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Fabrication and characterization of non-evaporable porous getter films

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Abstract

The porous Ti film getters on (100) silicon substrates were prepared using the glancing angle deposition of dc (direct current) magnetron sputtering method. The main deposition parameters that produce the porous Ti films are the low substrate temperature and high glancing angle. The larger the glancing angle is, the higher the porosity of the Ti films is. The porous films, grown at the glancing angle of 70° and room substrate temperature, are composed of nano-columnar crystalline crystals. The size and inter-distance between the columnar crystals are 70 nm and 30 nm, respectively. The porous Ti films have larger capability to absorb the oxygen than that of dense Ti films and Si substrate. The suitable operation condition of porous Ti film getters was also established.

Keywords: Porous films; Getter; Titanium; Glancing angle

1. Introduction

The non-evaporable getter (NEG) materials, such as titanium or titanium alloys, have been widely used in vacuum-type devices to upgrade and sustain the vacuum environment inside the cavity of the device by the chemical interaction between getters and gases [1–5]. Conventionally, bulk or sheet getters are used in the vacuum devices, such as the cathode ray tube (CRT) and the field emission display by the chip-level packaging process. With the progress of MEMS (microelectromechanical system) technologies, the development of the minimizing vacuum devices, such as high Q mechanical resonators, infrared detectors of focal plane array or tunneling sensors, has largely increased. The features of these devices are small vacuum cavity with several μm gap and wafer-level packaging fabrications. The conventional bulk or sheet getters can not be used in these minimizing devices due to the restricted space [6]. Additionally, the high porous or rough getters have the property of high pumping speed even at room temperature [6,7]. Therefore, it is highly required to develop the non-evaporable porous thin-film-type getters with several μm thickness for the applications of MEMS vacuum devices.

In this paper, the fabrication and characterization of surface morphologies and microstructures of the dense and porous Ti films will be first presented. Then, the gas-absorption performance of the film getters is discussed.

2. Experimental details

The Ti getter films were fabricated on (100) Si substrates by the glancing angle deposition of dc (direct current) magnetron sputtering method. The glancing angle is defined as the angle between the surface normal of the substrate and the surface normal of the target. The substrates were ultrasonically cleaned in the solutions of acetone and ethyl alcohol, respectively. Then, the substrate (1.57 in. × 1.57 in.)

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Table 1
Deposition conditions for dense and porous Ti films

Parameters	Dense Ti film	Porous Ti film
Flow rate of Ar	20 ml/min	20 ml/min
Target to substrate distance	3.54 in.	3.54 in.
dc power to Ti target	120 W	120 W
Working pressure	0.6 Pa	0.6 Pa
Glancing angle	0°	70°
Film thickness	1, 3 μm	1, 3 μm

was dipped into the dilute HF solution, diionized water and dried by purging nitrogen gas, sequentially. The Ti target (99.995% of purity; by Target Materials Inc., USA) with diameter of 3 in. and thickness of 0.25 in. was used. The deposition parameters were the pressure of sputtering gas Ar, dc power, glancing angle, target to substrate distance and deposition time, as listed in Table 1. The base pressure of deposition chamber was 2.7×10^{-4} Pa. The substrate was not intentionally heated during deposition. The thickness of the films was in the range of 1–3 μm.

The microstructures (phase, texture, crystallite size and lattice parameter) of the films were characterized by the grazing incident X-ray diffractometer (XRD, Rigaku D/MAX2500, Tokyo, Japan) with Cu K_α radiation and beam incident angle of 3°. A PHILIPS XL-40FEG field emission scanning electron microscope (Fe-SEM) was used to analyze the morphologies and the cross-sectional structure of the films. The surface roughness of the films was determined by an atomic force microscope (AFM, Digital Instruments Inc., NanoScope, USA). The gas absorption performance of the Ti films was characterized in a flowing oxygen atmosphere by a DuPont thermogravimetric analyzer (TGA). The evaluation of the suitable operation condition of the porous Ti film getters is made by the thermal desorption spectrometer (FSM 900TC-vac Integrated Metrology Chamber, USA).

3. Results and discussion

3.1. Microstructure analysis

The morphologies, microstructures and gas-absorption performance of the Ti films strongly relate to the deposition parameters, such as the pressure of sputtering gas Ar, dc sputtering power, deposition time and glancing angle. According to the Thornton's model [8], the continuous columnar structure of the films, grown by the sputtering process with zero glancing angle is obtained under the condition of low mobility of adatoms, such as low substrate temperature or high pressure of sputtering gas. However, the isolated columnar structure of the films, grown at high glancing angle, was presented by Ohring [9], Nieuwenhuizen [10], Messer et al. [11] and Robbie et al. [12]. This shows that the shadowing effect can be largely enhanced by increasing the glancing angle. There is a trend that the larger the glancing angle is, the higher the porosity of the film is [13,14]. In this study, we will accent the difference in morphologies and gas-absorption performance of the dense and porous Ti films, which were grown at the deposition condition of Ar pressure of 0.6 Pa, target-to-substrate distance of 3.54 in., dc power of 120 W, room substrate temperature and glancing angle of 0° and 70°, respectively, as listed in Table 1.

The surface morphologies and cross-sectional microstructures of the dense and porous Ti films are shown in the Fig. 1. Both of the films are composed of the nano-columnar crystals. The films grown at zero glancing angle have continuous columnar appearance, however the isolated columnar structure is formed in the films, grown at glancing angle of 70°. The former are the dense films, and the latter are the porous films. For the porous Ti films, the columnar size and inter-distance between the columnar crystals are 70 nm and 30 nm, respectively. The columnar crystals of the dense and porous Ti films have crystalline structure of Ti hexagonal closed package (hcp) phase, as shown in Fig. 2. The formation of the columnar structure is due to the low mobility of Ti adatoms on Si with low substrate temperature and non-perpendicular relationship between the sputtered flux and the substrate surface. This result has been thoroughly discussed in the Thornton's microstructure model [8]. As we know, the non-perpendicular relationship between the sputtered flux and the substrate surface becomes more marked with increasing the glancing angle. The effect of self-shadowing by the initial nuclei on the substrate surface is also increased with increasing the glancing angle. The porous films are formed when the glancing angle reaches the critical value (about 40°) or higher. Therefore, the formation of the porous columnar crystals of the films, grown with glancing angle of 70° and room substrate temperature, is due to the self-shadowing effect of the initial nuclei and little lateral diffusion of the adatoms. The feature of the porous columnar crystals is that there is a tilted angle between the columnar crystals and the substrate. The crystals are oriented toward the vapor sources (sputtering fluxes). This result is similar to other studies [9–12]. Additionally, the surface morphologies of the porous films have smoother appearance and better uniformity than the dense films, as shown in Figs. 1 and 3. The values of surface roughness (by AFM) of the dense and porous Ti films are 15.4 nm and 12.5 nm, respectively.

3.2. Performance characterization of Ti film getters

The apparatus for characterizing the thermal properties of the materials, such as the thermogravimetric analyzer (TGA), was used to evaluate the capability of oxygen absorption for the Ti film getters. The test procedure was to heat the sample from room temperature to 410 °C with a rate of 30 °C/min in atmosphere of flowing oxygen. Three types of the samples, such as pure Si substrate