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Characterization of activated non-evaporable porous Ti and Ti–Zr–V getter films by synchrotron radiation photoemission spectroscopy

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Abstract

Highly porous Ti and TiZrV film getters on (100) silicon substrates, grown by the glancing angle deposition of dc magnetron sputtering method, were used to study the activation process. The effect of activation temperature on the reducing degree of the porous Ti and TiZrV films were investigated by synchrotron radiation photoemission spectroscopy (SRPES). Elemental carbon absorbed on the surface of the Ti film, exposed in air, will be transformed to a Ti carbide phase, however, that which is on the surface of the TiZrV film will be completely removed by heat at 250 °C or above. The oxidized Ti in a porous TiZrV film is more easily reduced than that in the porous Ti films. The breakdown of V–O and Ti–O bonds on the TiZrV film surface is easier than that of the Zr–O bond. We suggest that the decrease of reducing temperature of oxidized TiZrV, comparing with that of oxidized Ti, is caused by the displacement reaction of Zr on oxidized Ti or oxidized V.

Keywords: Getter; NEG; TiZrV; BET; Porous films; Glancing angle; SRPES

1. Introduction

The development of various sealed-off devices requiring a vacuum for their operation have increased since the last decade. In order to upgrade and sustain the vacuum inside the cavity of vacuum-type devices, non-evaporable getter (NEG) materials, such as titanium or titanium alloys, have been widely used due to their high chemical activity, large solubility and high diffusivity for the adsorbed gases [1–6]. Some studies have shown that the pumping speed of the NEG for gases strongly depends on the geometrical area and the porosity of the activated getters [2,7–9].

With the development of microelectromechanical system (MEMS) technologies, the micro-miniature vacuum devices, such as high Q mechanical resonators, infrared detectors of focal plane arrays or tunneling sensors, play important roles in the development of the future micro-miniature devices. The features of these devices are small (micrometer) cavities with gaps typical of wafer-level bonding fabrication [10]. Therefore, porous thin-film-type NEGs with micron or sub-micron thickness are strongly required for the micro-miniature vacuum sealed-off devices in order to improve the vacuum.

When the NEG materials are exposed to air, their surfaces will be covered by reactive molecules such as oxygen, carbon dioxide, etc. The molecules absorbed on the NEG surface will desorb or diffuse into the NEG bulk during heating in a high vacuum. The process which heats the NEG in a vacuum to create a clean surface ready to absorb the reactive gases is called the activation process of the NEG. It is well known that the TixZryVz alloy with a well-defined composition range has the lowest activation temperature of 180 °C under the condition of activation time of 24 h [1,2,4]. The activation temperature of the NEG can be characterized by the ultimate pressure of the vacuum cavity [2] and the fully metallic surface state as determined by examination by X-ray photoelectron spectroscopy (XPS) [3,5], Auger electron spectroscopy (AES) [1,6], and static secondary ion mass spectroscopy (SSIMS) [4,5]. The essential factors to lower the activation temperature of the NEG

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materials are the following: The first is the composition of the NEG. It is well known that the TiZrV alloys exhibit the lowest activation temperature of 180 °C [1,2]. The second is the large solubility on the absorbed molecules at the activation temperature and room temperature. The third is the high bulk and surface diffusivity of the absorbed molecules in the NEG. The fourth is the microstructure and high specific surface area in the NEG, such as the porous microstructure, the microstructure with high density of grain boundaries or nanocrystalline grains [2].

In this paper, we will present the transition of the oxidized state to the metallic state for air-exposed porous Ti and TiZrV films by the consecutive heating steps in ultra-high-vacuum using the in-situ characterization of synchrotron radiation photoelectron spectroscopy (SRPES).

2. Experimental procedures

The highly porous Ti and TiZrV getter films were fabricated on (100) Si substrates by the glancing angle deposition of dc (direct current) magnetron sputtering method. The detailed processes were shown in our previous paper [11]. Targets of Ti (99.995% in purity; supplied by the Target Materials Inc., USA) and TiZrV (99.5% in purity; supplied by the Electric Materials Company, USA) with atomic composition of Ti/Zr/V = 30:20:50 were used. The main deposition parameters were the pressure of Ar sputtering gas, dc power, angle of deposition, and deposition time. The thickness of the films was about 3 μm. A field emission scanning electron microscope (Fe-SEM, Philips XL-40FEG, Eindhoven, Holland) with an integrated energy dispersive X-ray (EDX) spectrometer was used to analyze the composition, the morphologies and the cross-sectional structure of the films. The Brunauer-Emmett-Teller (BET) surface area of the films was determined by recording nitrogen adsorption/desorption isotherms at 77 K using a Micromeritics ASAP 2010 instrument (Micromeritics Instrument Corporation, USA). Before the physisorption measurements, the samples were outgassed at 383 K for 1 h in a vacuum.

To characterize the activated Ti and TiZrV getter films, the synchrotron radiation photoelectron spectroscopy (SRPES) was performed in a ultra-high-vacuum (UHV) chamber equipped with a Ta tape heater and a multichannel hemispherical energy analyzer at the National Synchrotron Radiation Research Center (NSSRC) in Taiwan. The light source is a high-performance U5-SGM undulator beamline, which covers photon energies from 60 eV to 1400 eV. The base pressure of the chamber was typically around 1.5×10^{-7} Pa. The thermal activation process was performed in five consecutive heating steps at 120 °C, 160 °C, 200 °C, 250 °C and 350 °C. The samples were kept at the indicated temperature for 0.5 h and then were cooled down to room temperature. The SRPES spectra were recorded at room temperature in each cycle. The binding energy (BE) scale was calibrated by measuring the carbon (1 s, 284.6 eV) core level signal of the molybdenum holder reference prior to and after measuring the sample.

3. Results and discussion

3.1. Microstructure and compositions of Ti and TiZrV films

The highly porous Ti and TiZrV films were used for the characterization of the activation process. The microstructure,

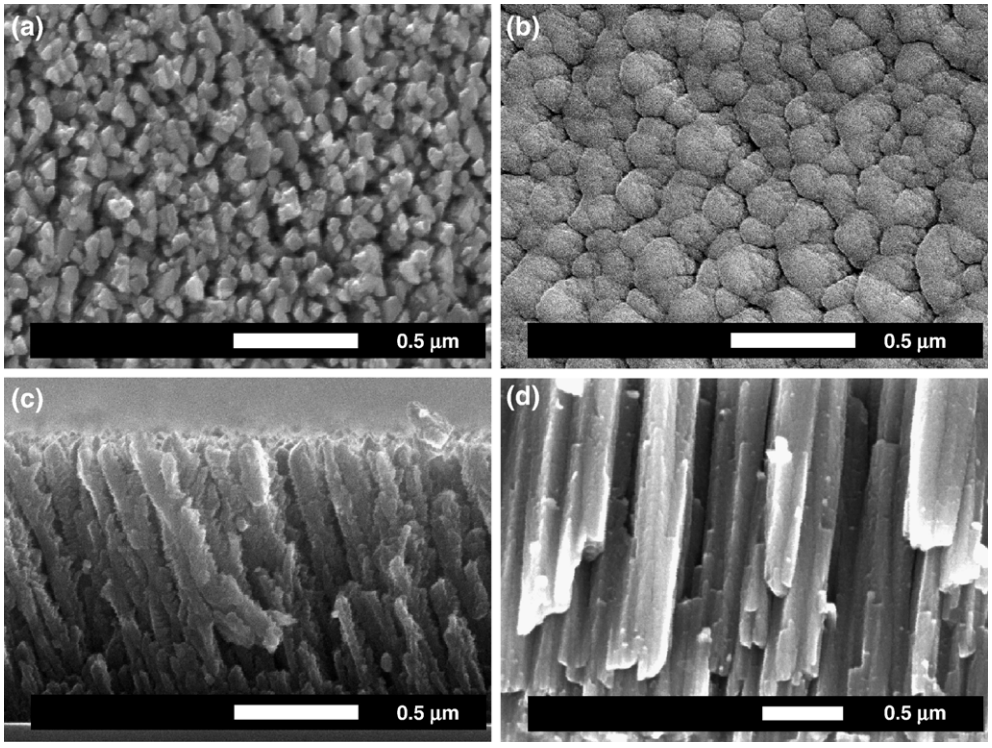

Fig. 1. SEM micrograph of the surface and fracture cross-section of films prepared on Si substrate of porous (a) Ti, (b) TiZrV, (c) Ti, and (d) TiZrV.