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# Activation characterization of non-evaporable Ti–Zr–V getter films by synchrotron radiation photoemission spectroscopy ☆

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**Abstract**

The effect of activation temperature on the degree of reduction of dense and porous TiZrV films was investigated by synchrotron radiation photoemission spectroscopy. The dense and porous TiZrV films have similar composition and thickness, and their specific surface areas are 2 $m^2/g$ and 13 $m^2/g$, respectively. Comparing the previous results of the porous TiZrV film [Chien-Cheng Li, Jow-Lay Huang, Ran-Jin Lin, Chia-Hao Chen, Ding-Fwu Lii, Thin Solid Films 515, (2006) 1121.], the degree of activation of the porous TiZrV film is lower than that of the dense TiZrV film. To complete the activation treatment of the dense and porous TiZrV films, the activation temperature must be higher than 350 °C or the activation time must be longer than 30 min.


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

## 1. Introduction

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 low activation temperature, high chemical activity, large solubility, and high diffusivity for gases [1–7]. When the NEG materials are exposed to air, their surfaces will be covered by the reactive molecules, such as oxygen, carbon dioxide, etc. The molecules adsorbed on the NEG surface will desorb or diffuse into the NEG bulk during heating in a high vacuum. The process during which the NEG is heated in a vacuum to create a clean surface ready to absorb the reactive gases is called the activation process of the NEG.

The activation temperature of the NEG can be characterized by the ultimate pressure of the vacuum cavity [1,3] and the fully metallic surface state by surface examination by X-ray photoelectron spectroscopy (XPS) [4,5,7], static secondary ion mass spectroscopy (SSIMS) [4,5], and Auger electron spectroscopy (AES) [2,6]. It is well known that the $Ti_xZr_yV_z$ alloy with a well-defined composition range has the lowest activation temperature of 180 °C with an activation time of 24 h [1–3,6].

In this paper, we characterized the effects of activation temperature on the oxidation state of surface layer of the air-exposed dense and porous TiZrV films on (100) Si substrates. The detailed results of the photoemission spectra of the activated TiZrV films and discussion of the evolution of surface oxides during consecutive activation processes will be presented.

## 2. Experimental procedures

The TiZrV getter films were fabricated on (100) Si substrates by the glancing angle dc (direct current) magnetron sputtering method. The detailed processes were as discussed in our previous paper [8]. The substrates were ultrasonically degreased and cleaned in acetone and ethyl alcohol, sequentially. Then, the substrate (4 cm × 4 cm) was dipped into the dilute HF solution,

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then washed with deionized water and dried by purging with nitrogen gas. The TiZrV target (30/20/50 at.% of composition, 99.5% of purity; supplied by the Electric Materials Company, USA) with a diameter of 7.62 cm and thickness of 0.64 cm was used. The deposition parameters were the pressure of Ar sputtering gas, deposition time, dc sputtering power and the glancing angle between the surface normal to the substrate and the surface normal to the target. The substrate was not intentionally heated during deposition. The thickness of the films was about 3 μm.

The microstructures (phase, texture, crystallite size and lattice parameter) of the films were characterized by a grazing incident x-ray diffractometer (XRD, Rigaku D/MAX2500, Tokyo, Japan) with Cu $K_\alpha$ radiation and beam incident angle of 3°. A Philips XL-40FEG field emission scanning electron microscope (Fe-SEM) with an integrated energy dispersive X-ray (EDX) spectroscopy was used to analyze the chemical composition, the morphologies and the cross-sectional structure of the films. The Brunauer–Emmett–Teller (BET) surface area of the TiZrV 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 vacuum.

To characterize the activated 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 photon energy of the excitation was 600±0.25 eV in the present experiment. The escape angle of the photoelectrons was 54.7°. The depth of the sampling was about 2 nm. These parameters were kept constant for the measurements on both samples. The surface composition of the films in atomic percent is calculated from the data of the photoelectron peak areas of the constituents and their atomic sensitivity factors at 54.7° [9] under the assumption that the sum of all constituents is 100%. The base pressure of the chamber was typically around $1.5\times10^{-7}$ Pa. The thermal activation process was performed by heating at intervals throughout 120, 160, 250 and 350 °C. The sample, mounted in a Molybdenum holder, was heated by a Ta tape heater. Sample temperature was monitored by a K-type (chromel–alumel) thermocouple, whose head was contacted with the Ta tape by mechanical force. The heating rate was 6 °C/min. The samples were kept at the indicated temperature for 0.5 h and then were cooled down to room temperature. During heating the sample, the pressure of the chamber generally increases with the increase of sample temperature. But, the chamber pressure did not exceed $7.9\times10^{-6}$ Pa even as the sample was heated to 350 °C for 30 min. The SRPES spectra were recorded at room temperature in each cycle. The binding energy (BE) scale was calibrated by measuring the carbon (1s, 284.6 eV) core level signal of the molybdenum holder reference prior to and after measuring the sample.

## 3. Results and discussion

The TiZrV films, sputter-deposited with an Ar pressure of 1.4 Pa at angles of 0° and 70°, were fabricated for this study. Fig. 1 shows the SEM micrographs of the surface and the cross-section of the TiZrV films grown with angles of 0° and 70°, respectively. For normal incidence or 0°, the appearance of the film is a dense fiber structure. Hereafter, this type of film is called the dense film. However, the film grown at the glancing angle of 70° is composed of porous and isolated columns, which are made of fine clusters. Hereafter, this type of film is called the porous film. The specific surface area of the dense and porous films is 2 $m^2$/g and 13.5 $m^2$/g, respectively. The dense and porous TiZrV films have similar composition. The average composition of the TiZrV films, measured by energy dispersive X-ray (EDX) analysis, is Ti 32 at.%, Zr 15 at.%, and V 53 at.% with the assumption that the sum of the atomic percentage of Ti, Zr and V is 100%. XRD analysis showed that both types of films are composed of amorphous and some nanocrystalline grains, which are dispersed in the amorphous matrix [8].

The activation process of dense and porous TiZrV films was characterized by the synchrotron radiation photoelectron spectroscopy (SRPES) in an ultra-high-vacuum (UHV) chamber. The thermal activation process was performed by heating at intervals throughout 120, 160, 250 and 350 °C. The samples were kept at the given temperature for 30 min and then were cooled down to

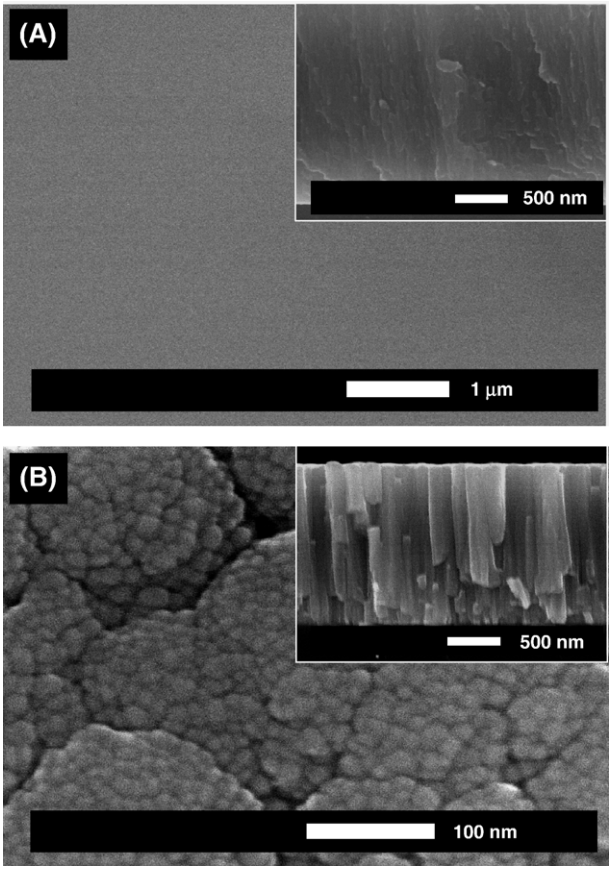


Fig. 1. SEM micrographs of the surface and fracture cross-section of films prepared on Si substrate of (A) dense TiZrV and (B) porous TiZrV.