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Enhanced thermal stability and thermochromic properties of VO_x-based thin films by room-temperature magnetron sputtering

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ABSTRACT

In order to enhance the thermal stability and thermochromic properties, three kinds of VO_x-based thin films with different structures (single-layer, triple-layer and multi-layer, respectively) were designed in this study. All of them were prepared by room-temperature reactive magnetron sputtering and subsequently rapid thermal annealing (RTA) in nitrogen atmosphere. The optical properties and microstructure of VO_x-based thin films were investigated. The results reveal that all samples are ascribed to pure VO_2 (M), and the VO_x-based thin films exhibit superior thermochromic properties with the solar modulation (ΔT_{sol}) up to 12.75%, 15.65% and 18.02%, respectively. The phase transition temperature (T_c) is as low as 54 °C for multi-layer thin films without doping, which indicates that the film design could effectively enhance optical switching and depress the T_c. After thermal treatment in the air, the phase of V_2O_5 appeared at 325 °C, 275 °C and 375 °C for single-layer, triple-layer and multi-layer thin films, respectively, which indicates the multi-layer thin films show the best thermal stability. According to the degradation mechanism in this paper, the unbalance of interfacial stress and oxygen vacancies in VO_x thin film accelerated the oxidation process, which results in the disappearance of thermochromic properties. Furthermore, the multi-layer thin films still show superior ΔT_{sol} of 16.56% and T_c of 56 °C, when it was taken out at 400 °C and cooled quickly in air. Meanwhile, the annealing period could be reduced by 75% in comparison to cooling in vacuum chamber. Our research set forth a new avenue in enhancing the thermal stability and production efficiency, which can promote the practical applications of VO_x-based thin films.

1. Introduction

Since the work reported by Morin in 1959 [1], vanadium dioxide (VO_2) has attracted much attention due to its metal-to-insulator transition at T_c of 68 °C for bulk VO_2. Owing to this unique characteristic, VO_2 film can respond to environmental temperature and regulate near-infrared (NIR) irradiation by transforming from a transparent state at low temperature to a more reflective state at high temperature. Therefore, it has been regarded as a promising intelligent windows material in architecture and automobile for saving energy [2,3].

Up to now, among the ways to prepare the VO_x-based thin films [4–9], the magnetron sputtering is one of the most promising routes on account of high production efficiency, high reproducibility and excellent uniformity on large scale substrates [10]. However, the preparation of VO_x-based thin films using magnetron sputtering is still faced with any key problems for the high deposition temperature (400–600 °C) [11–13], such as the stress relaxation of tempered glass substrate, the thermal stability of VO_2 thin films and so on, which may result in serious security risks and inferior products. The researchers have attempted to solve above problems by low temperature deposition and rapid thermal annealing. Aijaz et al. [14] and Loquai et al. [15] reported that the VO_2 thin films were deposited by High Power Impulse Magnetron Sputtering (HIPIMS) at 300 °C and 275 °C , respectively. In combination with the stress characteristics of glass substrate [16–18], the stress relaxation can be neglected. However, the thermochromic properties are obviously degraded due to poor crystallinity. In addition, the high performance VO_2 thin film was obtained at temperature as low as 380 °C by traditional annealing in air [19]. Nevertheless, it took two

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Nomenclature

RTA	rapid thermal annealing
ΔT_{sol}	solar modulation
T_c	phase transition temperature
T_{lum}	integral luminous transmittance
XRD	X-ray diffraction
SEM	scanning electron microscope
UV–vis–NIR	ultraviolet-visible-near infrared spectrophotometer
XPS	X-ray photoelectron spectroscopy

hours to complete annealing process. The results show that the VO_2 thin films fabricated at low temperature with poor thermochromic properties and low efficiency is difficult to acquire the practical application. The other researchers spent tens of seconds in fabricating VO_2 thin films by rapid thermal annealing (RTA) [20–22]. In comparison to traditional annealing method, the annealing time was significantly reduced, which is beneficial for improving stress relaxation, but it is difficult to get the pure phase VO_2 thin film for the poor thermal stability and poor anti-oxidation. A typical way to enhance the thermal stability of VO_2 thin films is obtained by the addition of overlying diffusion barrier [23–25], which leads to improving the weather resistance of VO_2 thin film, such as temperature resistance, humidity resistance and so on. This implies that the multi-layer thin films with barrier layer can enhance the thermal stability of VO_2 thin film. So far the studies of thermal stability are mainly focused on the VO_2 thin films prepared by high temperature deposition. There are few reports in combination with thermal stability and thermochromic properties of the VO_2-based thin films, and the degradation mechanism of VO_2 thin films is unclear. Therefore, it is necessary to expore the VO_2 thin films with good thermal stability and thermochromic properties by the combination of film design and rapid thermal annealing.

In this paper, the SiN_x and $NiCrO_x$ functional films [26–28] with excellent antioxidation and diffusion resistance are introduced into the film design. The three kinds of films are expressed as, single-layer with G/VO_x, triple-layer with $G/SiN_x/VO_x/SiN_x$ and multi-layer with $G/SiN_x/NiCrO_x/SiN_x/VO_x/SiN_x/NiCrO_x/SiN_x$. All of them were fabricated by magnetron sputtering at room-temperature and subsequently RTA in nitrogen atmosphere. The results show that the film design can improve the $\triangle T_{sol}$ and reduce the T_c. Furthermore, the annealed samples were heated in air to evaluate its thermal stability. The results show that the multi-layer thin films not only show superior ΔT_{sol} of 16.56% and T_c of 56 ℃, but also exhibit best thermal stability. It was cooled in air at 400 ℃ after annealing in vacuum and still kept similar thermochromic performance in comparison to cooling in vacuum chamber, and the annealing period has been reduced by 75%, which could improve stress relaxation of tempered glass substrate and increase the production efficiency. According to the degradation mechanism in this paper, it could be inferred that the unbalance of interfacial stress and oxygen vacancies accelerated the oxidation process. In this study, the VO_x-based thin films with excellent thermochromic properties and thermal stability have been obtained. And the stress relaxation during the preparation process of VO_2 thin films may be improved by reducing annealing period. It provides guidance for the preparation and application of VO_x-based thin films.

2. Experimental

2.1. Preparation and thermal treatment

The multifunctional coating machine was equipped with V, NiCr and SiAl targets. 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_x film and $NiCrO_x$ film were obtained at a Ar (96%) + O_2 (4%), Ar (90%) + O_2 (10%), respectively. The SiN_x film was obtained at a Ar (50%) + N_2 (50%). The three kinds of films were prepared on glass substrate using room-temperature (substrate without heating) reactive magnetron sputtering. Subsequently, the as-deposited films were then annealed in nitrogen atmosphere at 550 °C for 180 s using a rapid thermal annealing system. During the annealing process, when the background pressure was pumped down to 1 Pa, the nitrogen was introduced in the vacuum chamber. The annealing pressure was maintained at 250 Pa through the regulating valve. After annealing, the films were naturally cooled down to room temperature in vacuum chamber. The annealed samples were labeled as A_0, B_0 and C_0, respectively and used as reference samples for evaluating thermal stability. In order to investigate the thermal stability, the reference samples were divided into many samples and heated in air using a muffle furnace from room temperature to 250 °C, 275 °C, 325 °C and 375 °C with heating rate of 10 °C/min. These annealing temperatures were maintained for 10 min and 60 min, respectively. Then, the samples were naturally cooled down to room temperature. These samples were labeled as A_1-A_5, B_1-B_5 and C_1-C_5, respectively. The VO_x-based thin films and preparation processes were depicted in Fig. 1.

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 surface morphologies of the VO_x-based

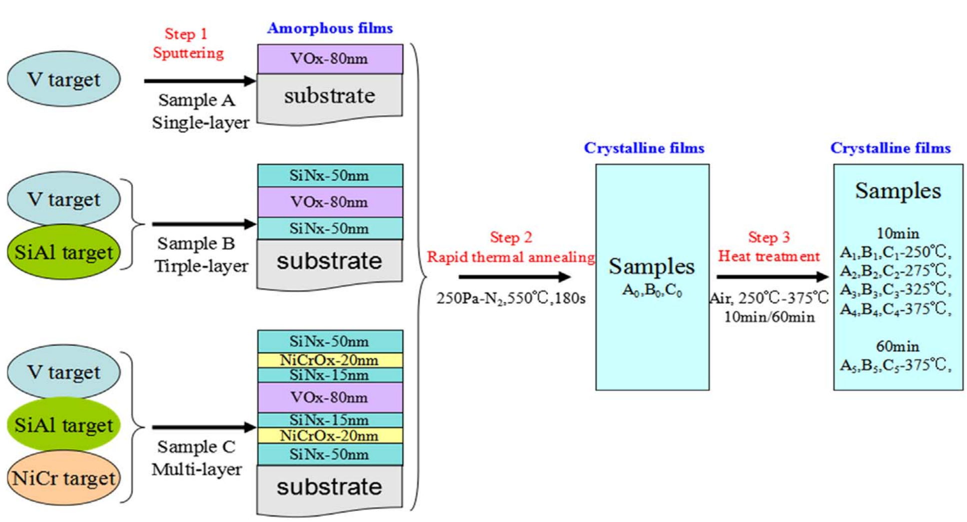

Fig. 1. The film design of VO_x-based thin films and preparation process.