Surfaces and Interfaces 8 (2017) 8–14

Contents lists available at ScienceDirect

Surfaces and Interfaces

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

Fabrication of a transparent and super-hydrophilic window by depositing WO_X nanoparticles via magnetron sputtering onto a glass

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ARTICLE INFO

Keywords:
WO_X nanoparticles
Magnetron sputtering deposition
Transparent superhydrophilic thin film
Thermal stability of nano-structure

ABSTRACT

Tungsten trioxide (WO_X) films were prepared on a glass substrate by depositing WO_X particles using a magnetron sputtering source, which imparted a nano-scale surface roughness to the glass. The chemical and geometric structures of the films were characterized with X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The AFM analysis revealed that the WO_X nanoparticles, with a lateral size of 65 nm, were randomly distributed on the glass substrate at room temperature. Only a slight rearrangement of particles was observed with no increase of mean particle size after annealing at 100 °C under air, while the annealing at 300 °C induced aggregation of the WO_X, forming larger WO_X particles (~85 nm). The formation of micro-sized 2-D islands of WO_X was observed upon increasing the annealing temperature to 500 °C. The adsorption capabilities of these WO_X/glass samples toward methylene blue from an aqueous solution decreased as the annealing temperature increased, which corresponded with the changes of the geometric structure (or number of surface adsorption sites) as annealing temperature increased. Lastly, the optical transmittance and water wettability of WO_X/glass samples was evaluated and it was found that the WO_X films with nano-scale surface roughness provided super-hydrophilic functionality to the glass substrate while maintaining good transparency over the entire visible light wavelength range. It is suggested that the WO_X/glass could be used in fog resistant windows.

1. Introduction

Nano-structuring of flat glass surfaces has attracted much attention over the last few decades since it can provide new functionality to the glass such as anti-condensation [1,2], anti-reflection [3-5], and super-hydrophobicity/hydrophilicity [1-3,6-8]. In particular, the super-hydrophilic surface of glass combined with high optical transparency can be useful in several applications including anti-fogging windows for optics, automobiles, buildings, and displays [9-15]. The hydrophilicity of a flat surface can be enhanced by the introduction of surface roughness, which can be, for example, understood in terms of the Wenzel equation [16-18]. However, an increase in the surface roughness can often make an originally clear glass turbid, reducing its optical transparency. Controlling the surface roughness of the glass at the nano-scale for enhanced hydrophilicity without large perturbations in its optical transparency can be a challenging issue.

Various techniques have been developed to fabricate functional glass via a nano-structuring process. One of the ways to achieve this is using etching processes; however, during most of the etching process, masks with the desired nano- or micro-patterns may be required in order to control the surface structure and roughness in the nano- and micro-size regime [3,9,11,19-23]. This process also often requires an additional etching processes to remove the mask as well as a lithography process to make the mask with the desired patterns. On the other hand, in the case of chemical etching processes without masking techniques, acidic or basic solutions are required, whose use is not environmentally benign and should be avoided [12,24].

Alternatively, the nano-structuring of glass can be done by depositing nanoparticles on the glass surfaces. Fabrication of metal and metal oxide nanoparticles has attracted great attention over the last few decades and many different techniques to generate and deposit metal nanoparticles have been developed based on either chemical or physical processes. Solution-based chemical processes require an additional organic stabilizer of nanoparticles to prevent the coalescence of nanoparticles during the fabrication process [13,15,25-27]. On the other hand, in the case of physical processes, e.g., magnetron sputter-

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http://dx.doi.org/10.1016/j.surfin.2017.04.005
Received 13 January 2017; Received in revised form 10 April 2017; Accepted 12 April 2017
Available online 13 April 2017

ing, nanoparticles are formed by the diffusion of metal atoms or clusters adsorbed on the substrate surface without use of a ligand as a stabilizing agent [28-32].

For practical applications, it is essential that the nanostructure of the glass is stable under atmospheric conditions. Also, the thermal stability of the structure can be an important issues for a glass covered with nanoparticles, since the nanoparticles can easily aggregate at elevated temperature, losing the nano-scale roughness of the surface, and in turn, losing the desired functionality of the nano-structured glass [33,34]. Here, we fabricated a nanostructured film consisting of tungsten oxide nanoparticles on the glass substrate using a magnetron sputtering source. The prepared WO_X/glass sample was studied in terms of its geometric structure, adsorption capability, wettability, and optical transparency. The influence of the post-annealing temperature on the geometric structure of the prepared WO_X film under atmospheric conditions was also studied. It was demonstrated that the nano-scale roughness of the WO_X film on a glass substrate was stable in air, even at elevated temperatures (~300 °C). Furthermore, the WO_X/glass sample exhibited good optical transmittance over the entire visible light range and super-hydrophilicity.

2. Experimental

2.1. Sample preparation

Tungsten clusters were generated by a magnetron sputtering source using a gas mixture of Ar and He (ratio of 1:10). A more detailed description of the magnetron sputtering source can be found elsewhere [35]. The base pressure of the sputtering source chamber, which was equipped with a turbo molecular pump, was 5×10^{-4} mbar and the pressure of the chamber was kept at 3×10^{-2} mbar during the sputtering process. The discharge was generated with a dc voltage of 470 V and the sputtering current was set at 0.4 A, respectively. Tungsten thin films, consisting of tungsten clusters, were obtained by placing slide glasses (a lateral size of 15 × 15 mm^2) in front of the sputtering source for 3 h. The distance between the glass samples and the tungsten target was 40 cm during the deposition process. After 3 h of tungsten cluster deposition, samples were taken out of the deposition chamber and annealed at three different temperatures (100, 300 and 500 C for 1 h) in air in order to study the effect of the post-annealing temperature on the morphology of the film surface.

2.2. Sample characterization

After the deposition of tungsten thin films, the samples were exposed to atmospheric conditions at room temperature, and then their surfaces were characterized using X-ray photoelectron spectroscopy (XPS). W 4f and Si 2p core-level spectra were measured at room temperature using a concentric hemispherical analyzer (Omicron EA 125) and a Mg K-α (1253.6 eV) X-ray source.

The topographic structures of as-prepared and annealed samples were investigated using ex-situ atomic force microscopy (Nanowizard® 3a Nanoscience AFM, JPK Instruments AG) in intermittent contact mode (tapping mode). The optical transmittance of the deposited tungsten film was measured by a UV–vis spectrometer (Agilent Technologies 8453 Spectrophotometer, Agilent) and the contact angle of water on the tungsten thin film was measured using a Theta Optical Tensiometer (KSV instrument, Ltd.) with a digital camera connected to a computer.

Methylene blue adsorption on the tungsten thin film was investigated by monitoring the optical absorbance of methylene blue at the maximum absorbance wavelength (λ_{max} = 665 nm). An as-prepared sample was placed in a polypropylene (PP) beaker filled with the methylene blue solution (10 ml, 2 ppm) and the change in the methylene blue concentration was evaluated by measuring the optical absorbance of methylene blue as a function of time. Every 30 min, 4 ml of the solution was transferred to a disposable cuvette to obtain the absorbance spectra of the solution with a UV–vis spectrometer, and then the solution was returned to the PP beaker. This experiment was done for 2 h for each sample. Following the dark-condition adsorption experiments, the reactor was illuminated by a blue light emitting diode (LED, λ_{max} = 454 nm) light in order to study photocatalytic activity of the tungsten film.

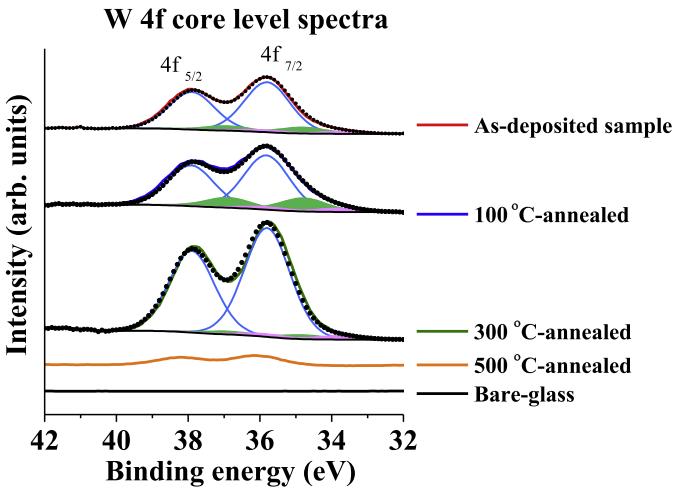

Fig. 1. W 4f and XPS core-level spectra of WO_X/glass, which are as-prepared and annealed at various temperatures, are compared. For the as-prepared and 100 °C- and 300 °C-annealed samples, fitting results are also presented.

3. Results and discussion

In Fig. 1, W 4f XPS spectra of bare, as-prepared tungsten-deposited glasses as well as those annealed at various temperatures (100, 300, and 500 °C for 1 h) in air are compared. The binding energy of the XPS spectra was calibrated by the Si 2p XPS spectrum at a binding energy of 103.3 eV (Si (IV)) [36]. Intensity of the W 4f peaks was normalized with respect to the respective Si 2p peak intensity. The W 4f peak appeared while the Si 2p peak from the glass substrate was reduced in its intensity after the deposition of tungsten films on the glass substrate. The W 4f peak of the as-prepared sample shows a doublet feature by the spin–orbit coupling of the final state (W $4f_{5/2}$ and $4f_{7/2}$) and the W $4f_{7/2}$ peak is centered at 35.8 eV corresponding to the fully oxidized W (VI) states [36,37]. Even though metallic W clusters were generated under vacuum conditions, W atoms were oxidized by the oxygen-containing molecules in air (H_2O and O_2), resulting in the formation of WO_X on the glass surface. When the sample was annealed at 100 °C, the peaks became slightly broader, whereas annealing at 300 °C resulted in an increase and sharpening of the peaks. For 500 °C-annealed samples, the W 4f level peaks became significantly lower, indicative of agglomeration of the WO_X clusters upon 500 °C-annealing.

In order to shed more light on the detailed nature of the WO_X clusters annealed at different temperatures, W 4f core level spectra of the as-prepared sample, and those annealed at 100, 300 °C, were de-convoluted using various oxidation states of W (Fig. 1). For each component, the function resulting from the linear combination Gaussian and Lorentzian functions with a ratio of 7:3 was used. For 500 °C-annealed sample, the de-convolution was not carried out due to its low intensity of the W 4f peaks. The results of the fitting procedure are quantitatively compared in Table 1. It is obvious that the as-prepared and 100 °C-annealed WO_X clusters consist of mixture of oxidation states of IV, V and VI, and the relative amount of VI state of W decreased upon annealing at 100 °C. As the annealing temperature increased to 300 °C, the amounts of W atoms with IV and V oxidation states were reduced, and relative amount of the VI state was significantly increased; though, the 300 °C-annealed sample still showed oxidation states of IV and V.