Physica E 52 (2013) 112–115

Contents lists available at SciVerse ScienceDirect

Physica E

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

The characteristics of Au:VO_2 nanocomposite thin film for photo-electricity applications

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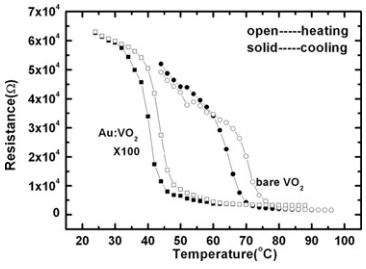
HIGHLIGHTS

- Au:VO_2 thin film was fabricated by NSL method and rf-magnetron sputtering method.
- The surface morphology, crystal structure and composition, electrical and optical properties were studied.
- Au doping in VO_2 thin films could reduce the transition temperature, which is better than that reported in reference.
- Au doping synchronizes influences the extent of transmittance is discussed.

GRAPHICAL ABSTRACT

The transition temperature of Au:VO_2 thin film is 25 °C lower than that of bare VO_2 thin film.



ARTICLE INFO

Article history:
Received 5 September 2012
Received in revised form
16 March 2013
Accepted 4 April 2013
Available online 12 April 2013

Keywords:
Au:VO_2 nanocomposite thin film
Transmittance
Semiconductor-to-metal phase transition
Nanosphere lithography
Radio frequency magnetron sputtering

ABSTRACT

Au nanoparticles have been fabricated on normal glass substrates using nanosphere lithography (NSL) method. Vanadium dioxide has been deposited on Au/glass by reactive radio frequency (rf) magnetron sputtering. The structure and composition were determined by X-ray diffraction and X-ray photoelectron spectroscope. Electrical and optical properties of bare VO_2 and Au:VO_2 nanocomposite thin films were measured. Typical hysteresis behavior and sharp phase transition were observed. Nanopartical Au could effectively reduce the transition temperature to 40 °C. The transmittance spectrum for both Au:VO_2 nanocomposite thin film shows high transmittance under transition temperature and low transmittance above transition temperature. The characteristics present the Au:VO_2 nanocomposite thin film can be used for applications, such as “smart window” or “laser protector”.

1. Introduction

Vanadium dioxide (VO_2) has been widely investigated due to its unique phase transformation since 1959. Low-temperature semiconductor phase of VO_2 abrupt transform to high-temperature metal phase as its crystal structure undergoes a monoclinic structure to a rutile structures near 68 °C. [1] It has been developed applications in optical switches, smart windows, laser protector, optical storage systems and thermistor, *etc*..[2–4] It is very important to reduce transition temperature to room temperature for all sorts of applications. However, the transmittance of VO_2 thin films was much decreased synchronized low transition phase temperature as W, Mo, and Nb doping in VO_2 thin films. [5,6] Besides, it is not reproducible to reduce the phase transition temperature and avoid affecting the optical properties by controlling the size of VO_2 grain in range of nanometer. [7] Au doping VO_2 thin film is another choice to depress phase transition and hold relatively higher transmittance. G. Xu et al. reported that the Au was randomly doped in VO_2 and the characteristic of electrical and optical was uncontrolled. [8] M. Maaza et al. also reported Au

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http://dx.doi.org/10.1016/j.physe.2013.04.005

doping VO_2 thin film by Reactive radio frequency inverted cylindrical magnetron sputtering (ICMS) exhibits plasmonic properties. [9,10] Recently, nanosphere lithography (NSL) has been explored to produce nanostructure for studying surface plasmon reasonance (SPR) and third-order optical nonlinearity. [11,12] To compare with electron-beam lithography (EBL) and focused ion beam lithography (FIB), NSL is a low-cost effective method. The size and shape were easily controlled using different sizes of polystyrene nanospheres. [13,14] In this article, firstly we fabricated Au particles on normal glass by NSL method. Secondly, VO_2 thin film was deposited on Au/glass by reactive radio frequency (rf) magnetron sputtering. The diameter of 233 nm triangular-shaped Au particles periodic arrays (PPAs) was observed in scanning electron microscopy (SEM) image. The optical and electrical properties were measured. Our result approaches to the best in references [8–10].

2. Experiment

The Au PPAs were fabricated using NSL method. Firstly, by dropping 10 ml of polystyrene sphere (in size of 1 μm) diluted solution onto a cleaned normal glass substrate, which was inclined about 5° in a chamber at room temperature for 48 h. A homogenous, dense monolayer colloid mask was successfully formed. Secondly, the colloid mask was set into vacuum chamber and sputtered gold target for 30 s. Thirdly, the colloid mask with Au film was immerged into chloroform, and the polystyrene sphere was ultrasonically removed for 10 min. Finally, the uniform and ordered Au PPAs with 50 nm height was obtained.

The Au PPAs and normal glass were put into reactive magnetron sputtering chamber. High purity argon gas (99.9999%) and oxygen gas (99.9999%) were induced into chamber with a partial pressure of ratio of 50:1. The vanadium target (99.99%) was bombarded and reacted with oxygen gas. The precursor of VO_2 thin film was deposited on Au PPAs and normal glass, respectively. Then the precursors were annealed for 60 min in the temperature 380 °C under air in Muffle furnace. The Au:VO_2 composite thin film and bare VO_2 thin film in 200 nm thickness were prepared.

The surface morphology image of Au PPAs was investigated using scanning electron microscopy (SEM) (Hitachi S4800). Atomic force microscopy (AFM) (Nanoscope V) was used to observe the surface of VO_2 and Au:VO_2 composite thin films. The crystal structure of Au:VO_2 was analyzed by X-ray diffraction (D/Mas-RB). X-ray photoelectron spectroscopy data (XPS) were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The data deal was performed using Avantage 4.15. The electrical property of samples was tested on a four-probe station with a temperature controller. The transmission of the samples was measured using high UV sensitivity thin back-illuminated CCD spectrometer (Avantes).

3. Results and discussion

Fig. 1 shows the SEM image of $5.6\times4.4\ \mu m^2$ area of Au PPAs. The image exhibits a typical hexagonal patterned 2D particle arrays consisting of triangular-shaped Au particles. The triangular-shaped Au particles are joined to each other because of larger empty of 1 μm polystyrene sphere. The particle diameter, defined as the perpendicular bisector of the equilateral triangle, is estimated to be about 233 nm, which can be calculated from formula $a=3/2(\sqrt{3}-1-(1/\sqrt{3}))D=0.233D$. [14] The average out-of-plane height of the particle arrays is about 50 nm.

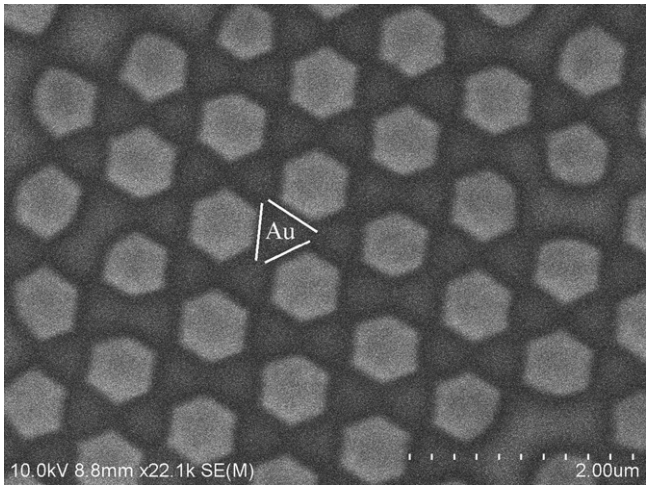

Fig. 1. SEM image for the surface of Au PPAs.

Fig. 2 shows the AFM images in size of $5\times5\ \mu m^2$ of bare VO_2 and Au:VO_2 thin films. Obviously, the crystal particle of bare VO_2 thin film (Fig. 2(a)) displays more random shape than that of Au:VO_2 composite thin film (Fig. 2(b)). The root mean square (RMS) value of roughness is 9.7 nm for bare VO_2 thin film and 11.7 nm for Au:VO_2 composite thin film, respectively. The average height of Au:VO_2 composite thin film is larger than that of bare VO_2 thin film. The reason is the Au particle was embedded under the VO_2 thin film. According to the height and area of Au particles, the Au PPAs constitute was estimated to be 12.5% by volume of Au:VO_2 thin films.

Fig. 3 exhibits typical θ-2θ scanning of the XRD pattern for Au:VO_2 composite thin film. For the reason on normal glass substrate, all peaks are small. Nevertheless, all peaks show the VO_2 thin film as monoclinic structure ($a=0.5752$ nm $b=0.4538$ nm $c=0.5383$ nm). One Au (111) peak appears in Fig. 3 although Au particles are underneath the VO_2 thin film.

Fig. 4(a) exhibits typical V2p and O1s X-ray photoelectron core lines for bare VO_2 thin film (solid) and the Au:VO_2 nanocomposite thin film (dot), respectively. Three peaks at 516.6, 524.2 and 529.9 eV, is corresponding to V2p3/2, V2p1/2 and O1s, respectively. The intensity ratio of V2p3/2 to V2p1/2 was constrained to about 2:1. The intensity ration of binding energy peaks of Au: VO_2 nanocomposite thin film are lower than those of bare VO_2 thin film because of doping Au. Two broad binding energy peaks at 84.1 and 87.6 eV, corresponding to Au 4*f*7/2 and Au 4*f* 5/2 in Fig. 4 (b) proved that the VO_2 thin film was doped by metal Au. The signal is weak and the ratio of Au shows less than 0.1 at%, which probably because the Au nanoparticles were embedded under the VO_2 thin film.

Fig. 5 shows resistance vs temperature curves of bare VO_2 and Au:VO_2 thin films. Typical heating and cooling hysteresis and tardily falling resistance are illustrated for both samples. The resistance value of Au:VO_2 thin film is two orders of magnitude lower than that of bare VO_2 thin film. The temperature of the phase transition (T_{MI}) is found to be around 40 °C for Au: VO_2 composite thin film and about 65 °C for bare VO_2 thin film, respectively. T_{MI} of Au: VO_2 thin film is 25 °C lower than that of bare VO_2 thin film, which is ascribed to more free electrons of Au injection into VO_2 thin film. According to G. Xu et al., the T_{MI} reduces with the Au particles height increasing. The rise in electron concentration in VO_2 triggers the phase transition at a lower temperature can be explained by Zylbersztejn and Mott. [15] D. W. Ferrara et al. reported Au array prepared by EBL reduced the threshold laser power required to result in the semiconductor-to-