

# NanoGetters for MEMS Hermetic Packaging

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**Abstract** — A new getter, we call it nanogetter, based on carbon nanotubes (CNTs) coated Ti films has been developed with the purpose of providing a more efficient material, capable of getting active at high vacuum environment ( $< 10^{-3}$ Torr, molecular state) and low temperature ( $< 400^{\circ}\text{C}$ ). Because of the large surface area of CNTs and its native gas adsorption ability, dense CNTs growth on silicon substrate is considered to be an effective skeleton structure of the nanogetters. All the tests have demonstrated that surface area of nanogetters do have been increased and the pumping speed is enhanced to large amount compared with some traditional getters, such as St175 of SAES in Italy.

**Keywords** — carbon nanotubes (CNTs), hermetic packaging, nanogetter

## I. INTRODUCTION

Vacuum and hermetic encapsulation technologies are essential for micro electro mechanical systems (MEMS) and devices to enhance their reliability and performance. Condensed moisture on a MEMS device surface and degassing of gaseous species during the operation may lead to the principle causes of failure in the field. Hermetic packaging is designed to prevent performance degradation caused by moisture deleterious effects and outgassing of gaseous species from packaging materials. Surface outgassing is the main obstacle to achieving ultrahigh vacuum (UHV) conditions during the MEMS encapsulation. A material called “getter” is needed to eliminate these problems and “kill” the undesirable substances such as  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{O}_2$ . But now there are still some limitations for the use of conventional getters [1], such as contamination, particles generated in the sintered getters during handling and cutting process, low efficiency with multi-layer, thin film, hard to assemble high porous thin film (HPTF) getters inside micro-cavity and incompatible with micro fabrication process, etc.

Thin film getter with high porous or rough appearance has the property of high adsorption characteristic even at room temperature [2, 3]. This work proposes and focuses on fabricating a novel getter based on CNTs to increase the adsorption performance by improving the efficiency of reaction between getter material and gases.

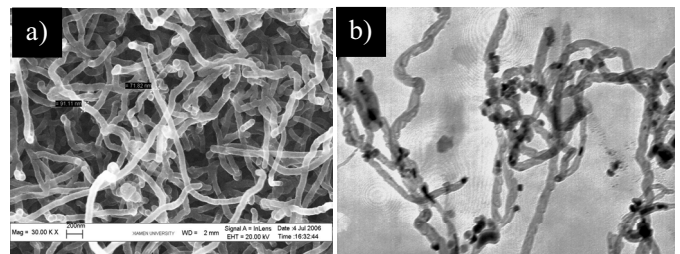
## II. FABRICATION

### A. Structural configuration

Porous structure allows the gases to diffuse through the pores inside the bulk getter thus ensures a large available surface area for the sorption process [4]. CNTs, due to its high

surface area-volume ratio in nature and gases absorption ability, is tried to be employed as the scaffold of the getter film.

In this paper, uniform CNTs have been synthesized on large area Si substrates by thermal chemical vapor deposition (CVD) methods using methane ( $\text{CH}_4$ ) as a carbon source and a binary alloy Ni/Fe as catalyst. Fig. 1 shows the scanning electron microscope (SEM, LEO 1530) image of CNTs. Fig. 1(a) illustrates the CNTs are uniformly distributed with a relatively high density. A comparison of the TEM image is shown by Figs. 1(b), which illustrates that no carbonaceous particles (carbon black) are observed over the entire surface area of the substrates, the average diameter of CNTs is about 81.47nm.



**Figure 1** (a) SEM image of CNTs on the Si substrates at 950 with the methane gas flowed at 40scem $\times$ 10min, (b) a comparison of the TEM image of CNTs.

High specific surface area of CNTs is proved by the usual Brunauer - Emmett - Teller (BET) technique with  $\text{N}_2$  as the test gas. The surface area of CNTs is up to 154.39m<sup>2</sup>/g according to testing reports.  $\text{N}_2$  adsorption/desorption isotherms of the CNTs sample weight 0.3721g are depicted in Fig. 2. As can be seen from this figure, both micropore and mesopore structures are present in the CNTs, the gradual increase from  $P/P_0 > 0.2$  is attributed to the wide range of mesopores. This can be proved by the BJH desorption cumulative pore volume which is shown in Fig. 3, above 90% pores are with the diameters range of 2~100nm, which indicates that CNTs do have an effect on the porosity and the increment surface area to be the skeleton structure of the nanogetters.

### B. Materials

The alloys from metals of the IVB group and thorium are normally used to be the non-evaporable getters materials [5]. The metals in the getters are capable of dissolving their own chemically formed oxides, nitrides and carbides in the solid-state form at elevated temperatures. Ti and Zr are the most common used metal elements for getters. Nevertheless Zr

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powders have high activity, they are easily flammable and explosive [6]. So Ti was chosen as the active element in our research. The characteristics of nanogetters with pores structure and Ti films thickness of 200nm is shown in Fig. 4. As can be seen from Fig. 4, CNTs based getter is a type of porous netlike and toothed structure, the rough appearance will increase the effective area of nanogetters to enhance the adsorption performance.

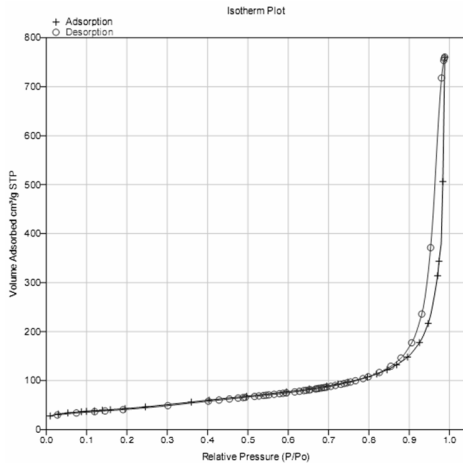


Figure 2 Nitrogen adsorption/desorption isotherms of CNTs.

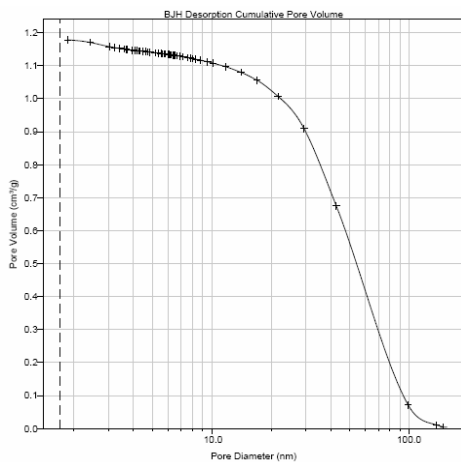


Figure 3 CNTs BJH desorption cumulative volume plot.

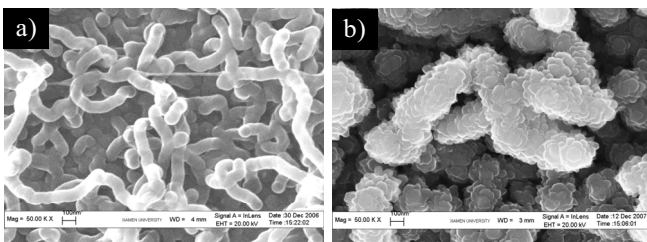


Figure 4 SEM images of Ti films sputtering on the CNTs before (a) and after (b).

### III. SORPTION CHARACTERISTICS

Thermogravimetric analyzer (TGA) is employed to prove the

adsorption performance of nanogetters with high surface area according to the weight loss.

The characteristics of the nanogetters have been investigated for H<sub>2</sub>, measuring the pumping speed as a function of the sorbed quantity by means of the standard dynamic method [7].

#### A. Tests

The TGA procedure was to heat the sample from room temperature to 500°C with a rate of 10°C/min in atmosphere. Four types of the samples: pure Si substrate, Si substrate with 5nm Ni/Fe coated, CNTs on Si substrate and CNTs with Ti films coated were used.

The nanogetter materials, like all other non-evaporable getter materials, must be activated. The following tests have been performed on nanogetter samples with the area of 215mm<sup>2</sup> and weight of 1.33mg in our experiment:

- 1) sorption of H<sub>2</sub> at room temperature at activation temperature 550°C × 10min with a constant pressure P<sub>g</sub> of 6.0 × 10<sup>-6</sup>Torr,
- 2) sorption of H<sub>2</sub> at room temperature at activation temperature 550°C × 10min and then 900°C × 30s with P<sub>g</sub> 1.5 × 10<sup>-6</sup>Torr,
- 3) sorption of H<sub>2</sub> at 320°C at activation temperature 550°C × 10min with P<sub>g</sub> 1.5 × 10<sup>-6</sup>Torr,
- 4) sorption of H<sub>2</sub> at 320°C at activation temperature 550°C × 10min with P<sub>g</sub> 6.0 × 10<sup>-6</sup>Torr.

#### B. Results and discussion

TGA was used to evaluate the capability of atmosphere absorption for the nanogetters. Fig. 5 shows the weight results of the four samples. It indicates that Ti films sputtering on the CNTs have larger capability to absorb atmosphere comparing to the other three samples from 75 to 500°C, the

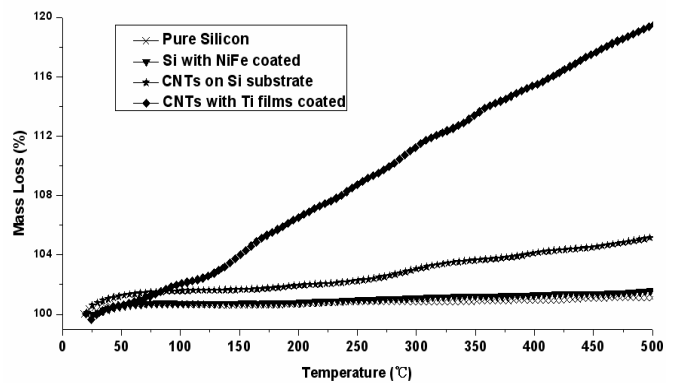


Figure 5 Weight gain vs. temperature for the pure Si substrate, Si substrate with 5nm Ni/Fe films coated, CNTs grown on the Si substrate and CNTs with Ti films coated on the Si substrate.

weigh gain is 8 times as great as Si when heat to 250°C and about 10 times at 500°C. This can be due to the higher surface area which can enhance the chemisorption according to the

adsorption mechanism. The sorption of the atmosphere on Ti films contains many complex reactions, such as physisorption and chemisorption between atmosphere and samples' surface, the adsorption and desorption on the samples' surface, solubility and diffusion of the atmosphere and the samples, etc.

Fig. 6 shows pumping speed decreases from  $1.8 \times 10^3 \text{ mL/s}$  to  $3.1 \times 10^2 \text{ mL/s}$  when the sorbed quantity changes from  $3.0 \times 10^{-2} \text{ mL}\cdot\text{Torr}$  to  $6.0 \times 10^{-2} \text{ mL}\cdot\text{Torr}$  after activation at  $550^\circ\text{C} \times 10\text{min}$  and constant pressure  $6.0 \times 10^{-6} \text{ Torr}$ . This is practically the same getting rate of descend when the absorbed quantity ranges from  $1.6 \times 10^{-2} \text{ mL}\cdot\text{Torr}$  to  $3.1 \times 10^{-2} \text{ mL}\cdot\text{Torr}$  in Fig. 7. Concerning the sorption of  $\text{H}_2$  at  $320^\circ\text{C}$  as the getter working temperature, the results are shown in Fig. 8 and 9 where it is possible to see the getter material performance is improved. Fig. 9 illustrates that the sorbed quantity ranges from  $0.06 \text{ mL}\cdot\text{Torr}$  to  $1.2 \text{ mL}\cdot\text{Torr}$  when getting rate decreases from  $200 \text{ mL/s}$  to  $10 \text{ mL/s}$  as illustrated in Fig. 9, which is up to 38 times as great as the sorbed quantity performed at room temperature and the same constant pressure after activation at  $550^\circ\text{C} \times 10\text{min}$  as observed in Fig. 6.

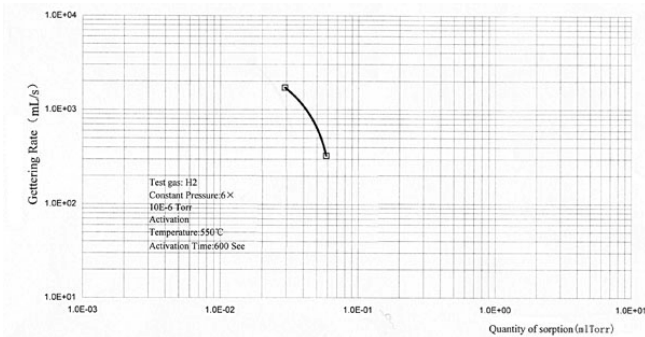


Figure 6 Sorption tests of  $\text{H}_2$  on nanogetter at room temperature at  $P_g 6.0 \times 10^{-6} \text{ Torr}$  and activation at  $550^\circ\text{C} \times 10\text{min}$ .

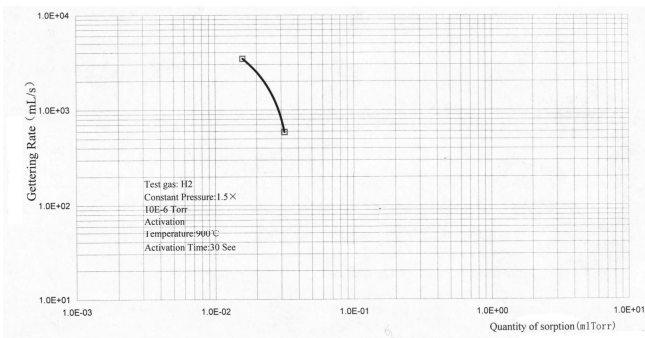


Figure 7 Sorption tests of  $\text{H}_2$  on nanogetter at room temperature at  $P_g 1.5 \times 10^{-6} \text{ Torr}$  after activation at  $550^\circ\text{C} \times 10\text{min}$  and then  $900^\circ\text{C} \times 30\text{s}$ .

Nanogetter was compared with the traditional getter St175, which is based on a powder of Ti and Mo in the weight ratio of 9:1 [8]. The specimens weight of  $0.8\text{g}$  were previously activated at  $500^\circ\text{C} \times 10\text{min}$  and  $750^\circ\text{C} \times 10\text{min}$ , the results of tests on the sorption of  $\text{H}_2$  at room temperature and  $400^\circ\text{C}$  at the pressure  $3 \times 10^{-6} \text{ Torr}$  are shown in Fig. 10. In comparison

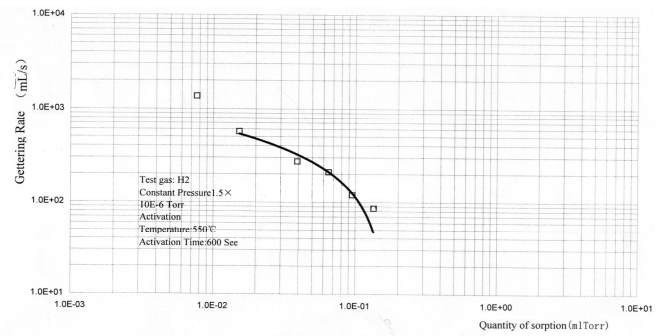


Figure 8 Sorption tests of  $\text{H}_2$  on nanogetter at  $320^\circ\text{C}$  at  $P_g 1.5 \times 10^{-6} \text{ Torr}$  and activation at  $550^\circ\text{C} \times 10\text{min}$ .

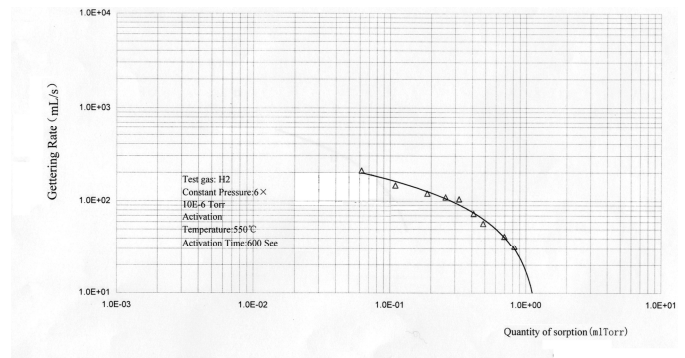


Figure 9 Sorption tests of  $\text{H}_2$  on nanogetter at  $320^\circ\text{C}$  at  $P_g 6.0 \times 10^{-6} \text{ Torr}$  and activation at  $550^\circ\text{C} \times 10\text{min}$ .

with the sorption unit-weight sorption characteristics of the two

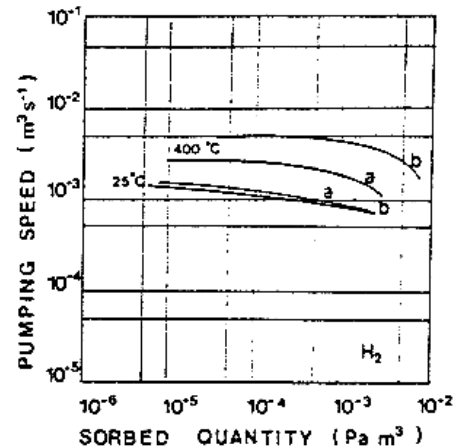


Figure 10 Sorption tests of  $\text{H}_2$  on Ti/Mo getter at room temperature and at  $400^\circ\text{C}$ , after activation at  $500^\circ\text{C} \times 10\text{min}$  (a) and at  $750^\circ\text{C} \times 10\text{min}$  (b). Gas pressure  $3.0 \times 10^{-6} \text{ Torr}$  [8].

getter materials which had been performed at room temperature, the results obtained in the present work are illustrated by the Fig. 11. In the case of room temperature sorption characteristics, the pumping speed and sorbed quantity seem to be less dependent on the activation temperature and constant pressure. As shown in Fig. 11, when the sorbed quantity is  $0.02 \text{ mL}\cdot\text{Torr}/\text{mg}$  after activation at  $550^\circ\text{C} \times 10\text{min}$ , the pumping speed of unit-weight nanogetters is up to  $1000 \text{ mL}/(\text{s}\cdot\text{mg})$ , which is near 1000 times greater than St175 at the same sorbed quantity after activation at  $500^\circ\text{C} \times 10\text{min}$ . But

the sorbed quantity of nanogetters per milligram is poor than St175 according to the pumping speed descending slope of nanogetters, which is near 2800 times as great as St175. Fig. 12 shows that nanogetters materials still have the strong pumping speed compared with St175. When the sorbed quantity is 0.04mL·Torr/mg after activation at 550 °C × 10min, the pumping speed of unit-weight nanogetters is up to 150mL/(s·mg), which is about 20 times greater than St175 at the same sorbed quantity after activation at 750 °C × 10min. Nevertheless the sorbed quantity of nanogetters per milligram is poor than St175 due to the pumping speed of nanogetters decreased sharply while the sorbed quantity of nanogetters is greater than 0.1 mL·Torr/mg.

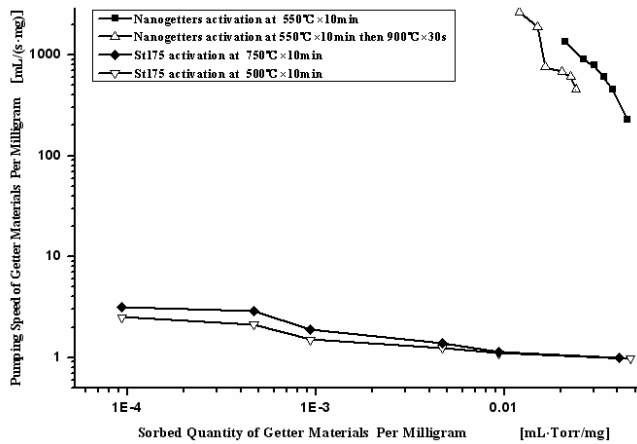
sputtering the alloy powders (such as Ti-Mo, Ti-Zr-V and Zr-V-Fe etc.) instead of Ti onto CNTs.

#### ACKNOWLEDGMENT

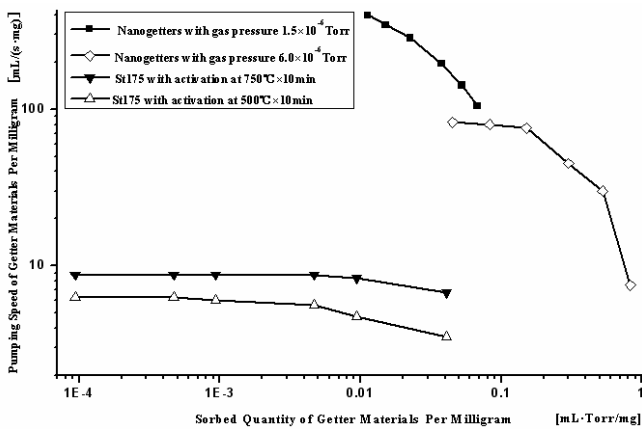
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**Figure 11** Sorption tests of H<sub>2</sub> on getter materials per milligram at room temperature with gas pressure  $3.0 \times 10^{-6}$  Torr for St175 and  $6.0 \times 10^{-6}$  Torr for nanogetters.



**Figure 12** Sorption tests of H<sub>2</sub> on nanogetters per milligram at 320°C and activation at 550 °C × 10min, St175 per milligram at 400 °C with gas pressure  $3.0 \times 10^{-6}$  Torr.

#### IV. CONCLUSIONS

In summary, nanogetter, based on CNTs coated with Ti films has been proven that it has high porosity and specific surface area, which allows a good pumping speed of unit-weight nanogetter at room temperature and at 320°C compared with St175, but the sorbed quantity is expected to be increased. The gettering capability can be envisioned to be enhanced if