Materials Chemistry and Physics 183 (2016) 131–135

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

On the interfacial reactions between VO_2 and thin metal films

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HIGHLIGHTS

- Competitive synthesis of VO_2(M1) phase that undergo MIT transition.
- Thin-film metal-VO_2 couples were annealed for 1 h up to 900 °C.
- Solid-state interfacial reactions between VO_2 and metals Co, Hf, Ni, Pd, Au and Pt.

ARTICLE INFO

Article history:
Received 10 March 2016
Received in revised form
4 August 2016
Accepted 6 August 2016
Available online 6 August 2016

Keywords:
Thin films
Powder diffraction
RBS
Annealing
Interfaces
Metals

ABSTRACT

We have investigated solid-state interfacial reactions between VO_2 and the metals Co, Hf, Ni, Pd, Pt and Au to establish possible criteria for whether a metal will react with VO_2 or not. Thin-film metal–VO_2 couples were annealed for periods ranging from 45 to 60 min at temperatures in the range 400–900 °C, and characterized using Rutherford backscattering spectrometry and X-ray diffraction. No interfacial reactions were detected between VO_2 and Co, Ni, Pd, Au and Pt, but Hf did react. Metals with a positive heat of reaction ΔH and electronegativity φ^*, as defined by Miedema, greater than 4.9 V did not react with VO_2 whereas Hf with $\varphi^* < 4.9$ V and a negative ΔH did. This correlation between the heats of reaction and the Meidema electronegativity of metals offers an empirical criterion for predicting whether a metal will react with VO_2 or not.

1. Introduction

Some vanadium oxides, such as V_2O_3, V_2O_5, V_6O_{13}, undergo a first-order phase transition at specific temperatures. This transition is accompanied by changes in their electrical, magnetic and optical properties [1–3]. VO_2 is the most-studied of these phases because its transition temperature (68 °C) is close to room temperature [1,4,5]. VO_2 behaves like a semi-metal above its transition temperature, reflecting a wide range of solar wavelengths, whereas below 68 °C it tends to reflect significantly less in the near infrared [5]. As a result, it has been suggested that this particular oxide can be used as a smart window coating [6]. The transition temperature of VO_2 can be increased or reduced by doping with metals [7,8]. Doping with W, Nb and Mo lowers the transition temperature, whereas doping with Ti and Sn raises it [8,9]. Zhou et al. [10] used Au (200 nm) and very thin Ti (20 nm) layer to fabricate and study electrically triggered ultrafast phase transition in VO_2 device switches with metal/VO_2/metal structure making this work valuable.

Some metals may react with VO_2 while others do not. Although work has been done on testing and predicting interfacial reactions between SiO_2 and various metals [11,12], we found no literature on the interfacial reactions between VO_2 and metals. In contrast, the Miedema electronegativity parameter φ^* indicates a correlation between a reactivity of SiO_2 and some metals and their calculated heats of reaction [13]. We therefore investigated the φ^* value of a metal and the calculated heat of reaction (ΔH_R), that results when a thin film metal is placed in contact with VO_2, in order to formulate a simple rule to predict whether the value of φ^* could be used to predict interfacial reactions between VO_2 and the metal.

2. Experimental procedure

Glass, chemically cleaned in an ultrasonic bath and then rinsed in de-ionized water, was used as the substrate for the prepared

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http://dx.doi.org/10.1016/j.matchemphys.2016.08.010
0254-0584/

samples. The thin films of VO_2 were then deposited on the glass substrates by means of an rf-inverted cylindrical magnetron sputtering system whose details are given elsewhere [2]. VO_2 was obtained by sputtering vanadium onto glass in atmosphere (10^{-2} mbar) containing oxygen. The deposited VO_2 film was made sufficiently thick that should the metal and VO_2 react, there would be enough VO_2 left on the substrate. The deposition time of the VO_2 (M1) phase films was 2–3 h and the substrate temperature was kept at 450 °C through-out the deposition. X-ray diffraction (XRD) was carried out on the samples to ensure that VO_2 had indeed been deposited on the glass substrate. The structure and morphology of the deposited films were further analyzed by grazing X-ray diffraction (GXRD) and Atomic Force Microscope (AFM), respectively, using a Bruker D8 Advance X-ray diffractometer using a Cu K_α ($\lambda = 0.154$ nm) radiation source. Data were recorded $2\theta = 10\text{-}70°$ range. An optical transmission spectrophotometry conducted on a Cecil 2000 unit in the spectral range 200–1100 nm was used to extract the hysteresis of the VO_2 (M1). The films were heated from 25 °C to 95 °C in the steps of 5 °C per measurement and subsequently cooled back.

The metals Co, Hf, Ni, Pd and Pt were then deposited individually on top of the VO_2 film using an electron beam evaporator in vacuum of better than 4×10^{-8} kPa, forming a composite sandwich structure glass/VO_2/metal. Annealing was conducted in vacuum of better than 2×10^{-8} kPa for times ranging from 45 to 60 min. The interfaces were analyzed using Rutherford backscattering spectrometry (RBS) and XRD.

3. Results and discussion

To find out whether we had managed to synthesize VO_2 (and not one of the many other oxides) we used XRD. The existence of VO_2 film was determined by using XRD. The XRD diffraction pattern of the deposited VO_2 films can be indexed according to the monoclinic phase, which is compatible with the standard value $a = 5.7430$ Å, $b = 4.5170$ Å, $c = 5.3750$ Å (JCPDS No. 72-514). Fig. 1 shows a pattern of the film showing a polycrystalline phases of VO_2 deposited on glass substrate. The first strong peak appearing at $2\theta = 27$ °C corresponds to an oxide of vanadium phase, VO_2 (M1). Other peaks falling between 27 °C and 65 °C show that VO_2 is polycrystalline.

The transmittance of the film is measured as function of temperature using UV–Vis spectrometer technique to further confirm the presence of the right VO_2 phase, the M1 phase. Fig. 2 shows an atomic microscopy image of VO_2 film showing the growth of the

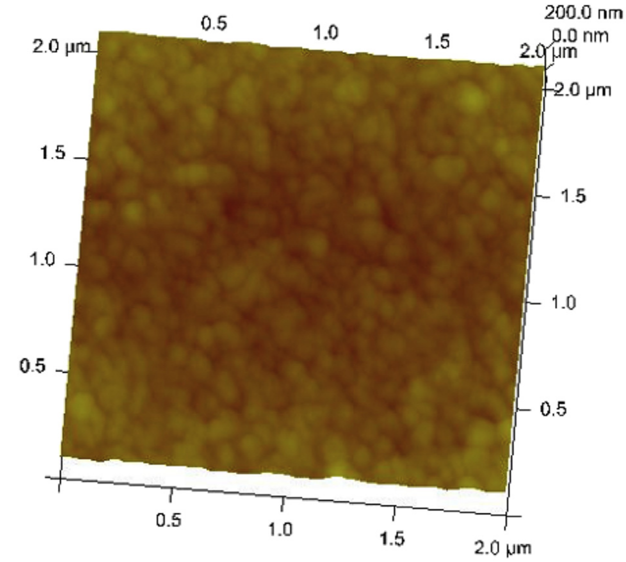

Fig. 2. X-Ray diffraction pattern of VO_2 deposited on a corning glass substrate.

film making small compact particles. Using Nanoscope software, the root mean square roughness (R_q) was calculated and found to be 14.3 nm.

Fig. 3 shows the experimental transmittance curves of VO_2 film at different temperatures, when the film temperature is raised from 25 °C (RT) to 95 °C and subsequently reduced back to 25 °C (RT) in small steps of 5 °C. From Fig. 3, we observe a change in the transmittance as function of wavelength. The spectrum transmittance of the low-temperature semiconducting phase and high-temperature metallic phase are sharply contrasting in the infrared region, furthermore this VO_2 film exhibited thermo-chromism. The transmittance of the VO_2 film on glass was observed as function of temperature as shown in Fig. 4.

The heating was done at the steps of 5 °C, and its transmittance at various temperatures was measured at a wavelength of 1100 nm. The transition temperature of the film was in a good range reported [13,14], it should be between 60 °C to 70 °C depending on number of thing like thickness nano-structuring etc. The semiconductor-to-metal transition of the deposited film was investigated using transmittance measurements as a function of temperature. The transmittance of the film shows a decrease with an increase in

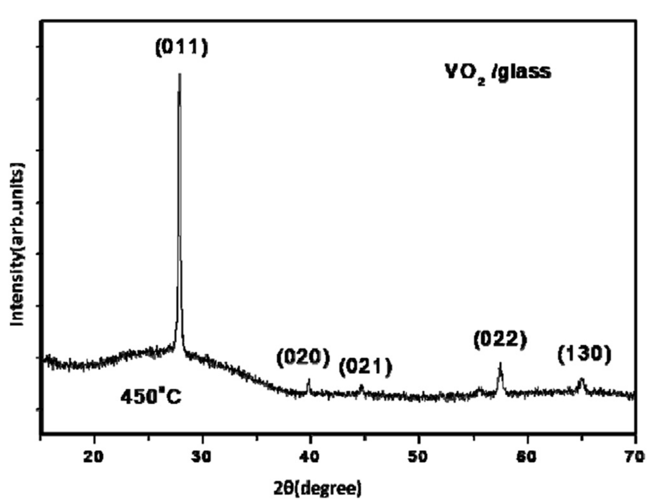

Fig. 1. X-Ray diffraction pattern of VO_2 deposited on a corning glass substrate.

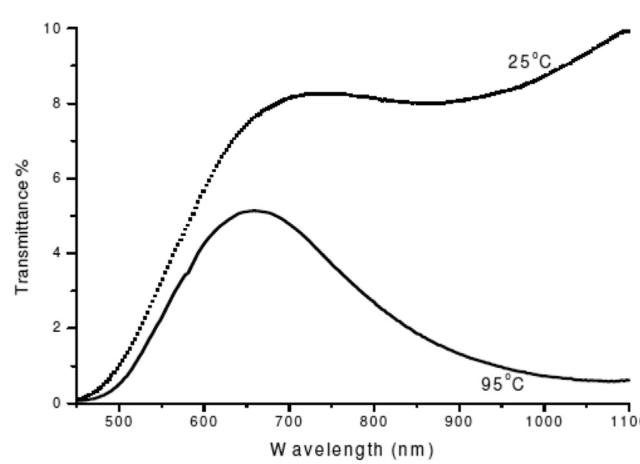

Fig. 3. Transmittance (%) vs. temperature (°C) for VO_2 film by reactive ion sputtering.