Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 516 (2008) 5541–5544
www.elsevier.com/locate/tsf

Preparation of silane-WO_3 film through sol–gel method and characterization of photochromism

Zhongkuan Luo [a,*], Jianjun Yang [b], Honghua Cai [a], Haiyang Li [a], Xiangzhong Ren [a], Jianhong Liu [a], Xun Liang [a]

[a] College of Chemistry and Chemical Engineering, Shenzhen University, Shenzhen 518060, Guangdong, PR China
[b] Xinyi Glass Holdings Limited, Shenzhen 518115, Guangdong, PR China

Available online 14 July 2007

Abstract

The sol of silane and WO_3 was prepared from tetraethyl orthosilicate (TEOS) and methacryloxy-propyl-trimethoxy silane (KH570) with a novel route as described in previous work, and the aqueous WO_3 solution was prepared from ammonium tungstate. These two sols were mixed by stirring for about 1 hour with a certain ratio. Through sol–gel method, the transparent hybrids coating of organic silane and tungsten oxide was prepared by spraying or dipping on the glass substrates, and then were heat-treated at a certain temperature. The photochromic properties were investigated. AFM was used to investigate the surface structure of the prepared coatings. The crystalline phase was studied through X-ray diffraction. UV lights with different wavelengths were used to get the coloration of the film. The results show that silane-WO_3 film exhibits better photo-chromic properties under UV light irradiation.

Keywords: Photochromic; Sol–gel; Silane; Tungsten oxide

1. Introduction

It is interesting to work on the research and development of materials and devices that can be used for optical switching of large-scale glazings. These potential switching technologies are available for glazings, including those based on the electrochromism, thermochromism and photochromism phenomena [1]. Tungsten oxide coatings can be used as the active layer in a range of electrochromic and photochromic devices [1], as catalysts for example in the photoassisted catalytic decomposition of organic pollutants [2], and as information storage systems [3]. Depending upon the application, the requirements vary from dense, optically transparent thin films, to porous thick layer coatings. The use of solution processing routes is advantageous for large-scale production of such coatings and a number of such routes are available. A variety of precursors can be used, for example tungsten alkoxide [4], sodium tungstate [5], dissolved tungsten metal [6], tungsten hexachloride [7] tungsten oxychloride [8], tungsten oxide [9] and hydrated ammonium metatungstate [10].

Electrochromism is defined as the electrochemical generation of color in conjunction with an electron transfer reaction. During the electrochromic reaction of thin-film metal oxide, the electrons responsible for the color state enter or leave the oxide film at the electrode/solution interface while the ions for the charge balance (electroneutrality) enter or leave via the ion-conductive electrolyte [11].

$$WO_3 + x(H^+ + e^-) \rightarrow H_xWO_3 \quad (1)$$

where the mobile ion is a proton.

The new method of injection of hydrogen in solid oxide was proposed by Gavrilyuk [12], and called photo-injection of hydrogen (PIH), because the hydrogen atoms injection is induced by light. Using this method, the photochromic properties of amorphous and crystalline WO_3 films were studied in this paper.

Since the photochromic process of WO_3 can be completely reversible if being exposed it to oxygen, has been considered to be one of the most promising candidates for technological

* Corresponding author. Tel.: +86 755 2653 6055.
E-mail address: luozhongkuan@126.com (Z. Luo).

0040-6090/$ - see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.tsf.2007.07.119

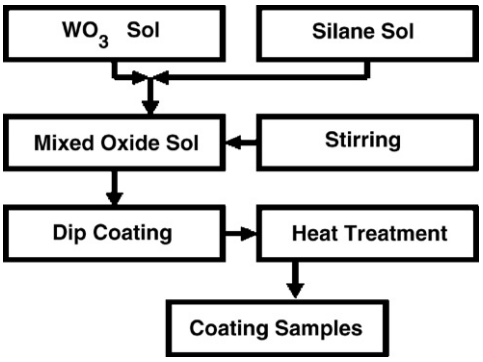

Fig. 1. Process flow chart for the preparation of hybrids coating.

applications such as large area displays and erasable optical storage devices. The UV light photochromism of WO_3 can be improved by supporting of water molecules existed in the silane or silica particles.

In this work silane sols were prepared by the sol–gel technique and hydrothermal treatment. The effects of silane and silica nanoparticles with different surface properties on the photochromism of WO_3 sol were investigated. The obtained results should be valuable for the practical applications of the WO_3 sol combined with silane sols.

2. Experimental

Tungsten oxide sol was prepared as follows: A commercial cation-exchange resin was immersed in an acid solution (HNO_3) for 1 h to convert from Na^+ type to H^+ type. After washing with distilled water five times, the resin was packed uniformly in a glass column and washed with distilled water repeatedly until pH of the effluent came close to 7. The ion-exchange capacity (content of protons) of the resin was about 2 meq/cm^3, as evaluated from the titration with an NaOH solution.

Sodium tungstate was purchased as its dihydrate (Na_2WO_4 $2H_2O$) and used without further purification. Its aqueous solution was let to flow down through the glass column at a fixed rate, and the effluent was collected into a beaker. After standing for 3 days, the effluent precipitated a yellow gel containing $WO_3 \cdot 2H_2O$. The particle size distributions of sols were analyzed on a laser particle size analyzer.

Silane sols were prepared as follows: The surface of nanosized silica sol is completed with hydroxyl (–OH) groups. Silane would dilute to different concentrations and mixed with different amounts of silica sol–gel. The solutions were stirred to promote strong chemical linking, and to form organic–inorganic nano-hybrid composites. During this process, chemical mixing make silica sol linked with silane forming the nana-hybrid composites. The precursor liquid would then be used to mixed tungsten oxide sol further. Methacryloxy-propyl-trimethoxy silane was diluted with ethanol in various ratios. The silane solutions were then filtered, the tetraethyl orthosilicate were added. Obtained solutions were stirred for 3 h. Twenty-four hours later the sol can be used to be mixed with other sol for preparing the coatings.

Tungsten oxide sol was added to silane sol with a certain ratio. Stirring lasted for about 1 h. Five days later, the mixed solution was used to coat the glass surface by dipping method. The times of dipping depend on the thickness demanded. Finally, the coatings were heat-treated for 30 min at 150 °C.

The substrates of glass were cleaned with acid acetone, extensive deionized water, and absolute ethanol sequentially. These glass substrates were air-dried. The cleaned substrates were dipped in a complete mixed precursor sol. The fabrication of multi-cycles coating was carried out. The glass substrates with a certain area were dipped in the obtained precursor for about 5–7 min. Coating fabrication can be seen from Fig. 1.

Particle size of the precursor solution was measured with N4 Plus particle size analyzer. The films were investigated using X-ray diffraction (Shimadzu), Atomic force microscope (DI–IIIa), and UV–Vis spectrophotometer (Shimadzu, UV–2401PC).

UV light within 325 nm–390 nm and 3.0 mW/cm^2 intensity was used as light source. UV irradiation time depended on the photochromic effect. Coloration process by UV light irradiation is as follows: samples were first UV irradiated for 1 min, and then the measurement of transmittance of visible light. Continual irradiation of UV was carried out for 5, 10, 15 or 20 min. Visible light transmittance was measured respectively.

3. Results and discussion

3.1. Particle size of sol

Particle size of mixed oxide sol was measured with laser diffraction particle size analyzer. The results of measurement showed that sol particle sizes were in the range of 5 to 100 nm, and the average size was 25 nm.

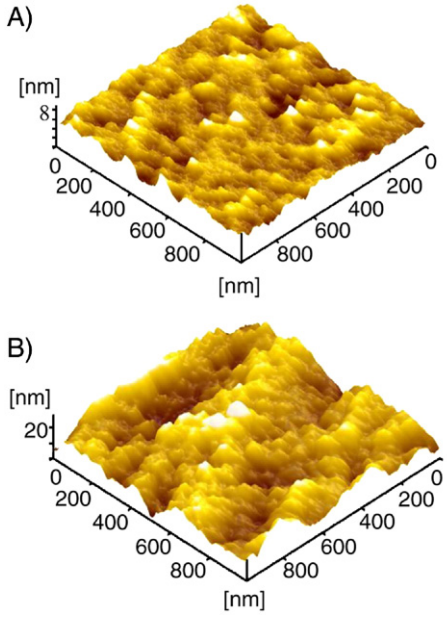

Fig. 2. AFM photos for different coating samples. (A: Concentration of WO_3 in sol is 5%. B: Concentration of WO_3 in sol is 9%).