

## Activation and gas sorption performance in Zr-Co-Y getters on Ge substrates

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The ternary ZrCo based getters are widely used in accelerator vacuum chambers and MEMS cavity. In this study, ZrCoY (Y is the rare earth element) getter thin films were deposited on polished Ge substrates in the uncooled infrared detectors by magnetron sputtering. Microstructure, sorption performance and activation mechanism were investigated. The grain size became larger and the FWHM of XRD diffraction peak decreased from 5.067 to 3.730 after the activation at 300°C for 45 minutes. The initial H<sub>2</sub> sorption speed reached 67.5 cm<sup>3</sup>·s<sup>-1</sup>·cm<sup>-2</sup> and the attenuation of sorption performance firstly was 11% but decreased to 4.4% at the fifth hour which indicated that the good effect of ZrCoY getters. The total sorption was calculated to 2743.57 Pa·cm<sup>3</sup>·cm<sup>-2</sup>. XPS showed that the getter film mainly existed as the form of ZrO<sub>2</sub> with a small amount of Zr. The addition of a Ni protective layer improved the sorption performance with initial sorption speed of 82 cm<sup>3</sup>·s<sup>-1</sup>·cm<sup>-2</sup>. The ZrCoY getter film on Ge substrates can be applied in uncooled infrared focal plane arrays (IRFPA).

**Keywords:** Non evaporable getters, ZrCoY, sorption performance, vacuum packaging

### INTRODUCTION

The vacuum packaging in micro-electro-mechanical systems (MEMS) such as low lost uncooled infrared focal plane arrays (IRFPA) detectors is very important procedure to improve the devices performances and reliability. Undesired residual gases like H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> after packaging have to be removed to maintain the vacuum conditions in the MEMS cavity [1-3]. Non-evaporable getters (NEG) are utilized for efficient sorption of sealed-off vacuum devices. The conventional bulk or sheet getters have been unsuitable for MEMS because of the limited space. The NEG thin films can be grown on the inner walls of vacuum chamber with lower activation temperature and better adhesion [4-5]. The pure metal or alloy like Ti, ZrTiV, ZrVFe have been applied in vacuum packaging for decades [6-9]. Recently, ZrCo based materials without toxic elements have attracted considerable interest because Co oxides can be deoxidized at low temperature which is benefit to decreasing the activation temperature. Zr-Co-RE (RE indicating rare earth elements) alloy getter materials exhibit a wide range of gas pumping and low activation temperature because of the excellent sorption performance of RE elements like Ce, La. In RE group [10], Yttrium (Y) is rich in the earth especially in China. Besides, it has been

demonstrated that the nickel (Ni) could reduce the activation temperature obviously because nickel plays a role of catalyst and can dissociate the hydrogen molecule at a lower energy level.

The NEG thin films in most of the research were grown on Si wafer. The NEG thin films in the vacuum MEMS devices usually need to be grown on the various substrates, such as germanium (Ge) window in IR detectors packing. It is important to understand the effect of Ge substrates on the film morphology, the activation property and sorption performance. In this paper, the highly porous ZrCoY thin films getters with Ni protect layer on Ge window substrates were firstly prepared by RF magnetron sputtering. The effect of Ni protect on the microstructure and morphology was discussed. Further, the effect of Ni protect layer on activation and H<sub>2</sub> gas sorption performance was studied.

### EXPERIMENT

#### *Films deposition*

ZrCoY getter films were deposited on Ge substrates by RF magnetron sputtering. The Ge substrates were ultrasonically cleaned with acetone and alcohol in sequence, followed by washing in deionized water and heating at 300 °C for 30 min. The structure of the getter films from down up is the adjusting layer, the getter layer and the protective layer denoting Ge/Ti/ZrCoY/Ni. Ti film

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about 1 μm thickness was sputtered using the Ti (99.999%) target under the power 150 W, the Ar flow rate 80 sccm and the deposition pressure 1.0 Pa. ZrCoY getter films about 2 μm thickness were deposited by sputtering the alloy target under the power 80 W, the Ar flow rate 40 sccm and the deposition pressure 4.0 Pa. Ni film about 500 nm thickness was deposited using the same parameters as Ti film. The sputtering parameters were shown in Tab.1. Then the getter films were activated by annealing in the vacuum of  $1.0 \times 10^{-5}$  Pa at 300 ??? for 45 minutes.

**Table 1.** The sputtering parameters of Ti/ZrCoY/Ni getter films on Ge substrates

Films	Sputtering Power/W	Sputtering pressure/Pa	Thickness /μm
Ni	150	1	0.5
ZrCoY	80	4	2
Ti	150	1	1

*Presentation of the experimental equipment*

The microstructure was studied by X ray diffraction (Rigaku MSAL XD2) operated at 36kV and 20mA. The field emission scanning electron microscope (FEI Quanta FEG 450) with an integrated energy dispersive X-ray spectrometer (EDS) was used to analyze the morphology, cross-section and surface composition of the film. The componential analysis of the Zr-Co-Y thin films was investigated using Thermo Fisher Scientific EscaLab 250Xi X-ray photo-emission electron spectroscopy (XPS) measurements.

Gas sorption performance was tested by the dynamic method according to national standard of PRC GB8763-88 [11]. The two gas chambers were connected by capillary or orifice. The pressure of one chamber with getter was  $P_g$ . The other with inlet  $H_2$  gas was  $P_m$ . In the test, the  $P_g$  remained  $1.0 \times 10^{-4}$  Pa unchanged and the  $P_m$ -time (t) relation was recorded. The sorption speed  $S$  ( $cm^3 \cdot s^{-1} \cdot cm^{-2}$ ) and the sorption quantity  $Q$  ( $Pa \cdot cm^3 \cdot cm^{-2}$ ) can be calculated by formula as followed:

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

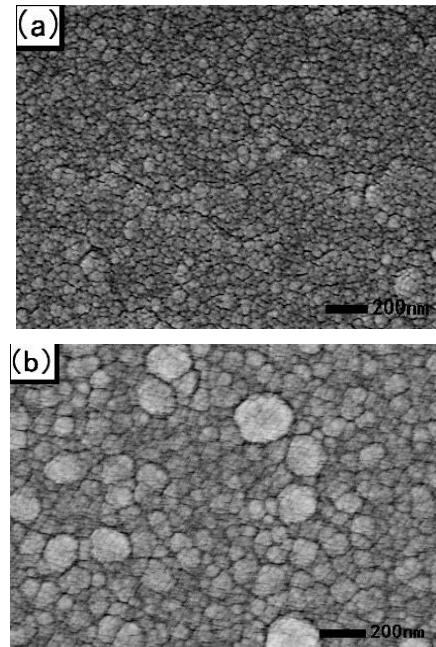
$$Q = \int_0^t Q_i dt = \frac{F}{A} \int_0^t (P_m - P_g) dt$$

where  $F = 71$  ml/s for  $H_2$  is the conductance of the capillary tube.  $A$  ( $cm^2$ ) is the area of the tested getter.

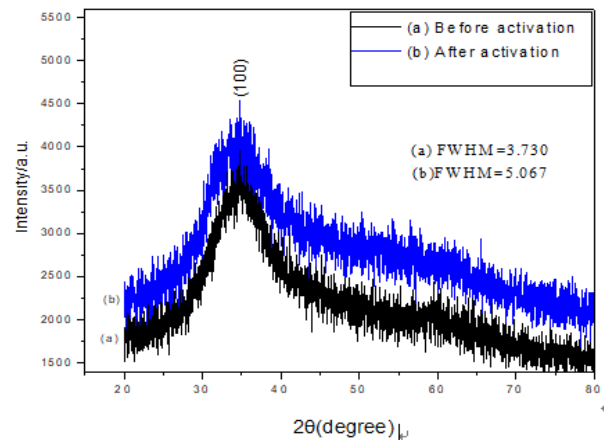
**RESULTS AND DISCUSSION**

*Films microstructure before and after the activation*

Fig.1 showed SEM images before and after activation of the films. The grain size became larger obviously from 20 nm to 60nm before and after the activation. During the heating activation process, the diffusion coefficient of the atoms increased. Therefore, the grain boundary was more likely to move which resulted in the growth of the grain. After the activation, the fresh and active surface was exposed [12-14,15].



**Fig.1.** SEM images of ZrCoY getter films before (a) and after (b) activation



**Fig.2.** XRD pattern of ZrCoY getter films before and after activation

The XRD pattern before and after activation was shown in the Fig.2. The diffraction peak around 2θ

= 35° was (100) orientation according to the  $\alpha$ -Zr hexagonal structure. The full width at half maximum (FWHM) of the peak became narrow from 5.067 to 3.730 because the activation process was accompanied by the growth of fine grains and the ordering of atoms [16].

*Inspiratory performance analysis*

Fig.3 showed the H<sub>2</sub> sorption performance of ZrCoY films after activation at 300 ° C for 45 min. The initial sorption speed reached 67.5 cm<sup>3</sup>·s<sup>-1</sup>·cm<sup>-2</sup>, then decreased slowly with the sorption quantity increasing. After activation, the bonds of the molecule broke and the gap between the grains increased, which significantly increased the surface area and improved the gas sorption properties of the

films. The rough surface and the interstitial space after activation are the main diffusion channels of the active gas molecules.

During the deposit of the vacuum MEMS devices, small amount of gas may release from the cavity materials. The change of the sorption speed with the time was investigated as shown in Tab.2. According to ASTM F798-97 (2002), the attenuation of the sorption speed is defined to the ratio of the real-time sorption speed to the initial sorption speed. The total sorption quantity is defined to the quantity at the termination of the sorption where the termination sorption speed is 5% of the initial speed that was 3.375 cm<sup>3</sup>·s<sup>-1</sup>·cm<sup>-2</sup> in our experiment.

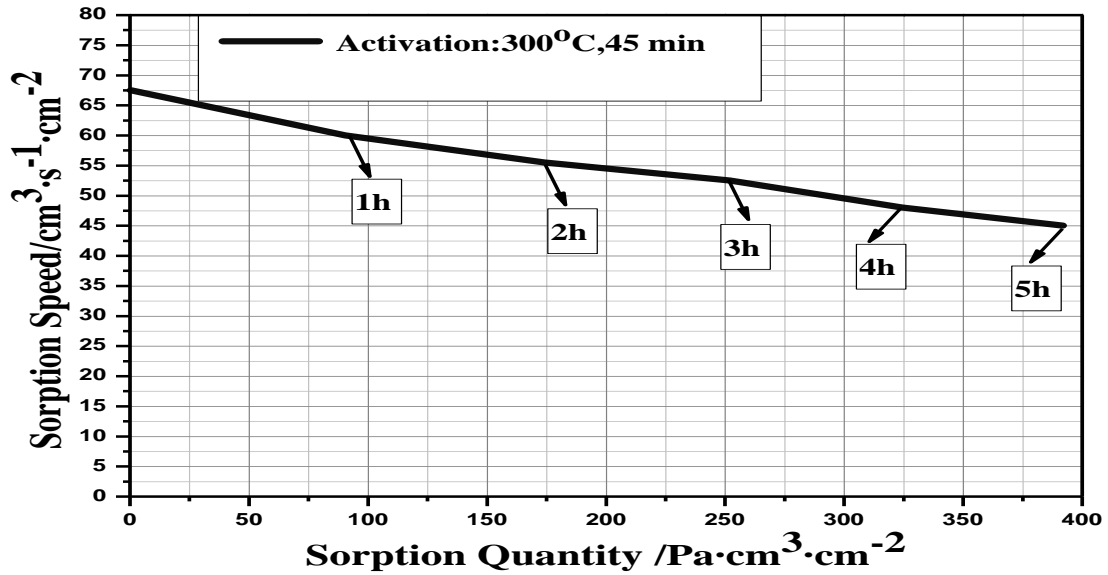


Fig.3. Hydrogen sorption performance curve of ZrCoY films on Ge substrates

Table 2. The change of the sorption speed with the time

Test time (h)	Real-time sorption speed (cm <sup>3</sup> s <sup>-1</sup> cm <sup>-2</sup> )	Attenuation (real-time/initial speed)
0	67.5	100%
0.5	63	93.33%
1	60	89%
1.5	58.5	86.7%
2	55.5	82.2%
2.5	54	80%
3	52.5	77.8%
3.5	51	77.6%
4	48	71.1%
4.5	46.5	68.9%
5	45	66.7%

The sorption speed gradually decreased with the time while the attenuation degree fade. From Tab.2, the attenuation rate decreased from 11% (100%-89%) in the first hour to 4.4% (71.1%-66.7%) in the fifth hour taking the initial sorption speed as the reference. It indicated that sorption of ZrCoY getters postponed the reduction of the vacuum degree. The empirical relation between the sorption speed and the quantity followed [17]:

$$\lg S = -\frac{Q}{A} + B \quad (1)$$

Where  $A$  and  $B$  are the parameters relating to the getter composition and the activation degree. The two parameters can be obtained by linearly fitting to  $A=2108.77$ ,  $B=1.83$  according to Fig.3. Then the formula (1) can be written as:

$$\lg S = -\frac{Q}{2108.77} + 1.83 \quad (2)$$

The total sorption  $Q$  can be obtained to  $2743.57 \text{ Pa}\cdot\text{cm}^3\cdot\text{cm}^{-2}$  by substituting the termination sorption speed  $3.375 \text{ cm}^3\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ .

#### Sorption mechanism analysis

The sorption mechanism of ZrCoY getter was studied by XPS analysis as shown in Figs.4-6. Fig.4 was a full spectrum after sorption at room temperature in which the main elements of Zr, Co, O, Y and C can be found. The measured data were related to the evolution of the XPS spectra of Zr 3d, Co 2p, Y 3d, O 1s, and C 1s orbitals. The oxygen element came from the oxidation of the surface. The strong O1s peak was located at about 540 eV. The weak peak at 284 eV accorded to the C 1s binding energy, indicated a small amount of CO and CO<sub>2</sub> were absorbed before activation.

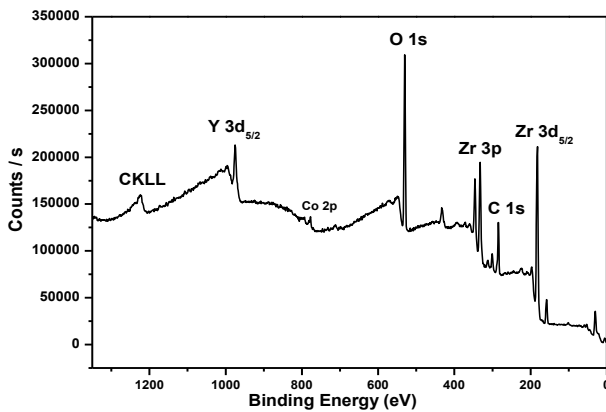


Fig.4. XPS spectrum of ZrCoY film after sorption

Fig.5 showed XPS spectrum of the Zr3d related peaks of ZrCoY films using the Gaussian-Lorentzian fitting after sorption. The two strong peaks at the electron binding energy 182 eV and 184.5 eV corresponded to Zr 3d5/2 and Zr 3d3/2 in ZrO<sub>2</sub> form or Zr<sup>4+</sup>. The weak peaks at 178 eV and 180.5 eV accorded to Zr 3d5/2 and Zr 3d3/2 in the natural form. The films mainly existed as the form of ZrO<sub>2</sub> with a small amount of Zr without metal hydroxide (Zr(OH)<sub>2</sub>) and metal suboxides (ZrO<sub>x</sub>, here  $x < 2$ ) as other reports [18]. The composition of ZrO<sub>2</sub> and Zr was 90.78% and 9.22% respectively according to the area calculation. Obviously the abundant O<sub>2</sub> were absorbed and reacted with ZrCoY getter films after the activation, which proved the good sorption ability of the getter films.

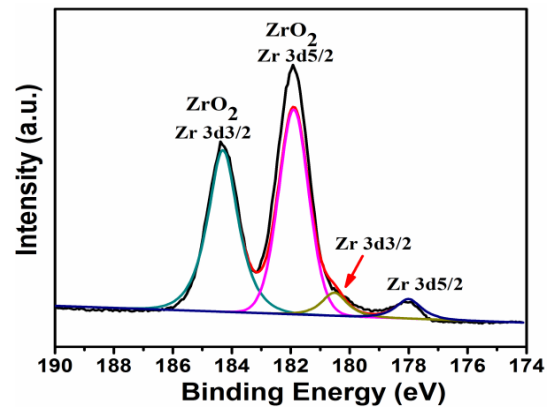


Fig.5. Zr 3d peaks in XPS spectrum after sorption

Fig.6 showed XPS spectrum of the Co 2p peak after sorping. The two characteristic peaks at 792 eV and 777 eV were accordance to Co 2p 1/2 and Co 2p 3/2 orbitals. There were obvious satellite peaks relating to the electronic vibration or Auger electron.

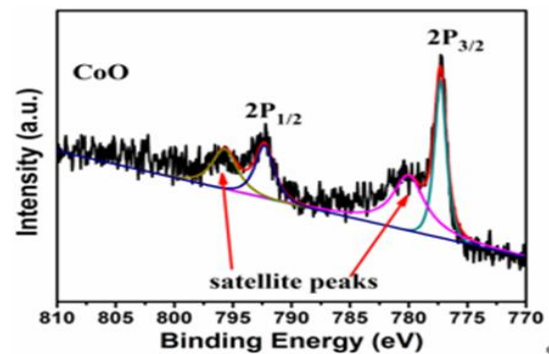


Fig.6. Co 2p XPS energy spectrum after sorption

The as-deposited and activated ZrCoY films were easily oxidized and absorbed the reactive gas in the air. The gas molecule was absorbed at the

surface and diffused to the certain depth from the surface which accompanied the energy absorption, the bond crack and new bond formation. So the gas molecule must be exhausted through the activation process. During the heating, Zr-O and Co-O bonds at the surface were broken resulted in the oxygen atoms diffusing into the bulk and Zr/Co metallic state appeared at the surface, which will realize the adsorption activity of the film.

*Effect of Ni protective layer on the sorption performance in ZrCoY getter*

Fig.7 showed the hydrogen sorption performance curve of ZrCoY getter films with and

without Ni protective layer. The Ni layer improved the sorption performance obviously. After being activated at 300 ° C for 45 min, the initial sorption speed improved from  $67.5 \text{ cm}^3 \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$  to  $82 \text{ cm}^3 \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$ , indicating that the protective layer played a significant protective effect on the getter and reduced oxidation of the film. The getter without Ni layer had an open surface and a large active area so that the active gas was more likely to oxidize the getter surface to form a passivation film. In the structure with Ni layer, the crystal bond broke and the gap increased which significantly improved the sorption performance.

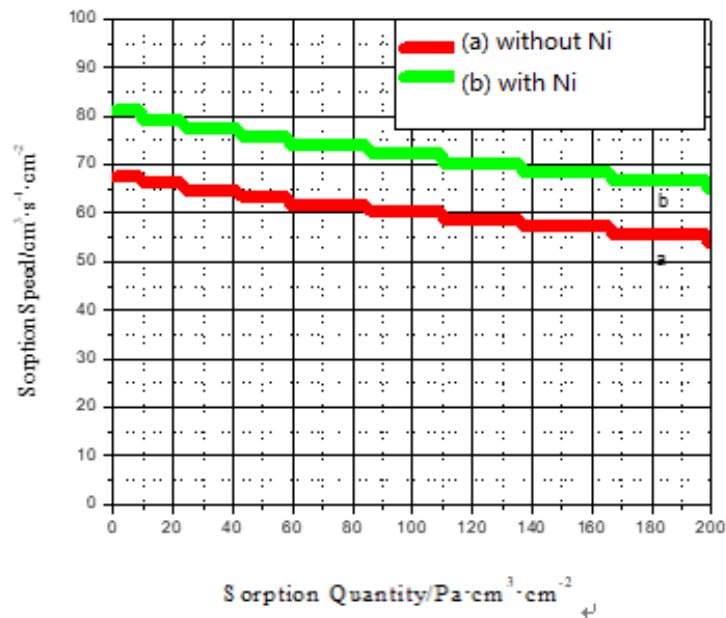


Fig.7. The sorption performance curves of ZrCoY film with and without Ni protective layer

CONCLUSIONS

ZrCoY (Y is the rare earth element) getter thin films were deposited on polished Ge substrates by magnetron sputtering. The microstructure, the surface morphology, the sorption performance and the activation mechanism were investigated. The total H<sub>2</sub> sorption quantity of ZrCoY getter films was estimated to about 2743.57 Pa·cm<sup>3</sup>·cm<sup>-2</sup>. The sorption speed of Ni/ZrCoY film getters was 82 cm<sup>3</sup>·s<sup>-1</sup>·cm<sup>-2</sup> which is 1.3 times than that of ZrCoY film getters. With the development to the inside of the film, O<sub>2</sub> gradually changed from adsorption state to oxidation state. The Ni protective layer effectively reduces the oxidation degree of ZrCoY film getter. The sorption properties of Ni/ZrCoY/Ti getter films in this paper ensure its application in

the uncooled infrared focal plane arrays (IRFPA). In addition, Ni protective layer provides a new passivation layer to improve the sorption properties in many vacuum sealed devices such as gyroscopes, accelerometers, micro-bolometers, pressure sensors, frequency resonators and atomic clocks. In the future, thicker Ni layer and other metal alloy protective layer can be applied to improve the sorption speed. ZrCo alloy with other rare earth elements like Ce will be investigated.

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