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Influence of the sputtering glancing angle on the microstructure and adsorption characteristics of Zr-Co-RE getter films

Chao Zhou, Detian Li, Hui Zhou, Xingguang Liu and Zhanji Ma
Science and Technology on Vacuum Technology and Physics Laboratory, Lanzhou Institute of Physics, Lanzhou 730000, People’s Republic of China
E-mail: 1987zhouchao@163.com

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Abstract

Zr-Co-RE non-evaporable getter films have excellent gas adsorption performance therefore can be used in vacuum sealed electronic devices. The microstructure of getter films has vital effect on adsorption performance. In this paper, Zr-Co-RE films deposited by DC magnetron sputtering at different glancing angles are investigated including microstructures and adsorption characteristics. The surface and cross-sectional morphologies demonstrate loose, porous and columnar-like structure which forms because of low lateral mobility of Zr and Co atoms and shadowing effect of non-perpendicular sputtering. Zr-Co-RE films are amorphous or nanocrystalline structure. The films deposited at 90° glancing angle show large grain size. After Zr-Co-RE films are heated at 350 °C for 15 min, the H2 adsorption capacity and pumping speed at ambient temperature are tested. The films grown at 90° glancing angle have highest initial pumping speed (103.9 ml s$^{-1}$ cm$^{-2}$), which owe to its more gas diffusion path and active surface, meanwhile, the adsorption capacity is lower than 60° because of difficult and limited diffusion process into getter matrix. The films grown at 60° glancing angle have best adsorption capacity (71.5 Pa.ml cm$^{-2}$) and pumping speed stability.

1. Introduction

Non-evaporable getter (NEG) films have widespread use in electronic devices vacuum sealing to adsorb the residual active gas and gas outgassing of devices [1–3]. With the advantages of suitable shape, adsorption performance and heat activation compatible with wafer bonding and sealing technologies, NEG films play a significant role in micro electro mechanical system (MEMS) devices vacuum sealing to maintain the internal vacuum level [4–7]. The low pressure of the internal vacuum environment determines the properties even lifetime of MEMS devices. Conventional sealing of MEMS devices is placing bulk getters in cavity which occupy valuable space and may cause tiny particles contamination. However, NEG films deposited in the cavity can be heat activated while the device bonding process at high temperature and maintain the vacuum environment [8, 9].

Titanium alloy and zirconium alloy are typical NEG compositions, such as Ti–V, Zr–V–Fe, Ti–Zr–V, etc Ti and Zr have special enthalpy and entropy of combining with gas atoms to form compound (oxide, carbide and hydride) and solid solution [10–13]. V can improve gas diffusion speed in NEG materials [14]. Therefore, Ti–Zr–V NEG film with lowest activation temperature (180 °C) has been used in vacuum chambers of accelerators, which are made of stainless steel and aluminum alloys. Recently, Zr-Co-RE (RE indicates rare earth) alloys attract more attention in many different sealed devices to fulfill some specific integration needs in the shape of patterned film on silicon, glass, metallic or ceramic substrates. Zr-Co-RE NEG is developed from hydrogen storage alloy and has better safety (low probability of self-ignition), better adhesion to substrate, higher gas adsorption property and no environment risks compared with other Zr alloys getters. Especially, the heat activation temperature coincides with MEMS device sealing process, which span a temperature range from 250 °C to 600 °C [15–17]. Zr-Co-RE films can be prepared by magnetron sputtering from Zr-Co-RE alloy targets. The active surface area of films, diffusion process and matrix solubility are directly related to gas...
adsorption performance [18–21]. For Zirconium alloy getters, adding cobalt can enlarge the lattice parameter then increase gas diffusion speed, meanwhile, rare earth elements can deplete vacancy near Zr from oxygen or hydrogen to enhance getter activity [16, 22–24]. Generally, NEG films prepared by magnetron sputtering with high porosity and grain boundaries of microstructures have better adsorption performance [25–28]. The sputtering parameters have significant effects on most other Ti or Zr alloys films microstructures and properties. Previous studies show that the main sputtering parameters of fabricating Ti and Ti-Zr-V films include temperature, sputtering gas pressure and the glancing angle (angle between substrate surface and target surface) [29–33]. However, the correlation of adsorption performance, microstructures and fabrication parameters of Zr-Co-RE films has not been reported before. In this paper, influences of the sputtering glancing angle on the microstructure and adsorption characteristics of Zr-Co-RE getter films are investigated.

2. Experiment part

2.1. Preparation of Zr-Co-RE films
The film samples are deposited on (100) Si wafer substrates which are ultrasonically cleaned in acetone and ethyl alcohol, sequentially. The Zr-Co-RE films are grown by DC magnetron sputtering method from Zr75Co22RE3 (atomic percent, RE = Ce45La34Nd21) target which is fabricated by HIP (hot isostatic pressing). To avoid the gas contamination in vacuum chamber, the background pressure is less than $1 \times 10^{-4}\text{Pa}$. As is shown in figure 1, each sample is placed on the special stainless steel shelf which is fixed to rotating holder and the glancing angles are $0^\circ$, $30^\circ$, $60^\circ$ and $90^\circ$, respectively. The arrangement ensures the same distance between target and substrates, meanwhile, the target edge effects can be prevented at the most extent.

The deposition process is carried out in high purity Ar atmosphere at 2 Pa sputtering pressure. The distance between substrates and target is 11 cm. Before the deposition process, the substrates are applied of 300 V bias voltage and cleaned by ion beam for 10 min. The target is pre-sputtered for 15 min to eliminate the surface adsorptive contamination. The Zr-Co-RE films are deposited for 70 min. In the Zr-Co-RE films depositing process, the holder is non-rotating.

2.2. Adsorption test process
For NEG films, one remarkable characteristic is the large adsorption speed for active gases, especially for H$_2$ at ambient temperature [34]. Further, H$_2$ is the main residual gas in ultra-high vacuum (UHV) to affect the performance of most MEMS devices. So, the research chose to measure hydrogen adsorption property. The Zr-Co-RE films need to be heat activated to refresh the getter surfaces which have passive layer after be prepared and exposed in the air. The H$_2$ adsorption tests are proceed by dynamic method (keep the pressure was constant) at the special vacuum system built according to ASTM F798-97 [35, 36].
in figure 2. The specimens are placed in a quartz glass chamber and the heating system with thermocouple is attached to the specimens. The vacuum system is heated at 280 °C to outgas for base pressure less than $1 \times 10^{-7}$ Pa. Then the getter films are activated by heating power source which control and show the heating temperature. The Zr-Co-RE getter films are activated by 350 °C for 15 min. When the specimens temperature decreases to ambient temperature, $H_2$ (high purity, 99.999%) is accessed by the valve to maintain the pressure of test chamber ($P_g$) at $4 \times 10^{-4}$ Pa. In the test process, $P_m$ is the instantaneous pressure of the test gas inlet chamber.

The adsorption speed ($S$) and capacity ($Q$) are calculated according to the formula as follows [36],

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

$$Q = \frac{F}{A} \int_0^t (P_m - P_g)\,dt$$

Where $A$ is the surface area of test specimens, and $F$ is the known flow conductance of capillary tube ($0.07$ l s$^{-1}$ for $H_2$) as described in previous paper [37].

2.3. Characterization
The surface and cross-sectional morphologies of getter films are analyzed by a field emission scanning electron microscope (FEI, Apreo S), which has an integrated energy dispersive x-ray spectroscopy (EDS) for measuring the chemical composition. The microstructures are characterized by x-ray diffraction (APD 2000 PRO) with Cu K-α radiation. The grain size of Zr-Co-RE films is calculated according to the Scherrer’s formula.

3. Results and discussion

3.1. Microstructure characteristic of Zr-Co-RE getter films
The gas adsorption performance of getter films has relation to active surface area. 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 and cracks. Figure 3 shows the surface and cross-sectional morphologies of the Zr-Co-RE getter films. The films are deposited at the glancing angles of 0°, 30°, 60° and 90°, respectively. The films exhibit loose, porous and columnar-like structures. The films grown at large glancing angle show more porous surface, denser interface and looser columnar cross-section. The formation of the columnar-like structure is mainly because of the low lateral mobility of Zr and Co atoms on Si substrate at low temperature and the shadowing effect of the non-perpendicular relationship between the sputtered flux and the substrate surface. This indicates that the specific surface area of Zr-Co-RE getter films is increasing with the glancing angle. However, when the glancing angle is 90°, the atoms grow vertically to the substrate as the figure 3(d). Generally, this highly loose porous microstructure has poor adhesion to the substrate and causes particles to fall off when suffer a severe impact.

Figure 4 presents the effect of the glancing angle on the composition of Zr-Co-RE films. The composition is analyzed by EDS with the assumption that the sum of the atomic percentage of Zr, Co, Ce, La and Nd is 100%. All samples are coincident with the target, and there is no significant difference in composition with the glancing angle.
Microstructures of the getter films can change with sputtering glancing angles. The x-ray diffraction patterns of the Zr-Co-RE films are demonstrated in the figure 5. As can be seen, there is no obvious high intensity diffraction. All films have almost same pattern and exhibit only one broad diffraction peak at around $2\theta = 36^\circ$, which suggest that the Zr-Co-RE films are amorphous or nanocrystalline structure [17, 32, 38]. The full-width at half maximum (FWHM) of the peaks is 4.98 ($0^\circ$), 5.73 ($30^\circ$), 5.58 ($60^\circ$), 4.38 ($90^\circ$), respectively. According to the Scherrer’s formula, the grain size of Zr-Co-RE films is about 3 ~ 4 nm. At 90$^\circ$ glancing angle, the FWHM decreases and indicates the nanocrystallines grow up or amorphous structures crystallize.
Figure 5. X-ray diffraction patterns of the Zr-Co-RE films.

Figure 6. H₂ adsorption curves of Zr-Co-RE getter films. Activation: 350 °C, 15 min Adsorption temperature: 25 °C Pressure: 4 × 10⁻⁴ Pa.

Table 1. Adsorption capacity and initial pumping speed of the Zr-Co-RE films.

| Glancing angle | 0°  | 30° | 60° | 90° |
|---------------|-----|-----|-----|-----|
| Adsorption capacity (Pa.ml cm⁻²) | 53.3 | 50.2 | 71.5 | 54.6 |
| Initial pumping speed (ml s⁻¹ cm⁻²) | 37.3 | 57.4 | 73.6 | 103.9 |
3.2. Adsorption characteristics of Zr-Co-RE getter films
The getter films should be heat activated to refresh the surface before testing the gas adsorption performance. Zr-Co-RE films are heated at 350 °C for 15 min then the temperature cools to ambient temperature. H2 adsorption capacity and pumping speed are tested keeping H2 pressure in test chamber is $4 \times 10^{-4}$ Pa. Figure 6 demonstrates the films adsorption curves for H2 and the calculated results were shown in the table 1. The films grown at 90° glancing angle own the highest initial pumping speed because of the microstructure which has more gas diffusion path and active surface. However, the adsorption capacity increase with increasing the angles up to 60°, and then decrease for sample deposited at 90°. The reason is that the deposited atoms grow perpendicularly to the substrate surface then lead to the accumulation layer by layer. The gas diffusion in getter matrix is difficult and limited [8, 15, 32].

Compared with SAES getter film which has the best adsorption performance as reported, the Zr-Co-RE film of this study (LIP) has higher initial pumping speed but lower pumping speed stability as demonstrated in figure 7 [8]. The adsorption process of Zr-Co-RE getter films is combination of dynamic physical diffusion and chemical reaction. The active surface ensures the high initial pumping speed. With the adsorption capacity increasing, the pumping speed decreases which attributes to the covered surface and slow diffusion process.

4. Conclusion
Zr-Co-RE getter films are prepared by DC magnetron sputtering at different glancing angles. The films grown at large glancing angle show more porous surface, denser interface and looser columnar cross-section. Specific surface area of Zr-Co-RE getter films is increasing with the glancing angle. The formation of loose and columnar-like structure is mainly because of the low lateral mobility of Zr and Co atoms on Si substrate at low temperature and the shadowing effect of the non-perpendicular relationship between the sputtered flux and the substrate surface. Zr-Co-RE films are amorphous or nanocrystalline structure according to XRD analysis. Films deposited at 90° glancing angle have smallest FWHM and indicate the nanocrystallines grow up or amorphous structures crystallize. The H2 adsorption capacity and pumping speed at ambient temperature are tested after be heat activated at 350 °C for 15 min in $4 \times 10^{-4}$ Pa vacuum environment. The films grown at 90° glancing angle have highest initial pumping speed (103.9 ml s$^{-1}$ cm$^{-2}$), which owe to its more gas diffusion path and active surface, meanwhile, the adsorption capacity is lower than 60° because of difficult and limited diffusion in getter matrix. Therefore, improving the pumping speed stability is necessary and become the focus of following studies.

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ORCID iDs

Detian Li @ https://orcid.org/0000-0001-6842-6217

References

[1] Ramesham R and Kullberg R 2009 J. Micro/Nanolith. MEMS MOEMS 8 031307
[2] Tencchine L, Baillien X, Faure C, Nicolas P, Martinez and Papon A-M 2011 Sens. Actuators, A 172 233–9
[3] Choa S H 2005 Microsyst. Technol. 11 1187–96
[4] Górecka-Drzazga A 2009 Vacuum 83 1419–26
[5] Lee B, Seok S and Chun K 2003 J. Micromech. Microeng. 13 663–9
[6] Zhang J, Jiang W, Wang X, Zhou J and Yang H 2012 J. Micromech. Microeng. 22 125022
[7] Amiotti M, Moraja M, Conte A and Florence H 2004 IEEE Int. Ultrasonics, Ferroelectrics, and Frequency Control Joint 50th Anniversary Conf. 678–81
[8] Zhou C, Li D, Zhou H, Zhang K and Cao S 2019 Materials Reports 33 438–43
[9] Vivek C, Xie L and Chen B 2001 Titanium-Based Getter Solution for Wafer-Level MEMS Vacuum Packaging J. Electron. Mater. 42 485–91
[10] Benvenuti C, Chiggiato P, Costa Pinto P, Escudeiro Santana A, Hedley T, Mongelluzzo A, Ruzinov V and Wessels I 2001 Vacuum 60 57–65
[11] Chiggiato P and Costa Pinto P 2006 Thin Solid Films 515 382–8
[12] Benvenuti C, Cazeneuve J M, Chiggiato P, Cicoira F, Escudeiro Santana A, Johanek V, Ruzinov V and Fraxedas J 1999 Vacuum 53 219–25
[13] Jin Y, Wang Z, Zhao L, Lim P C, Wei J and Wong C K 2004 J. Micromech. Microeng. 14 687–92
[14] Cui J, Guo C, Zou L, Li C and Du Z 2018 Galphad 55 189–98
[15] Bu J, Mao C, Zhang Y, Wei X and Du J 2012 J. Alloys Compd. 529 69–72
[16] Pettit D, Cantoni M, Leone M, Bertacco R and Rizzi E 2010 Appl. Surf. Sci. 256 6291–6
[17] Bu J, Mao C, Zhang Y, Zhang X, Wei X and Du J 2013 Rare. Metal. Mat. Eng. 42 1889–92
[18] Malsheov O B, Valizadeh R and Hannah A N 2014 Vacuum 100 26–8
[19] Sutara F, Skala T, Malek K and Matolin V 2009 Vacuum 83 824–7
[20] Ferreira M J, Seraphim R M, Ramirez A J, Tabacniks M H and Nascente P A P 2012 Phys. Proc. 32 840–52
[21] Li C-C, Huang J-L, Lin R-J, Lii D-F, Chen C-H, Chen L-C and Chen K-H 2009 Thin Solid Films 517 3672–6
[22] Moghadam A H, Dashiizad V, Kafiou A and Youzbashizadeh H 2015 TMS Middle East-Mediterranean Materials Congress on Energy and Infrastructure Systems (MEMA 273
[23] Mozaftari N, Elahi S M and Parhizgar S 2019 Int. J. Thermophys. 40 67
[24] Mozaftari N, Elahi S H, Parhizgar S S, Mozaftari N and Elahi S M 2019 Mater. Res. Express 6 116428
[25] Wang J, Zhang B, Xu Y, Wei W, Fan L, Pei X, Hong Y and Wang Y 2015 Chin. Phys. C 39 127007
[26] Prodromides A E, Scheuerlein C and Taborelli M 2001 Vacuum 60 35–41
[27] Zhang B, Wang Y, Wei W, Fan L, Wang J and Li W 2012 Phys. Proc. 32 802–6
[28] Wu H, Cui J, Xu Y and Xu X 2018 Mater. Sci. Forum 913 700–6
[29] Benvenuti C, Chiggiato P, Costa Pinto P, Prodromides A and Ruzinov V 2003 Vacuum 71 307–15
[30] Li C-C, Huang J-L, Lin R-J, Lii D-F and Chen C-H 2007 J. Vac. Sci. Technol. A 25 1373–80
[31] Malsheov O B, Valizadeh R, Collignon J S, Hannah A, Middleton J K, Patel S and Vishnyakov V M 2009 J. Vac. Sci. Technol. A 27 521–30
[32] Li C-C, Huang J-L, Lin R-J and Lii D-F 2006 Surf. Coat. Tech. 201 3977–81
[33] Li C-C, Huang J-L, Lin R-J, Lii D-F and Chen C-H, 2009 Thin Solid Films 517 5876–80
[34] Li D and Cheng Y 2011 Vacuum 85 739–43
[35] Malsheov O B, Middleton J K, Collignon J S and Valizadeh R 2009 J. Vac. Sci. Technol. A 27 321–7
[36] 798–97 ASTM 2002 Standard Practice for Determining Gettering Rate, Sorption Capacity, and Gas Content of Non-evaporable Getters in the Molecular Flow Region. (West Conshohocken: ASTM International)
[37] Zhang Y, Wei X, Mao C, Li T, Yuan P and Du J 2009 J. Alloys Compd. 485 200–3
[38] Mozaftari N, Mirzakosseini A H S, Sadri A H and Aval L F 2019 Journal of Theoretical and Applied Physics (https://doi.org/10.1007/s40094-019-00360-6)