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Synthesis of colloidal VO_2 nanoparticles for thermochromic applications

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ABSTRACT

Vanadium dioxide (VO_2) thin films are key materials for thermochromic smart windows and commonly have a typical phase transition (insulator to metal phase) at a transition temperature of 68 °C. This research, however, found that highly crystallized VO_2 nanoparticles can be successfully coated on a glass substrate with added functionalities, such as higher luminous transmittance and transition efficiency. The transition temperature revealed that the VO_2 nanoparticles with post thermal treatment at 600 °C also clearly exhibited a reduced transition temperature of 69 °C in the heating curve, 59 °C in the cooling curve, and a transition width of 10 °C. By nanopatterning the thin films, we were able to prepare VO_2 thin films with higher luminous transmittance than that attained with non-patterned VO_2 thin films. The enhanced transition property was demonstrated using highly crystallized VO_2 nanoparticles induced by post thermal treatment, and the luminous transmittance was improved by the nanopatterns on the surface of the VO_2 thin films.

1. Introduction

Smart windows are currently being intensely investigated so that they can be effectively implemented in modern energy saving buildings. For smart windows, chromogenic materials have been researched for many years and a large number of practical applications have been found because of reversible changes in their optical characteristics occurred due to some external stimulus. Many chromogenic materials are reported in field of thermochromic, photochromic, and electrochromic, which are changed material properties of physical and chemical by temperature, light [1–5], and electric field [6], respectively. In particular, thermochromic windows have effectively reduced energy consumption in residential and commercial buildings because the phase transition effectively regulates the solar irradiation in a wavelength of 800–2500 nm [7–9].

Thermochromic materials are capable of a reversible change in optical transmittance and electrical resistance in response to environmental temperature. Vanadium dioxide (VO_2) is well known as one of the most promising thermochromic materials [10]. At below the transition temperature, VO_2 has a semiconductor or insulator state with a monoclinic structure. When VO_2 is heated above the transition temperature, it undergoes changes in the electrical resistance and optical transparency, particularly in the near-mid infrared wavelength regime, due to the structural change from monoclinic to tetragonal [11–13]. Because of their distinctive optical and electrical switching characteristics, VO_2 thin films hold potential to be used for a number of practical applications, including smart windows [14–16], infrared sensors or detectors [17], and Mott transistors [18].

A number of methods have been studied to fabricate VO_2 thin films with better phase transition characteristics, including physical vapour deposition (PVD) such as DC or RF reactive sputtering [19–21], ion beam assisted sputtering [22], pulsed laser deposition [23], and chemical vapour deposition (CVD) [24,25]. However, it is difficult to perform large-area deposition on the substrate and achieve low cost production due to the high process temperature. These temperatures are still too high to use soda-lime glass as a substrate for smart window applications because it is difficult to prevent ion diffusion from a soda-lime substrate. Recently, solution-based processes, such as sol-gel deposition [26], an electrochemical process [27], a hydrothermal process [28,29], and polymer-assisted deposition [30], have been used to fabricate pure VO_2 thin films to obtain high thermochromic characteristics.

Sol-gel deposition is a typical solution-based synthesis process with various chemical materials and creates a vanadium oxide network by the polymerization of chemical precursors, such as vanadyl triisopropoxide ($VO(OC_3H_7)_3$) [31], vanadium oxyacetylacetone ($VO(acac)_2$) [32], and ammonium meta-vanadate (NH_4VO_3) [33]. VO_2 nanoparticles have attracted much attention due to their size- and shape-tunable properties, which are more highly desirable for low-cost industrial production of VO_2 thin films than those produced with conventional gas phase deposition such as PVD and CVD. However, synthesized VO_2 thin films are significantly limited in their use because of a number of issues, including a relatively low luminous transmittance in

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the visible regime and low transition efficiency in the solar transmittance.

In order to enhance the luminous transmittance, some researchers have introduced doping in the VO_2 thin films with fluorine (F) [34], magnesium (Mg) [35], and titanium (Ti) [36]. Another way to enhance the optical properties introduced index matching layers in the VO_2 thin films, like an anti-reflection coating with TiO_2, Al_2O_3, Nb_2O_5, or SiO_2 layers, which provide a significant enhancement in the transmittance and successfully maintain the infrared transmittance [37]. Such layering not only suppresses the reflectance in the visible wavelength regime but also shifts the peak position of the optical transmittance to the short or long wavelength region, however additional processes and materials are needed to make index matching layers.

In this paper, we describe the synthesis of colloidal VO_2 nanoparticles with a high luminous transmittance. The highly crystallized VO_2 nanoparticles exhibited a VO_2 phase through post thermal treatment. In addition, using a nanoimprinting method, we patterned the VO_2 thin films to control the aperture ratio with striped lines and spaces. We also discuss the thermochromic characteristics of the nanopatterned VO_2 thin films.

2. Experimental procedure

2.1. Synthesis of colloidal VO_2 nanoparticles

In a typical synthesis procedure, ammonium meta-vanadate (NH_4VO_3, 99%, Sigma-Aldrich) and ethylene glycol ($C_2H_6O_2$, 99.8%, Sigma-Aldrich) were used as received to prepare the vanadium precursor. To reduce or depress the aggregation of nanocrystals during synthesis, oleic acid ($C_{18}H_{34}O_2$, Sigma-Aldrich) was utilized as a structure directing agent with the VO_2 nanoparticles. As shown in Fig. 1(a), 3 g of NH_4VO_3, 3 g of oleic acid and 60 mL of $C_2H_6O_2$ were mixed in a 250 mL round-bottomed flask. The mixture was purged by N_2 gas, and then the flask was placed in a heating mantle at 160 °C under vigorous stirring. The temperature of the solution was monitored by thermocouples. The color of the reaction solution turned from yellow to blue after 60 min. The blue precipitate was washed and filtered several times with 60 mL of $C_2H_6O_2$ by a 0.1 μm pore sized PTFE membrane under reduced pressure. The filtered precipitate was placed in a convection oven at 200 °C for 30 min to remove most of the $C_2H_6O_2$ and water and to form crystalline VO_2 nanoparticles. After cooling to room temperature, the resulting particles were mixed with 10 mL of $C_2H_6O_2$ and sonicated for 10 min to form a suspension. The suspension was filtered again and the resulting precipitate was treated in a convection oven at 200 °C for 30 min [38].

2.2. Post thermal treatment

The resulting particles were further annealed in a vacuum furnace to enhance the crystallinity of the VO_2 nanoparticles. When the base pressure in the tube furnace reached 5×10^{-3} Torr, the nanoparticles were annealed at a temperature of 600 °C with different annealing times from 60 to 180 min. The annealing temperature was controlled by a temperature controller with a heating rate of about 10 °C/min. For an accurate reading of the furnace temperatures, temperature calibration was performed using K-type thermocouples directly attached to the surface of the furnace tube. The annealing atmosphere with Ar gas was kept at 50 sccm, which was precisely controlled with a mass flow controller (MFC). After thermal treatment, the VO_2 nanoparticles in ethanol were treated by ultra-sonication and syringe filtering with a 0.45 μm pore size to reduce the average size of the nanoparticles because larger particle sizes could not be used to fabricate VO_2 thin films because they could not be dispersed in the solvent.

2.3. Preparation of nanopatterned VO_2 thin film

As shown in Fig. 1(b), the nanopatterned VO_2 thin films were fabricated through a polydimethylsiloxane (PDMS) mold and spin coating. The Si trench master mold with a pattern width of 250 nm and different patterns for different pattern periods was fabricated using KrF photolithography followed by reactive ion etching (RIE). A positive photoresist with a thickness of 400 nm was spin coated on 200 mm Si wafers, which was exposed by a KrF scanner (Nikon, NSR-S203B), followed by developing using a developer solution (tetramethylammonium hydroxide, TMAH). The photoresist patterns were used as an etch mask to pattern the Si surface by reactive ion etching by CF_4 gas. After the stripping of the remaining photoresist, trench patterns with a width of 250 nm, a depth of 200 nm, and a different period were obtained and used for VO_2 nanofabrication. To fabricate the PDMS mold, pre-polymers and a curing agent (Sylgard 184, Dow Corning Co. Ltd.) were mixed with a weight ratio of 10:1, and the resulting air bubbles in the mixture were eliminated by degassing in a vacuum. The mixture was then poured on a silicon wafer and baked at 150 °C for 30 min using a convection oven. Poly-4-vinylpyridine (P4VP) film was spin coated on the elastomeric PDMS mold, which was prepared by thermal curing pre-polymers on surface-patterned silicon templates. To remove the top-

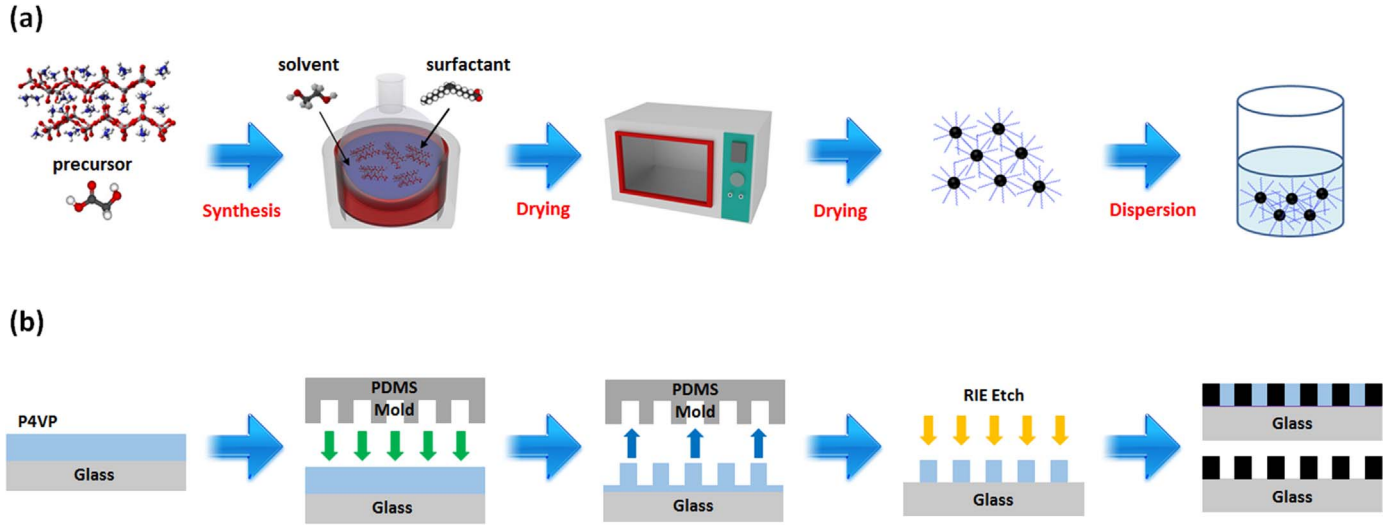

Fig. 1. A schematic of the general procedure for nanopatterned VO_2 thin films. (a) Preparation of VO_2 nanoparticles with ammonium meta-vanadate, oleic acid, and ethylene glycol. (b) Nanoimprinting method to fabricate nanopatterns by a PDMS mold.