Rare Metal Materials and Engineering
Volume 54, Issue 6, June 2025
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Zhou Chao, Ma Zhanji, Li Gang, et al. Effect of Magnetron Sputtered Gas on Microstructure and Hydrogen Adsorption Performance of ZrCoRE Films[J]. Rare Metal Materials and Engineering, 2025, 54(06): 1451-1456. DOI: https://doi.org/10.12442/j.issn.1002-185X.20240265.

ARTICLE

Effect of Magnetron Sputtered Gas on Microstructure and Hydrogen Adsorption Performance of ZrCoRE Films

Zhou Chao, Ma Zhanji, Li Gang, Yang Lamaocao, Zhang Huzhong

Science and Technology on Vacuum Technology and Physics Laboratory, Lanzhou Institute of Physics, Lanzhou 730000, China

Abstract: ZrCoRE (RE denotes rare earth elements) non-evaporable getter films have significant applications in vacuum packaging of micro-electro mechanical system devices because of their excellent gas adsorption performance, low activation temperature and environmental friendliness. The films were deposited using DC magnetron sputtering with argon and krypton gases under various deposition pressures. The effects of sputtering gas type and pressure on the morphology and hydrogen adsorption performance of ZrCoRE films were investigated. Results show that the films prepared in Ar exhibit a relatively dense structure with fewer grain boundaries. The increase in Ar pressure results in more grain boundaries and gap structures in the films. In contrast, films deposited in Kr display a higher density of grain boundaries and cluster structures, and the films have an obvious columnar crystal structure, with numerous interfaces and gaps distributed between the columnar structures, providing more paths for gas diffusion. As Kr pressure increases, the film demonstrates more pronounced continuous columnar structure growth, accompanied by deeper and wider grain boundaries. This structural configuration provides a larger specific surface area, which significantly improves the hydrogen adsorption speed and capacity. Consequently, high Ar and Kr pressures are beneficial to improve the adsorption performance.

Key words: NEG film; magnetron sputtering; krypton; sputtering pressure; hydrogen adsorption performance

1 Introduction

As the most advanced adsorption method that can meet the requirements of micro-scale vacuum packaging devices, the non-evaporable getter (NEG) film has advantages such as low active temperature, space efficiency, patternability, absence of particle pollution and elimination of pressure gradient. It can be applied in the vacuum chambers of large ultra-high vacuum pipes, such as particle accelerators and micro-electro mechanical system (MEMS) devices, which can maintain the vacuum level inside the vacuum pipes and microstructure devices[1–8].

There is a passivation layer on the surface of getter film, which needs to be activated by high temperature. The activation temperature and time vary depending on the material systems. Commonly used getter film material systems are titanium alloy and zirconium alloy, including ZrVFe, TiZrV, ZrCoRE (RE denotes rare earth elements), etc[9–23]. ZrCoRE alloy has wide-range applications in vacuum packaging of MEMS devices because of better adsorption performance, excellent compatibility with activation process and no environmental risk. The adsorption process differs depending on the types of gas. For H_2, the gas can be rapidly diffused into getter, forming a solid solution. Due to the weak force between hydrogen atom and getter alloy, hydrogen absorbed at low temperatures can be released when heated to higher temperature. In contrast, other active gases, such as CO and O_2, are adsorbed on the surface of getter materials, where they decompose into atoms and chemically bond with getter to form oxides or carbides[24–27]. The getter combines strongly with these elements, and no gas is released at high temperature. High temperature promotes the solid solution of gas atoms into the getter, exposing fresh film surfaces and enabling further adsorption of active gases. Therefore, the specific surface area, porosity, gas diffusion process and solid solubility of the substrate materials directly affect the

---

Received date: June 07, 2024
Foundation item: National Natural Science Foundation of China (62171208); Natural Science Foundation of Gansu Province (23JRRA1355)

Corresponding author: Zhou Chao, Ph. D., Senior Engineer, Science and Technology on Vacuum Technology and Physics Laboratory, Lanzhou Institute of Physics, Lanzhou 730000, P. R. China, E-mail: 1987zhouchao@163.com

adsorption performance of the film.

ZrCoRE thin films can be deposited by DC magnetron sputtering. In traditional magnetron sputtering, argon (Ar) is used as sputtering gas. During sputtering, parameters such as sputtering pressure, power and grazing angle have a great impact on the morphology and structure of the thin films, thereby further affecting their overall properties. In this study, krypton (Kr) was used as sputtering gas due to its relatively high sputtering yield, which enhances the ionization efficiency and facilitates the preparation of high-performance films. In addition, ZrCoRE getter films with different microstructures and hydrogen absorption properties were prepared by changing the sputtering pressure in both Ar and Kr sputtering atmospheres, and the mechanism of the influence of sputtering pressure on the structure and properties of the films was analyzed.

2 Experiment

2.1 Deposition of ZrCoRE films

The ZrCoRE films were deposited on (100) Si wafer substrates by DC magnetron sputtering using Ar and Kr as sputtering gas (purity⩾99.999%). The Si wafer substrates were ultrasonically cleaned with acetone, anhydrous alcohol and deionized water. The ZrCoRE alloy target (Zr 75%/Co 20%/ RE 5%, RE includes 3% Ce and 2% La, wt%; purity>99.9%; *Φ*100 mm×6 mm) was prepared by hot pressing. The target prepared by this method has fine grain, uniform structure and high density which are beneficial for preparation of high-performance films. The deposition parameters include the pressure of sputtering gas, DC power, target-substrate distance, deposition temperature and time, as shown in Table 1. The background pressure of vacuum chamber was less than 1.0×10^{-4} Pa, avoiding the gas contamination in deposition. Before deposition process, the substrates were applied with bias voltage at 600 V for 10 min to clean and to improve the adhesion between film and substrate.

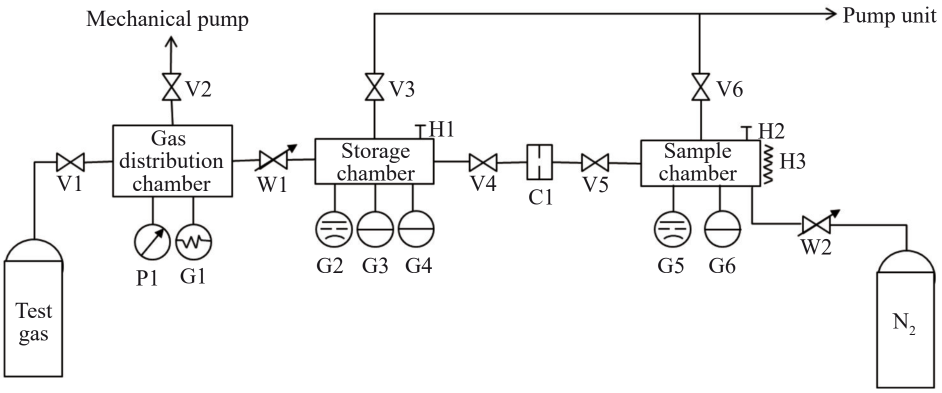
Table 1 Deposition parameters of Zr-Co-RE films

Parameter	Value
Sputtering gas	Ar, Kr
Sputtering pressure/Pa	3.0–6.0
Sputtering power/W	350
Target-substrate distance/cm	7
Substrate temperature	Ambient temperature
Deposition time/min	30
Background pressure/Pa	⩽1.0×10^{-4}
Bias voltage before deposition	600 V for 10 min

2.2 Adsorption test method

The remarkable feature of getter films is their exceptional hydrogen adsorption capability at room temperature. Given that hydrogen is the most important gas affecting the vacuum level of large ultra-high vacuum pipes and MEMS devices, the hydrogen absorption performance of ZrCoRE films was tested. The surface of the prepared ZrCoRE film forms a passivation layer upon exposure to the atmosphere, which needs to be activated by high temperature to refresh surface for gas adsorption. The adsorption tests were conducted using a dynamic method (the pressure is constant) within a special vacuum system built according to ASTM F798-97, and hydrogen was used as the standard testing gas[28]. The diagram of testing system is demonstrated in Fig. 1. The specimens were placed on a heating platform in the stainless-steel chamber. The vacuum system was heated to 150 °C to outgas, achieving a base pressure less than 1.5×10^{-6} Pa. Then, the getter films were activated at 300 °C for 15 min before cooling down to ambient temperature. H_2 (high purity, 99.999%) was accessed by the valve to maintain the pressure of test chamber (P_g) at 3×10^{-4} Pa. In the test process, P_m was the instantaneous pressure within the test gas inlet chamber. The adsorption speed (S) and capacity (Q) were calculated according to the following formulas.

$$S = F\cdot\frac{P_m - P_g}{P_g A} \tag{1}$$



V1-manual stop valve; V2-manual high vacuum angle valve; V3 and V6-all metal sealed high vacuum angle valve; V4 and V5-bellows valve; W1 and W2-micrometering valve; P1-absolute pressure sensors; G1-pirani gauge; G2 and G5-hot cathode gauge; G3-1330 Pa capacitance diaphragm gauge; G4 and G6-13.3 Pa capacitance diaphragm gauge; H1 and H2-heater; H3-heater for activating getter; C1-flow limiting element

Fig.1 Testing system diagram of ZrCoRE getter films

$$Q = \frac{F}{A}\int_0^t (P_\mathrm{m} - P_\mathrm{g})\mathrm{d}t \quad (2)$$

where A is the surface area of test specimens, and F is the known flow conductance of capillary tube (1.08 mL·s^{-1} for H_2).

2.3 Microstructure characterization

The surface morphologies and cross-sectional structures of the film were analyzed using Zeiss Sigma 500 scanning electron microscope (SEM), equipped with energy dispersive X-ray spectroscope (EDS) for measuring the chemical composition. The microstructures were characterized by X-ray diffractometer (XRD, Rigaku) with Cu Kα radiation at glancing angle of 1°.

3 Results and Discussion

3.1 Morphology and microstructure characteristics of ZrCoRE films

Gas diffusion through surface and interface are faster than bulk diffusion, so the getter films with large specific surface have better gas adsorption performance because of more interfaces, grain boundaries and gaps. Fig.2 shows the surface and cross-sectional morphologies of the ZrCoRE getter films, which were deposited at the argon pressure of 3, 4 and 5 Pa.

The films deposited at 3 Pa have relatively dense structure. At the pressure of 4 Pa, the sputtering particles undergo preferred growth and diffusion on the substrate, so the surface structures become relatively loose and grain boundary structure appears. The cross-sectional morphologies show that the film grows in a discontinuous columnar shape. At the pressure of 5 Pa, more grain boundaries appear in the loose ZrCoRE film, and the columnar structure is more obvious. These structures are attributed to different energies of the sputtered alloy particles. At low pressures, the low collision probability between sputtered ZrCoRE particles and gas particles causes surface diffusion of atoms with sufficient energy, then forming a dense structure. At higher sputtering pressures, sputtered atoms on substrate have low mobility, resulting in rapid preferential growth into island structures. The continued growth of island structures leads to a deposition shadow effect, which further hinders the capturing of sputtering atoms at the gap, thus forming a large number of grain boundaries, gaps or interfaces.

Morphologies of ZrCoRE films deposited at different Kr gas pressures are shown in Fig.3. The film deposited at 3 Pa exhibits a small number of grain boundaries. The cross-sectional

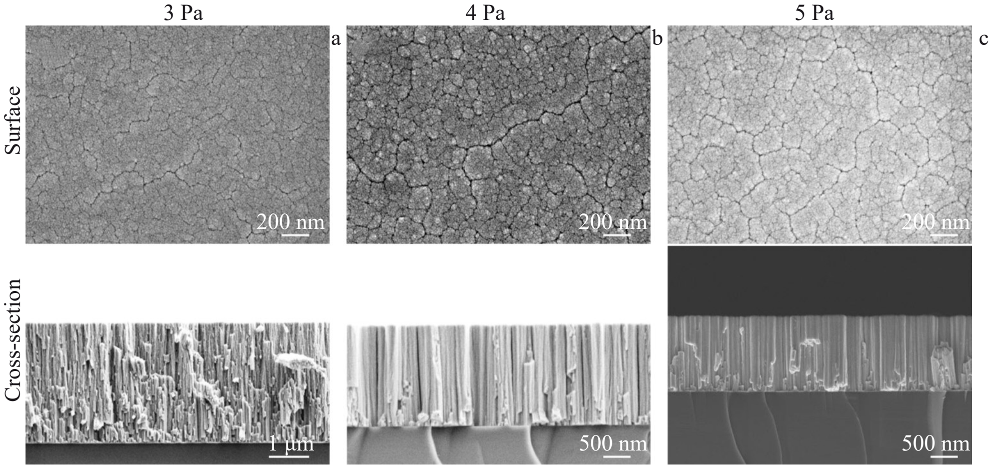


Fig.2 SEM surface and cross-sectional micrographs of ZrCoRE films sputtered at different argon pressures: (a) 3 Pa, (b) 4 Pa, and (c) 5 Pa

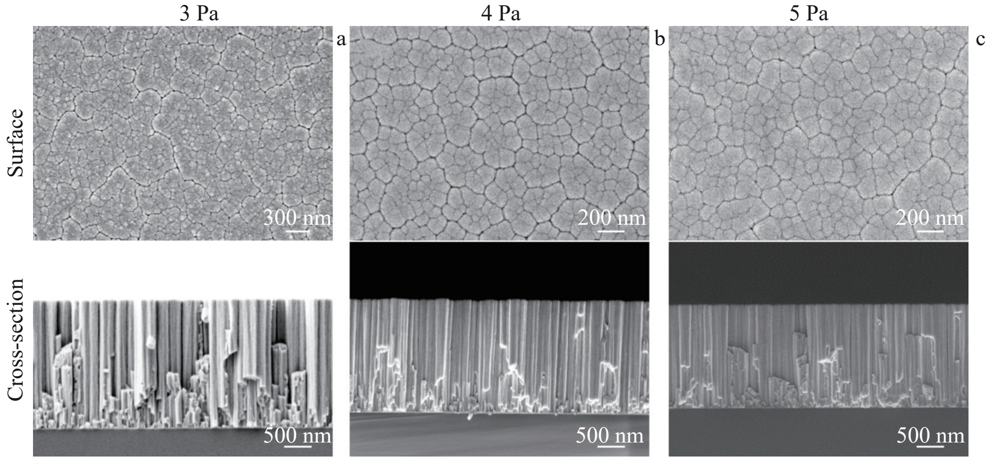


Fig.3 SEM surface and cross-sectional micrographs of ZrCoRE films sputtered at different krypton pressures: (a) 3 Pa, (b) 4 Pa, and (c) 5 Pa

morphologies show that the film grows in a discontinuous columnar pattern. There are quantities of grain boundaries and cluster structures distributed uniformly in the film deposited at 4 Pa. These cluster structures grow individually, eventually forming more distinct columnar crystals, as shown in cross-sectional morphologies. The film deposited at 4 Pa exhibits more grain boundaries and pores, and the grain boundaries are deeper and wider, including a large number of penetrating grain boundaries, as shown in Fig. 4. In contrast, the film deposited at 5 Pa shows a reduction in the depth and width of the grain boundary structures. The formation of columnar structure is due to the combination of self-shadowing effect of the initial atoms and lateral diffusion mobility of atoms arriving at substrate surface. The ZrCoRE atoms have sufficient energy for surface diffusion at low Kr pressures. At higher Kr sputtering pressures, sputtered atoms on substrate have low lateral mobility, resulting in preferential growth into a columnar structure. The surface is characterized by cluster structures, which contain quantities of gaps and grain boundaries. Moreover, the grain boundaries are distributed uniformly in the structure. As the Kr pressure increases, the kinetic energy of the sputtered atoms reaching the surface will be greatly reduced, and thus the lateral diffusion of atoms is further restricted. Obviously, the columnar structure becomes finer and less marked at even higher pressures.

From the above research, it is evident that the films deposited in a Kr atmosphere, compared with those sputtered in an Ar atmosphere at the same pressure, contain more grain boundaries and gap structures. The grain boundaries divide the surface into uniform cluster structures with larger surface area, more obvious continuous columnar structures and deeper and wider grain boundaries, enhancing the films' capacity for gas adsorption and diffusion. Because Kr has relatively high sputtering yield, it has higher ionization efficiency at the same gas molecular density, which is conducive to the preparation of high-performance films.

Microstructures of the getter films change with sputtering gas pressures. XRD patterns of ZrCoRE films deposited in Ar gas are demonstrated in Fig. 5. The diffraction peaks in the curve correspond to the (110), (200) and (211) orientations of the α-Zr phase. With the increase in gas pressure, the full width at half maximum of the diffraction peak increases. This phenomenon can be attributed to the lower kinetic energy of the deposited atoms at higher pressures, which restricts diffusion during the film formation process, forming amorphous regions and grain boundaries with irregular arrangement of grains and atoms, weakening the diffraction intensity in the Bragg direction, increasing the scattering intensity in the non-Bragg direction, and ultimately resulting in the broadening of diffraction peaks.

XRD patterns of the film deposited in Kr gas are shown in Fig. 6. All films have almost the same pattern and exhibit one broad diffraction peak at around $2\theta=36°$. Compared with the film deposited in Ar atmosphere, the (200)- and (211)-oriented diffraction peaks of α-Zr phase do not appear, and the broad diffraction peaks of (110) orientation exist, which indicates that there are more non-crystalline regions and grain

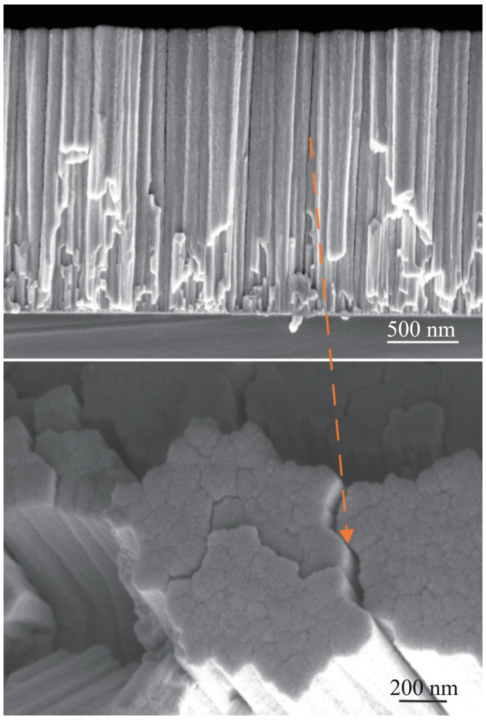


Fig.4 Cross-sectional morphologies of penetrating crack

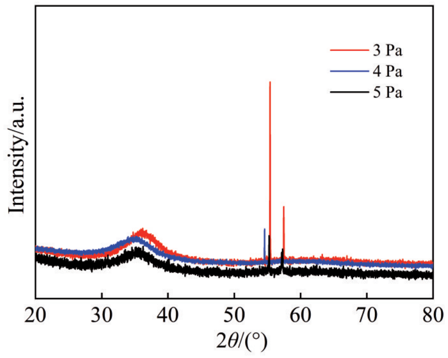


Fig.5 XRD patterns of ZrCoRE films sputtered at different argon pressures

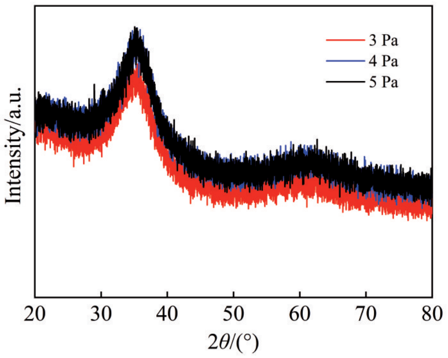


Fig.6 XRD patterns of ZrCoRE films sputtered at different krypton pressures

boundaries in the film structure.

Fig. 7 presents the effect of the gas pressure on the composition of ZrCoRE films. The composition is analyzed by EDS with the assumption that the sum of the mass percentage of Zr, Co, Ce and La is 100%. The composition of all samples has no significant difference under different gas pressures, which indicates that the sputtering yield of each element in the target is not affected by the pressure.

3.2 Adsorption characteristics of ZrCoRE getter films

The getter films should be heat activated to refresh the surface before the gas adsorption test. ZrCoRE films were heated at 300 °C for 15 min and then cooled to ambient temperature. H_2 adsorption capacity and rate were evaluated under a constant hydrogen pressure of 3×10^{-4} Pa in the test chamber. Fig. 8 demonstrates the hydrogen adsorption curves of the films deposited in Ar gas. The initial adsorption rate is 58.4, 62.2 and 69.5 $mL\cdot s^{-1}\cdot cm^{-2}$ at 3, 4 and 5 Pa, respectively. Fig. 9 demonstrates the influence of Kr sputtering gas pressure on adsorption characteristics. The initial adsorption rate is 88.9, 113.5 and 108.3 $mL\cdot s^{-1}\cdot cm^{-2}$ at 3, 4 and 5 Pa, respectively. It indicates that at the same gas pressure, ZrCoRE films deposited in Kr exhibit more grain boundaries and gap structures, and the specific surface area is larger, which is conducive to gas adsorption and diffusion. In different atmospheres, the increase in gas pressure is beneficial to improve the hydrogen absorption performance of the film. This is because the film deposited at high gas pressure contains more grain boundaries and gap structures, and the grain boundaries divide the surface into uniform cluster structures with larger surface area, more obvious growth of continuous columnar structures and deeper and wider grain boundaries.

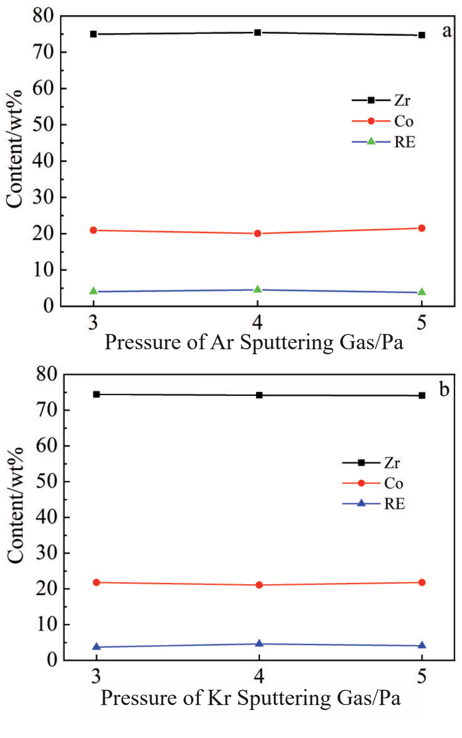


Fig.7 Composition of ZrCoRE films sputtered in Ar (a) and Kr (b) atmospheres

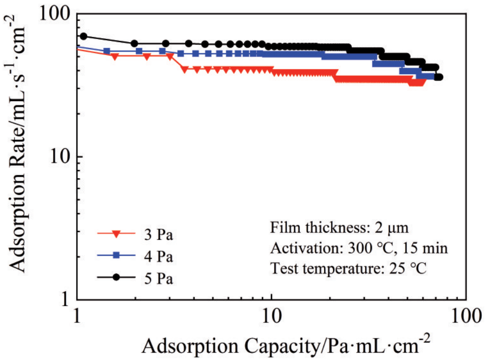


Fig.8 Hydrogen adsorption curves of ZrCoRE films deposited in argon atmosphere

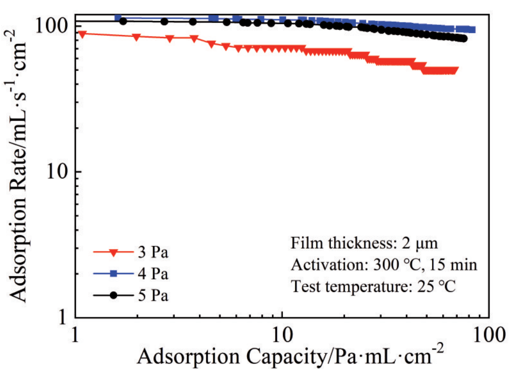


Fig.9 Hydrogen adsorption curves of ZrCoRE films deposited in krypton atmosphere

4 Conclusions

1) For ZrCoRE films deposited in Ar atmosphere, the increase in gas pressure is beneficial to the gas adsorption and diffusion. When the gas pressure is 5 Pa, the ZrCoRE particles deposited on the substrate have low diffusion ability, and the short-range aggregation forms island-like crystal nuclei. The deposition shadow effect of the island-like structure becomes stronger, and numerous gaps or grain boundaries further form, so the film has a large specific surface area.

2) For the ZrCoRE films deposited in Kr atmosphere, with the increase in pressure, the shadow effect makes the particles grow into a columnar structure in the preferred direction, and the surface presents a cluster structure with a large number of grain boundaries and gap structures which are uniformly distributed. At higher deposition gas pressures, the kinetic energy of particles is greatly reduced, which affects the lateral diffusion of atoms and the preferential growth. When the air pressure is 4 Pa, the grain boundaries become deeper and wider, including a large number of penetrating grain boundaries, and the film has the highest hydrogen absorption rate.

3) At the same gas pressure, the film deposited in Ar atmosphere is denser, while the film deposited in Kr atmosphere has more cluster structures and penetrating grain boundaries, and the columnar crystal structure is more

obvious, providing more paths for gas diffusion and higher hydrogen absorption rate.

References

1 Ramesham R, Kullberg R. *Journal of Micro-Nanolithography, MEMS and MOEMS*[J], 2009, 8(3): 031307

2 Górecka-Drzazga A. *Vacuum*[J], 2009, 83(12): 1419

3 Vivek C, Xie L, Chen B T. *Journal of Electronic Materials*[J], 2013, 42(3): 485

4 Zhou Chao, Li Detian, Zhou Hui *et al. Materials Reports*[J], 2019, 33(3): 438 (in Chinese)

5 Zhang J W, Jiang W, Wang X *et al. Journal of Micromechanics and Microengineering*[J], 2012, 22: 125022

6 Wu M, Moulin J, Bosseboeuf A. *ECS Transactions*[J], 2018, 86(5): 95

7 Tenchine L, Baillin X, Faure C *et al. Procedia Engineering*[J], 2011, 172: 233

8 Lee B, Seok S, Chun K. *Journal of Micromechanics and Microengineering*[J], 2003, 13: 663

9 Širvinskaitė R, Malyshev O B, Valizadeh R *et al. Vacuum*[J], 2020, 179: 109510

10 Benvenuti C, Chiggiato P, Costa-Pinto P *et al. Vacuum*[J], 2001, 60: 57

11 Chiggiato P, Costa-Pinto P. *Thin Solid Films*[J], 2006, 515: 382

12 Bu J G, Mao C H, Zhang Y *et al. Journal of Alloys and Compounds*[J], 2012, 529: 69

13 Bu J G, Mao C H, Zhang Y *et al. Rare Metal Materials and Engineering*[J], 2013, 42(9): 1889

14 Jin Y F, Wang Z F, Zhao L *et al. Journal of Micromechanics and Microengineering*[J], 2004, 14: 687

15 Xu Y H, Cui J D, Cui H *et al. Journal of Alloys and Compounds*[J], 2016, 661: 396

16 Wang J, Zhang B, Xu Y H *et al. Chinese Physics C*[J], 2015, 39(12): 127007

17 Yang Xiaowei, Li Jishan, Wang Xufeng *et al. Rare Metal Materials and Engineering*[J], 2010, 39(11): 1960 (in Chinese)

18 Cui J, Guo C, Zou L *et al. Computer Coupling of Phase Diagrams and Thermochemistry*[J], 2016, 55: 189

19 Jiang B, Wang J X, Xu L F *et al. Materials*[J], 2018, 11(6): 947

20 Miyazawa T, Kurihara M, Ohno S *et al. Journal of Vacuum Science & Technology A*[J], 2018, 36: 051601

21 Matsumoto M, Okada T, Miyazawa T *et al. Journal of Vacuum Science & Technology A*[J], 2019, 37: 051601

22 Feng T Y, Cheng Y J, Chen L *et al. Vacuum*[J], 2018, 154: 6

23 Shi X, Xiong Y H, Wu H T. *Materials*[J], 2023, 16(7): 2916

24 Petti D, Cantoni M, Leone M *et al. Applied Surface Science*[J], 2010, 256(21): 6291

25 Hörz G. *Gases and Carbon in Metals: Thermodynamics, Kinetics, and Properties. Group VA Metals (1), Vanadium (V)*[M]. Germany: Cheminform Press, 1981

26 Zhou C, Li D T, Zhou H *et al. Materials Research Express*[J], 2020, 7: 036402

27 Li C C, Huang J L, Lin R J *et al. Thin Solid Films*[J], 2009, 517: 5876

28 ASTM 798-97[S]. West Conshohocken: ASTM International, 2002

磁控溅射气体对ZrCoRE薄膜微观结构和吸氢性能的影响

周　超，马占吉，李　刚，杨拉毛草，张虎忠

(兰州空间技术物理研究所 真空技术与物理重点实验室，甘肃 兰州 730000)

摘　要：ZrCoRE（RE为稀土元素）吸气剂薄膜具有气体吸附性能好、活化温度低和无污染等优点，在微机电系统器件真空封装中具有重要应用。研究了直流磁控溅射气体的种类和压强对薄膜微观结构和吸氢性能的影响。结果表明，采用氩气（Ar）进行磁控溅射，沉积的薄膜较致密，晶界结构较少，随着Ar气压增大，薄膜中晶界和间隙结构增多。采用氪气（Kr）进行磁控溅射，沉积的薄膜中含有较多的晶界和团簇结构，薄膜具有明显的柱状晶结构，柱状结构之间分布着大量的界面和间隙，能为气体扩散提供更多路径。随着Kr气压增大，薄膜的连续柱状结构生长更明显，晶界扩展的更深、更宽，该结构具有更大的比表面积，可提高氢气在薄膜中的吸附速率和吸附量。因此，Ar和Kr气压增大有利于提高薄膜的气体吸附性能。

关键词：NEG薄膜；磁控溅射；氪气；溅射气压；吸氢性能

作者简介：周 超，女，1987年生，博士，高级工程师，兰州空间技术物理研究所真空技术与物理重点实验室，甘肃 兰州 730000，E-mail：1987zhouchao@163.com