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Microfabrication of VO_2 Thin Films via a Photosensitive Sol-Gel Method

Chuanbao Wu [1,2,*], Yunwei Wang [3] and Guangqiang Ma [3]

[1] College of Vanadium and Titanium, Panzhihua University, Panzhihua 617000, China
[2] Vanadium and Titanium Resource Comprehensive Utilization Key Laboratory of Sichuan Province, Panzhihua University, Panzhihua 617000, China
[3] School of Biological and Chemical Engineering, Panzhihua University, Panzhihua 617000, China; pzhuwyw001@163.com (Y.W.); magq3218@sina.com.cn (G.M.)
* Correspondence: wuchuanbao@pzhu.edu.cn

Abstract: VO_2 films are widely used in photoelectric switches, smart glasses, storage media, and terahertz communications. In these applications, microfabrication technology is a very important process for producing microdevices or even improving film properties. In this paper, a novel photoetching microfabrication method is proposed for VO_2 thin films. First, a VO_2 precursor sol with ultraviolet photosensitivity was prepared using vanadyl acetylacetonate as the raw material and anhydrous methanol as the solvent. The dip-coated VO_2 gel film can be directly subjected to photolithography processing without coating additional photoresist by using the photosensitive sol. A fine pattern on the VO_2 film with good phase-transition performance can be obtained after annealing in a nitrogen atmosphere at 550 °C for 1 h. This method can be used to prepare grating, microarray, and various other fine patterns with the remarkable advantages of a low cost and simplified process, and the as-obtained material performances are unaffected using the method. It is a potential alternative method for optics, electronics, and magnetics devices based on VO_2 thin films.

Keywords: vanadium dioxide; photoetching; micro patterns; sol-gel method; phase transition

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1. Introduction

Vanadium dioxide (VO_2) undergoes a metal-insulating phase transition (MIT) under thermal excitation at 68 °C, and its crystal structure will change from a low-temperature monoclinic M1 phase to a high-temperature rutile tetragonal phase [1–3]. The MIT process is accompanied by reversible saltation in optical, electrical, and magnetic properties [4–6]. Although the MIT behavior is observed in other transition-metal oxides, the phase-transition temperature of VO_2 is the closest to room temperature, and the phase transition is fast and reversible [7,8]. The unique properties of VO_2 near room temperature provide broad applications in the fields of photoelectric switches, smart glasses, storage media, and terahertz communications [9–12].

With the development of integration and miniaturization of micro-optoelectronic devices, microfabrication technology has gradually become more and more important, typically in the field of data storage and photoelectric switches [13,14]. In addition, one of the most promising applications of VO_2 is smart glasses, and a large number of studies on it have been reported. However, the low visible-light transmittance for coated VO_2 glass is one of the key issues [15–17], limiting its development. Recently, it has been reported that the preparation of moth-eye micro-nano structure patterns on the surface of VO_2 film can significantly improve its transmittance and also increase its infrared modulation ability [18]. In that study, the preparation method of its fine structure involves expensive equipment, and the process is complex, not suitable for large-scale production. Furthermore, the terahertz application of VO_2 has gradually become a new focus recently [19–21], and a low-cost and short-term microfabrication technology is urgently needed to prepare antenna patterns for terahertz communications.

In this study, a novel photoetching microfabrication method was developed to prepare micropatterns on VO_2 thin films via a photosensitive sol-gel process based on our previous study [22]. The process does not require photoresist, and it also does not require expensive ion etching equipment to instantly produce micron-level fine patterns. Moreover, the thin film micropattern process precedes the film annealing, which can avoid probable damage to the film performances observed in traditional microprocessing technologies. In particular, in our previous study, it is necessary to add a chelating agent or stabilizer to provide the sol photosensitive characteristic. In this study, a photosensitive VO_2 sol can be obtained only using the vanadyl acetylacetonate as the vanadium source and absolute methanol as the solvent without adding additional chelating agents or stabilizer. Owing to the simplification of composition of VO_2 sol, the pattern preparation process can be more easily controlled, and thus the VO_2 patterns of grating and microarray structures can be easily prepared.

2. Experiments

2.1. Preparation of VO_2 Micropatterns

A photosensitive VO_2 sol was prepared using vanadyl acetylacetonate as the raw material and anhydrous methanol as the solvent. The concentration of VO_2 sol was fixed at 0.1 mol/L by adjusting the amount of anhydrous methanol. The VO_2 sol was standing for 24 h at room temperature for aging. A VO_2 gel film was obtained on single-crystal silicon (100) or quartz substrates (only for UV-vis spectra test) by dip-coating with a withdrawal rate of 2 mm/s on a dip coater (DC-II, Xi'an University of Technology, Xi'an, China). Then, UV lithography was directly performed on the photosensitive gel film, as shown in Figure 1. A UV point light source (152 mW/cm^2, SP-9, Ushio, Tokyo, Japan) was used to irradiate the gel film at room temperature for different times. The spot size is about 59 mm in diameter when the distance between the light source and film is 100 mm. The sample dimension is about 20 mm × 10 mm. The mask was fabricated by depositing Cr film onto a quartz substrate (processed by Shaopu Co. LTD, Changsha, China), according to the self-designed patterns. The irradiated gel film was then immersed in a mixture of ethanol and *n*-butanol (3:1 in volume) for 10 s and then blow-dried using nitrogen to develop the pattern. Thus, a fine pattern consistent with the negative image of the mask was obtained. Finally, the patterned gel film was annealed in a nitrogen atmosphere at 550 °C for 1 h to obtain a patterned VO_2 ceramic film.

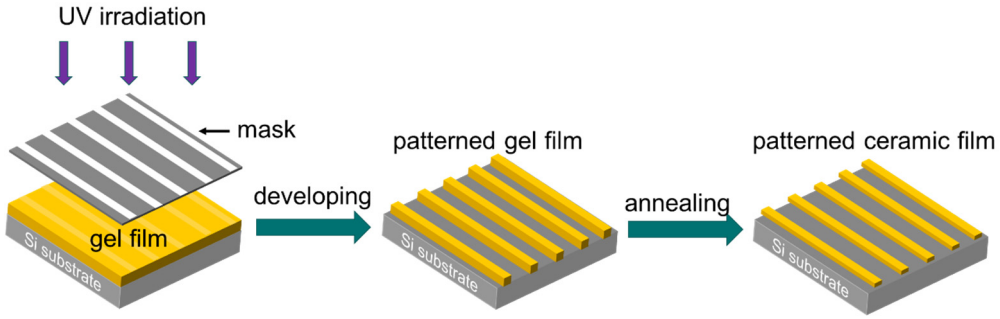

Figure 1. Schematic diagram of preparation process for patterned VO_2 ceramic film.

2.2. Characterization Techniques of VO_2 Micropatterns

The photodecomposition process of VO_2 gel film was studied by UV-Vis spectroscopy (D-7PC, Philes, Nanjing, China). The fine patterns of the film were observed by optical microscopy (DFC320, Leica Microsystems Ltd., Weztlar, Germany), an atomic force microscope (MFP-3D Infinity, Oxford Instruments, Oxford, England) and a scanning electron microscope (MCE, Tescan, Brno, Czech Republic). The phase structure of the film was tested using an X-ray diffractometer (X'Pert^3 Powder, PANalytical, Almelo, The Netherlands) in θ–2θ scan mode. The set voltage and current are 40 kV and 40 mA, respectively, the scanning angle is 20–60°, and the scanning step is 0.01°. To characterize the phase

transition of VO_2 film after microfabrication, the film was processed into a 50-micron-wide microbridge, and the resistance was tested using a four-lead method in the temperature range of 25–100 °C.

3. Results and Discussion

3.1. Photosensitivity of VO_2 Gel Film

During the dissolution of vanadyl acetylacetonate in methanol, the carbonyl group of vanadyl acetylacetonate provides electrons to coordinate to the sixth vacant site of vanadium ions, forming a cyclic chelate [23]. The cyclic chelate can be maintained in the dip-coated VO_2 gel film, and it is gradually decomposed under UV-light irradiation to form an –O–V–O– network structure, which is insoluble in organic solvents, similar to the report in references [24,25]. On the other hand, the cyclic chelate still exists in the non-UV-irradiated gel film, and the gel film is easily dissolved in organic solvent. In this manner, the UV-irradiated VO_2 gel film will be retained, and the non-UV-irradiated gel film will be washed away after developing in organic solvents. Finally, a fine pattern consistent with the negative image of the mask can be obtained.

To study the photolysis kinetics process of VO_2 gel film under UV-light irradiation, a UV-vis spectrum test was carried out after UV exposure for every 20 min, and the time-gradient spectrum results are shown in Figure 2. A strong UV absorption peak for the VO_2 gel film appeared at about 302 nm, corresponding to π–π* transition in the cyclic chelate of vanadium [22]. The absorption intensity of cyclic chelate gradually decreased with increasing UV exposure time owing to the photodecomposition of cyclic chelate in the VO_2 gel film. Moreover, the rate of peak reduction gradually decreased. The peak intensity between the gel film irradiated for 60 min and irradiated for 80 min is similar, indicating that the cyclic chelate is nearly completely decomposed after UV irradiation for 60 min.

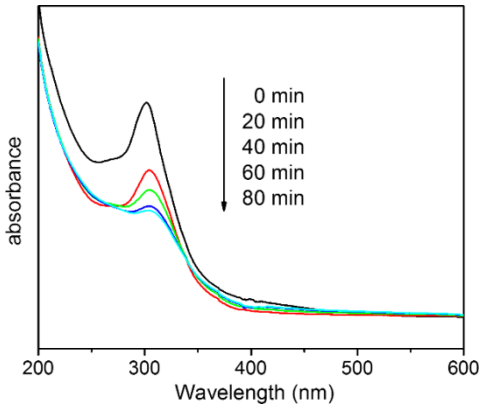

Figure 2. Time-gradient UV-vis spectra of VO_2 gel film coated on a quartz substrate.

3.2. Patterns of VO_2 Films

In our experiments, it was found that, when a mixture of ethanol and *n*-butanol with a volume ratio of 3:1 was used to develop the UV-irradiated VO_2 gel film, a fine pattern with expected morphology can be obtained, as shown in Figure 3. In these patterns, the bright areas are the Si substrate, and the dark areas are the patterned VO_2 gel films apart from (i) and (j). Figure 3d shows that the film has a regular pattern and a uniform surface. The lithographic resolution can be evaluated to be about 5 μm according to the radial-shape pattern in (c). Moreover, the microfabrication method can be used to produce both grating structures and dot array structures as shown in Figure 3e–j. It is believed that arbitrary micrographs with a size limit of more than 5 μm can be obtained using the photosensitive sol-gel method as long as the mask patterns can be designed appropriately.

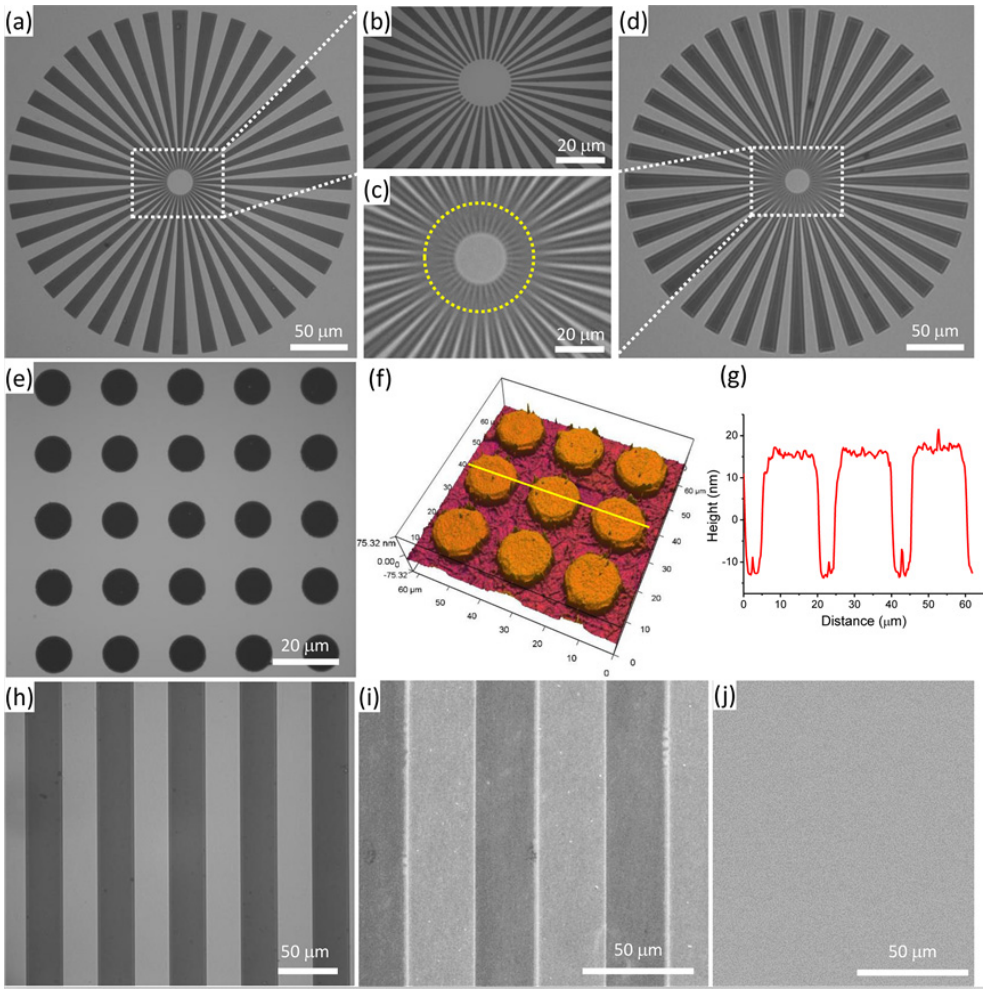

Figure 3. Mask plate of radial shape, patterned and also whole VO_2 gel/ceramic films. (**a**) is a mask plate and (**d**) is the corresponding pattern on VO_2 gel film. (**b**,**c**) is enlarged views of the boxed area in (**a**,**d**). The lines inside the circles in (**c**) can no longer be distinguished, so the lithographic resolution is evaluated to be 5 μm. (**e**–**j**) are patterned or whole VO_2 ceramic films; (**e**) is a dot array with a periodicity of 20 μm, and (**f**,**g**) are the results from the atomic force microscope. (**h**) is grating with a periodicity of 60 μm; (**i**,**j**) are scanning electron microscope pictures for grating patterns and whole films, respectively. There is almost no difference between the patterns and films.

3.3. Characteristics of VO_2 Ceramic Film

The VO_2 film with a monoclinic M1 structure exhibits a remarkable phase-transition characteristic. To determine the phase structure of as-prepared film, a powder X-ray diffraction (XRD) experiment was performed on the VO_2 film. Notably, the VO_2 film was prepared by repeating the dip-coating and annealing processes for ten times to establish the film thickness (about 310 nm) so as to enhance the XRD signals. Figure 4 shows the XRD pattern of VO_2 ceramic film. Diffraction peaks are observed at angles of 27.8°, 37.0° 39.8°, 55.5°, and 57.5°, corresponding to the diffractive crystal planes of (011), (−211), (020), (211), and (022) of VO_2 material, consistent with the standard diffraction peaks of VO_2 (JCPDS Card No. 82-0661) [26,27]. Notably, the peak intensity of (020) plane of obtained VO_2 film is significantly higher than the corresponding intensity in the standard powder diffraction card. This indicates that the VO_2 film has a certain (020) preferred orientation, which is derived from the single-crystal Si (100) substrate [28]. In addition, except for the diffraction peaks from VO_2 film, no peaks were detected from the other impurities, demonstrating that a single-phase VO_2 film with monoclinic M1 structure was obtained.

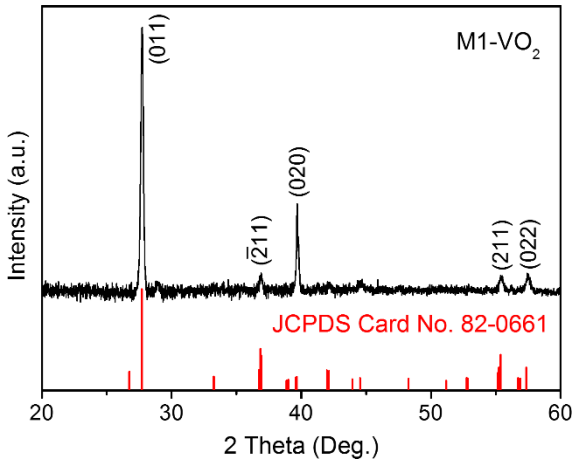

Figure 4. XRD pattern of VO_2 ceramic film grown on a single-crystal Si (100) substrate.

The phase-transition behavior of patterned VO_2 ceramic film was further investigated, and the resulting *R*–*T* curve is shown in Figure 5. To eliminate the contact resistance, a four-lead method was used to test the resistance of patterned VO_2 ceramic film, as shown in the inset of Figure 5, which shows that, as the temperature increases, the resistance of patterned VO_2 film gradually decreases. The resistance then drops sharply at about 66 °C, indicating that the patterned film underwent a phase transition from a low-temperature insulating phase to a high-temperature metal phase at this temperature. The phase-transition process is completed at about 79 °C, and the resistance slowly decreases again as the temperature increases. During the cooling, a reversible phase transition occurs at about 63 °C, returning to the low-temperature insulating phase. During the entire phase transition, the saltation amplitude of resistance reaches about two orders of magnitude, similar to the phase transition of the VO_2 film reported in the literature [13,29]. It seems that the microfabrication method proposed in this study does not affect the phase-transition behavior of VO_2 film.

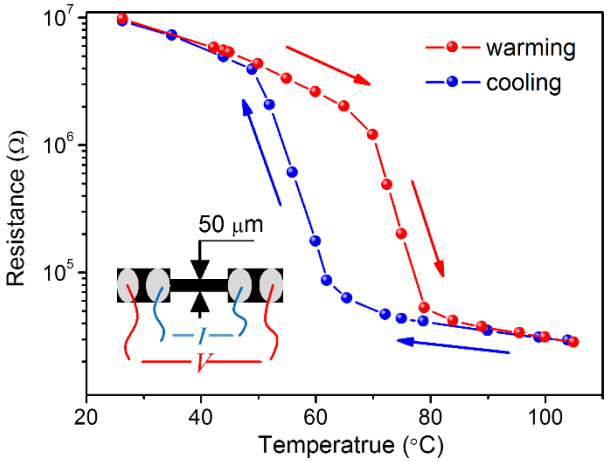

Figure 5. *R*–*T* curve of patterned VO_2 ceramic film.

The microfabrication method proposed in this study can be used to prepare gratings, microarray structures, and other various micropatterns, and it can be widely used in micro devices such as photoelectric switches, storage media, and terahertz antenna. Although the resolution of patterns can achieve about 5 μm in this research, it is likely that the resolution can reach 1 μm by further improving the photosensitivity of VO_2 sol. In particular, if laser interferometry rather than UV irradiation is used for photolithography in the future, it will be able to achieve submicron resolution. In that case, the photosensitive sol-gel method might provide a new process route for improving the color of VO_2 film, increasing

the visible-light transmittance, and endowing superhydrophobic properties by designing applicable patterns [18].

4. Conclusions

We developed a photosensitive sol-gel method to prepare micropatterns on VO_2 thin films. In this method, the UV-photosensitive VO_2 precursor sol was prepared using vanadyl acetylacetonate as the raw material. After UV-photoetching and developing in organic solvents, a VO_2 film micropattern consistent with the negative image of the mask was obtained. Finally, a remarkable phase-transition behavior was observed in the patterned VO_2 ceramic film after annealing in a nitrogen atmosphere at 550 °C for 1 h. The method does not require photoresist and expensive ion etching equipment, and the microfabrication process is simple. Furthermore, the obtained film has a regular pattern and uniform surface. In particular, the microfabrication process precedes the annealing process, so it does not affect the performances of the film. It is demonstrated that the microfabrication method proposed in this study can be used to prepare gratings and microarray structures. Therefore, the microfabrication process is a potential method for producing various photoelectric devices based on VO_2 film.

Author Contributions: C.W. conceived and conducted the experiments and wrote the preliminary version of the manuscript. Y.W. and G.M. discussed the results with C.W. and revised the paper. All authors have read and agreed to the published version of the manuscript.

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