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The growth mechanism of VO_2 multilayer thin films with high thermochromic performance prepared by RTA in air

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ABSTRACT

In this paper, the multilayer thin films with SiN_x/NiCr/$NiCrO_x$/VO_2/$NiCrO_x$/NiCr/SiN_x structure were prepared by reactive magnetron sputtering at room temperature and subsequently rapid thermal annealing (RTA) in air. The effects of annealing temperature on the microstructure and thermocheromic performance of the VO_2 multilayer thin films were systemacially investigated by UV–Vis-NIR, XRD, SEM, XPS and TEM. The results showed that the crystalline VO_2 multilayer thin films can be obtained as the temperature rose from room temperature to 301 °C within 6 s, and the high thermochromic performance with solar modulation (ΔT_{sol}) of 17.2%, luminous transmittance (T_{lum}) of 26.9% and phase transition temperature (T_c) of 60 °C can be acquired as the temperature rose from room temperature to 571 °C within 10 s, which indicates the VO_2 multilayer thin films show the good antioxidation. Based on growth mechanism of VO_2 multilayer thin films, it can be found that the atomic diffusion may form crystal nucleation and induce the rapid crystallization of VO_2 thin film at low temperature, the drastic diffusion reaction results in the degeneration of crystallinity and performance of VO_2 film with increasing temperature. Finally, the unbalance of interfacial stress lead to the rupture of the films, and the VO_2 was completely oxidized into V_2O_5. The exploration of the growth mechanism provides the basis for the optimization of the film structure and annealing parameters, so as to promote the practical application of VO_2 multilayer thin films with high thermochromic performance.

1. Introduction

Vanadium dioxide (VO_2) presents a reversible metal-to-insulator transition (MIT) at a critical temperature T_c of 68 °C [1], accompanied by a large modulation of its infrared (IR) transmission. For this reason, the VO_2-based thin film materials with high thermochromic performance have great application prospects in smart windows [2–5]

At present, various methods, such as sol-gel spin coating [6], chemical deposition (CVD) [7], pulsed laser deposition (PLD) [8] and magnetron sputtering [9,10], have been employed for preparing VO_2 thin film. Among them, the magnetron sputtering is a most promising method. However, it still faces the problem of high deposited temperature (about 400 °C–600 °C) for crystallization of VO_2 thin film [11,12]. The fabrication of VO_2 thin film by annealing in air has attracted more and more attention on account of its simple process, which can avoid a series of problems caused by the heating and cooling in vacuum environment, and improve production efficiency. Nowadays, the precursor oxidation method is the most popular routes to prepare VO_2 thin films by annealing in air [13–16]. The VO_2 thin films with high thermochromic performance were prepared by the traditional resistance annealing. However, in order to reduce oxidation risk, it took a long time to obtain crystalline films due to the low annealing temperature [15]. Other researchers have attempted to prepare VO_2 thin films by RTA in air for high preparation efficiency [17–19]. The results show that the exposed vanadium based precursor film is often oxidized to various valence vanadium oxides owing to the poor antioxidation. According to our previous work [20], it is known that the VO_2 multilayer thin films show good antioxidation, but its thermochromic

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performance is influenced by annealing temperature. Therefore, in order to realize the preparation of VO_2 thin films in air, it is necessary to investigate the growth mechanism and evolution process of VO_2 thin film at different temperature.

In this paper, the VO_2 multilayer thin films with SiN_x/NiCr/$NiCrO_x$/VO_2/$NiCrO_x$/NiCr -/SiN_x structure were deposited by magnetron sputtering at room temperature. The barrier layers with $NiCrO_x$ + NiCr + SiN_x show good antioxidation. The best thermochromic performance with ΔT_{sol} of 17.2%, T_{lum} of 26.9% and T_c of 60 °C can be obtained at 571 °C, which indicates that SiN_x/NiCr/$NiCrO_x$/VO_2/$NiCrO_x$/NiCr/SiN_x shows good antioxidation. The growth mechanism and evolution process of the VO_2 thin film were studied based on thermochromic performance at different temperature. The results show that the atomic diffusion induces crystalization and rapid growth of VO_2 thin film at low temperature. So that the crystalline phase of VO_2 (M) can be observed at 301 °C within 6 s. The drastic diffusion reaction between $NiCrO_x$ and VO_2 thin film results in deterioration of the thermochromic performance with increasing temperature. Then, the unbalance of interfacial stress caused by softening of glass leads to oxidation of VO_2 thin film and delamination of barrier layer. Finally, when the VO_2 is oxidized to V_2O_5, the thermochromic performance of the films disappear. In this paper, the results will be beneficial to the preparation of high performance VO_2 multilayer thin films by RTA in air.

2. Experimental

2.1. Preparation and annealing

The multifunctional coating system was equipped with V (99.9%) metal, NiCr (80/20 mol.%) alloy and Si targets. The VO_2 multilayer thin films were prepared on glass substrate using reactive magnetron sputtering at room-temperature. Before the sputtering process, the vacuum chamber was pumped down to a background pressure of 8×10^{-4} Pa. During sputtering process, the gas pressure was maintained at 0.5 Pa. Typically, VO_2, NiCr and NiCrOx films were obtained at Ar (96%) + O_2 (4%), Ar (100%) and Ar (80%) + O_2 (20%), respectively. The SiN_x film is obtained at a Ar (50%) + N_2 (50%). The substrate moved under different targets. Finally, the film structure was formed as follows: Glass/SiN_x-80 nm/NiCr-20 nm/$NiCrO_x$-15 nm /VO_2-130 nm/$NiCrO_x$-15 nm/NiCr-20 nm/SiN_x-80 nm. Subsequently, the as-deposited films were then annealed in air by RTA. A temperature sensor was attached to the side of film on glass. The power density of the annealing system remains 250 kW/m^2 during the annealing process.

To investigate the effect of temperature on the growth process of films, the heating temperature is indirectly controlled by a predetermined heating time because the direct controlling of temperature is very difficult in short heating time and high heating rate. It means that the infrared lamps automatically turn off when the samples are heated for a predetermined time, then the samples were naturally cooled in air. In fact, the specific heating time corresponds to the instantaneous heating temperature. The image of the annealing system and the temperature as a function of annealing time were exhibited in Fig 1(a) and (b), respectively. It can be observed from Fig. 1(b) that the temperature of sample (e) increased rapidly from room temperature to 806 °C after heating for 18 s. All of the samples that were prepared at the end of the annealing process are summarized in Table 1. It can be found that the annealing temperature in air rose up to 152 °C, 301 °C, 571 °C, 731 °C and 806 °C after heating within 4 s, 6 s, 10 s, 14 s and 18 s, respectively. An important feature about the annealing process is that each sample has not been set in the heating preservation process.

2.2. Characterizations

The X-ray diffraction (XRD) measurements were performed by X' Pert Pro MPD diffractometer, using Cu-Kα as radiation source at a scan rate of 0.05°2θ S^{-1}. The cross-section morphologies of the VO_2 multilayer thin films were investigated using a field emission scanning electron microscope (FESEM, S-4800, Hitachi). Ultraviolet-visible-near infrared spectrophotmeter (UV–Vis-NIR, Lambda 750) was employed to characterize the optical switching properties of the films ranging from 300 to 2500 nm at temperature 30 °C and 90 °C. Temperature was measured by a sensor, which is in contact with the films and connected with FP23 temperature controlling unit. Hysteresis loops were measured by recording the transmittance for 2000 nm wavelength against the temperature with a heating /cooling rate of 2 °C/min. The distribution of the elements were determined by transmission electron microscopy (TEM, JEOL 2100F). X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250 Xi) was performed to determine the chemical states and composition. The T_c was defined as a temperature at the half-maximum of the heating curve, as described in an earlier article [21]. The T_{lum} (380–780 nm) and T_{sol}(300–2500 nm) were calculated based on the recorded spectra using the following expression:

$$T_{lum/sol} = \int_{\varphi_{lum/sol}} (\lambda) T(\lambda) \mathrm{d}\ \lambda / \int_{\varphi_{lum/sol}} (\lambda) \mathrm{d}\ \lambda$$

where $T(\lambda)$ is the recorded film transmittance, φ lum is the standard luminous efficiency function for the photopic vision of human eyes, and φ sol is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon) [22]. $\Delta Tsol$ is attained by equation $\Delta T_{sol} = T_{sol}(30\ \bigcirc C) - T_{sol}(90\ \bigcirc C)$.

In order to obtain the valence states of the VO_2 thin film, the Ar^+ was used to etch the multilayer thin films on top of VO_2 thin film. The total sputtering time was 2600 s, which the O1s and V2p XPS signal were recorded. The XPS data analysis was performed with the advantage 5.52. The V2p3/2 and V2p1/2 signal areas have a 2:1 ratio, a proportion, which is used in the curve fitting of all the V2p XPS spectra.

3. Results and discussion

3.1. UV-Vis-NIR spectra analysis

The transmission spectra and hysteresis loops of the VO_2 multilayer thin films are shown in Figs. 2 and 3, respectively. In addition, the T_{lum}, ΔT_{sol} and T_c were calculated and listed in Table 2. It can be found that the optical switching cannot be observed at 152 °C, which implies that the sample (a) remained amorphous due to the low temperature. When the annealing temperature rose up to 301 °C, the crystalline phase may be formed in sample (b), thus the optical switching can be observed. With increasing temperature, the migration of atoms is enhanced, and the crystallinity of the VO_2 film is improved. Therefore, the optical switching of sample (c) is obviously improved in comparison to sample (b), the maximum ΔT_{sol} of 17.2% can be obtained. When the annealing temperature rose up to 731 °C, the softening of the glass substrate may deteriorate the antioxidation of the barrier layers, which may result in the formation of a small amount of V_2O_5 in sample (d), so that the optical switching gradually reduced from 17.2% to 10.3%. When the annealing temperature rose up to 806 °C, the VO_2 in the sample (e) may be completely oxidized into V_2O_5 for the degeneration of barrier layers, which is accompanied by the disappearance of the optical switching from 30 °C to 90 °C. Based on above results, the highest thermochromic performance can be observed after heating at 571 °C, which exhibits the T_{lum} of 26.9% and ΔT_{sol} of 17.2%, and the VO_2 multilayer thin films show the high thermal stability. This performance is comparable to the other several typical structures in Table 3, such as porosity [23], composite [3], periodicity [24,25] and multilayer structure [26,27]. Although it can be found that the T_{lum} in this paper is the lowest of all structures, and that is an important direction for improvement, the ΔT_{sol} is superior to that of most other structures except for VO_2/hydrogel nanothermochromic material [28]. Generally speaking, commercial application of VO_2-based thin films requires not only excellent thermochromic performance, but also requires the simple and efficient