min with a 3.4 MeV protons beam during  
7 continuous heating starting from room temperature with a 10 K/min ramp. Depending on  
8 the kinetic of He release final temperature, and eventual isothermal annealing, were  
9 selected.

### 10 **Films characterization by SEM and TEM analyses:**

11 The thickness and microstructure of the Co and Si films (before and after annealing) were  
12 examined by scanning electron microscopy (SEM) employing a HITACHI S-4800 SEM-  
13 FEG microscope operated at 1-2 kV. Thickness and morphology of the Zr films were  
14 determined by scanning electron microscopy (SEM) using a Zeiss Supra 40 FEG-SEM  
15 operating at 3 kV. In addition, Energy Dispersive X-ray Spectroscopy (EDS) at the  
16 accelerating voltage of 15 kV was carried out with a detector Bruker QUANTAX to draw  
17 a chemical cartography after annealing. Samples deposited on silicon or glassy carbon  
18 substrates were analyzed on top and cleaved for cross-sectional views. The nanostructure  
19 of the Co and Si nanocomposite films was investigated at the Laboratory of Nanoscopies  
20 and Spectroscopies (LANE-ICMS, Sevilla, Spain) by Transmission Electron Microscopy  
21 (TEM) using a Jeol 2100Plus TEM operated at 200 kV. For the Zr samples an ARM  
22 CFEG JEOL TEM working at 200 kV and equipped with 2 Cs aberration correctors was  
23 used. The cross-sectional TEM lamellas were prepared by mechanical polishing and  
24 dimple grinding of the coatings deposited on silicon or glassy carbon, followed by  $\text{Ar}^+$

1 ion milling to electron transparency. Representative porous areas were selected for  
2 imaging and analysis.

3

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## 32 DATA AVAILABILITY

33 **The datasets** used and/or analyzed during the current study are available from the  
34 corresponding author on reasonable request.

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**Author Contributions**

Fabrication and microstructural characterization of Si and Co films were conducted in Seville by D.H., M.C.J.H., O.M. and A.F. Fabrication and microstructural characterization of Zr films were conducted in Orléans by A.C. P.B. and A.L.T. Films composition by IBA analyses were done by T.S. in Orléans and F.J.F. in Seville. “*In-situ*” IBA analyses during thermal annealing were done in Orléans by T.S. The manuscript was written by A.F and A.L.T. All the authors reviewed the manuscript.

**Competing interests’ statement**

The authors declare no conflicts of interest.

1 **Figure captions**

2

3 **Fig.1.-** (a) Helium and Cobalt content evolution for sample **1** derived from proton-EBS  
4 spectra during *in-situ* annealing in vacuum at indicated temperatures. (b) SEM top-view  
5 and cross-section images of sample **1** as prepared and after annealing in vacuum.

6 **Fig.2.-** TEM cross-section images of sample **1** as prepared and after *in-situ* annealing.

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8 **Fig.3.-** (a) Helium and Silicon content evolution for sample **2** derived from proton-EBS  
9 spectra during *in-situ* annealing in vacuum at indicated temperatures. (b) SEM top-view  
10 and cross-section images of sample **2** as prepared and after annealing in vacuum.

11 **Fig.4.-** TEM cross-section images of sample **2** as prepared and after *in-situ* annealing.

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13 **Fig.5.-** (a) Helium and Silicon content evolution for sample **3** derived from proton-EBS  
14 spectra during *in-situ* annealing in vacuum at indicated temperatures. (b) SEM top-view  
15 and cross-section images of sample **3** as prepared and after annealing in vacuum.

16 **Fig.6.-** TEM cross-section images of sample **3** as prepared and after *in-situ* annealing.

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18 **Fig.7.-** (a) Helium 3 and Silicon content evolution for sample **4** derived from proton-  
19 EBS spectra during *in-situ* annealing in vacuum at indicated temperatures. (b) SEM top-  
20 view and cross-section images of sample **4** as prepared and after annealing in vacuum.

21 **Fig.8.-** TEM cross-section images of sample **4** as prepared and after *in-situ* annealing.

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23 **Fig.9.-** (a) Helium and Zirconium content evolution for sample **5** derived from proton-  
24 EBS spectra during *in-situ* annealing in vacuum at indicated temperatures. (b) SEM top-  
25 view and cross-section images of sample **5** as prepared and after annealing in vacuum.

26 **Fig.10.-** TEM cross-section images of sample **6** as prepared.

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2 **Table 1.-** Nomenclature and deposition parameters for investigated samples (“as deposited”)

Sample nr. Description	Substrate	Deposition time (h)	Sputtering gas and pressure (Pa)	Power (dc or rf) (W)	Deposition rate <sup>a)</sup> (nm/min)
E49 1. Co:He-RF	Silicon	4	4 (He)	200 (rf)	4.9±0.1
E101 2. Si:He-DC <sup>b)</sup>	Glassy Carbon Silicon	4	4.8 (He)	100 (dc)	8.0±0.1
E102 3. Si:He-RF <sup>b)</sup>	Glassy Carbon Silicon	4	4.8 (He)	150 (rf)	5.7±0,2
E69 4. Si: <sup>3</sup> He-RF(static) <sup>b), c)</sup>	Glassy Carbon Silicon	4	5 ( <sup>3</sup> He)	150 (rf)	4.8±0.1
G1 5. Zr:He+Ar-DC	Silicon	1	1 (95% He and 5% Ar)	300 (dc)	16±0.3
G2 6. Zr:He-DC	Silicon	2	1 (He)	410 (dc)	2±0.3

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- a) Calculated from deposition time and the thickness determined by SEM. Note that the target to substrate distance during deposition was 8 cm for Co, 10 cm for Si and 12 cm for Zr.
- b) Samples grown on: (i) glassy carbon for IBA analyses and (ii) silicon to facilitate TEM lamella preparations.
- c) This sample was prepared using a low gas consumption procedure in static operation mode. See Ref. 19 and section “Methods” for details.

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**Table 2.-** Areal density for Helium and matrix elements (Co, Si, Zr) and average porosity for the total thickness of investigated films

Sample nr. Description	Thickness <sup>a)</sup> ( $\mu\text{m}$ )	Areal density ( $10^{15}$ at/cm <sup>2</sup> )			Atomic ratio <sup>4</sup> He/M	Atomic ratio <sup>3</sup> He/M	Porosity (%)
		<sup>4</sup> He	<sup>3</sup> He	M: Co/Si/Zr			
E49 1. Co:He-RF	1.19 $\pm$ 0.02	925 $\pm$ 50	-	5150 $\pm$ 100	0.18	-	47 $\pm$ 1
E101 2. Si:He-DC	1.92 $\pm$ 0.03	3250 $\pm$ 100	-	5000 $\pm$ 100	0.65	-	46 $\pm$ 2
E102 3. Si:He-RF	1.37 $\pm$ 0.05	2350 $\pm$ 50	-	3250 $\pm$ 75	0.72	-	50 $\pm$ 3
E69 4. Si: <sup>3</sup> He-RF(static) <sup>b)</sup>	1.16 $\pm$ 0.01	-	917 $\pm$ 7	4378 $\pm$ 48	-	0.20	22 $\pm$ 0.5
G1 5. Zr:He+Ar-DC	0.96 $\pm$ 0.02	890 $\pm$ 45	-	2980 $\pm$ 60	0.30	-	27 $\pm$ 1
G2 6. Zr:He-DC	0.25 $\pm$ 0.02	125 $\pm$ 6	-	586 $\pm$ 12	0.21	-	45 $\pm$ 4

5 a) Measured from SEM cross-section (at different positions and cleaved areas).  
6 b) The “static” methodology aims to reduce the <sup>3</sup>He gas consumption [19].