RESEARCH PAPER

Hydrophilicity of Silica Nano-Porous Thin Film " Calcination Temperature Effects "

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ABSTRACT

In this research work, silica nano-porous thin films were deposited on glass substrates by layer by layer method. The thin films were calcinated at various calcination temperatures (200, 300, 400, and 500 °C). The morphology, surface characteristics, surface roughness and hydrophilic properties of the thin films were investigated by field emission scanning electron microscopy, attenuated total reflectance fourier transform infrared spectroscopy, atomic force microscopy and water contact angle analyzer. The surface characteristic showed that silica nano-porous thin film had an amorphous structure. The hydrophilic results indicated that the water contact angle of the glass coated silica nano-porous surface is decreased by increasing the calcinations temperatures to 300 °C and at higher temperature, it is increased. The deposition of silica nano-porous thin film on the glass surface at the optimum calcination temperature (300 °C) decreased water contact angle of the glass surface from 67° to 3°. Therefore, silica nanoporous thin film calcinated at 300 °C showed superhydrophilicity which greatly encourages the antifogging functions of the thin film.

INTRODUCTION

Hydrophilic materials due to their antifogging effects and self cleaning properties have attracted a great deal of attention in recent years in special applications such as building, automobile and glass industry [1-2]. The hydrophilicity allows water to spread completely across the surface rather than remain as droplets, thus making the surface easy to wash. In recent years, hydrophilic titania thin film has a high potential for practical applications such as mirrors, window panes and automobile windshields [3-4]. However, titania thin film only displays hydrophilicity under UV light irradiation. In practical uses, UV irradiation light on the titania surface does not always occur [2]. Therefore, it is preferable that the thin film obtains its hydrophilicity without UV irradiation. It is observed that textured surface induced hydrophilicity without UV irradiation. Such hydrophilic surfaces structures have been created by lithographic patterning techniques or by formation a porous structure by creation of surface roughness. Surface roughness will perform the hydrophilic surface material more wettable [5]. Then, it is possible to obtain hydrophilicity by incorporation nanoporous into hydrophilic coatings. Recently, it is observed that silica nano-porous coating can show hydrophilicity without UV irradiation. Silica nano-porous thin films can be fabricated by various methods such as sol–gel

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process, phase-separation, layer-by-layer (LBL) deposition method, plasma-enhanced chemical vapor deposition. Among these methods, the layer- by- layer method (LBL) is a desirable technology for fabrication of silica coatings since it allows deposition of coatings on large area, non-flat surfaces and wide range of substrates [6-9]. It was found that the properties of silica nano-porous thin films are strongly dependent upon the preparation conditions such as the pH of solution, thin film thickness and calcination temperature [10-11]. On the other hand, the characteristics of a nano porous thin film like hydrophlicity can vary strongly with the size and shape of the particles and pores. It is well known that the calcination temperatures (the as synthesized samples were calcined at different temperatures) strongly affect the crystal structure, particle size, surface area and thus the properties of nanocrystalline thin films. Among the literatures, few studies report the influence of calcination temperature on the characteristics of the silica nano-porous thin films. Then, the main purpose is to understand the effect of calcination temperature on the hydrophilic properties of the silica nanoporous thin film. In this study, silica nano-porous thin films were deposited on glass substrates using LBL assembly method. Then, the effects of calcination temperatures on the hydrophilic properties of the silica nano-porous thin films were investigated.

MATERIALS AND METHODS

At first, silica nano-porous thin films were prepared. The procedure for fabrication of silica nano-porous thin films was described in details in earlier our published work [12]. After thin film preparation, the coated slides were calcinated at various temperatures (200,300, 400 and 500°C) for 4 hours at air atmosphere. The thicknesses of the thin films were approximately same as 128 nm. Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR; Bruker Germany, Tensor 27), field emission scanning electron microscopy (FE-SEM, Hitachi S4160, Cold Field Emission, Voltage 20KV) and Atomic force microscopy (AFM, Veeco CPR USA contact mode) were used to study the surface characteristics, morphology and surface roughness of the thin films. The surface properties of the thin film was analyzed by X-ray photoelectron spectroscopy (XPS) using Mg kα source (1253/6 eV). The film hydrophilicity was evaluated by measuring the water contact angle of a droplet on the film surfaces. A droplet was injected on to the film surface using a 1μL micro-injector. The water contact angle was averaged from five measurements.

RESULTS AND DISCUSSION

The surface characteristics of the film calcinated at 300 °C were studied by ATR-FTIR. Fig. 1 shows the ATR-FTIR reflection spectra of the silica nanoporous thin film. The adsorption band at about 850 and 1070 cm^{-1} is assigned to the stretching vibration of the Si–O–Si band which indicates the existence of amorphous silica [12-13].

Fig. 2 shows FE-SEM images of the silica nano-porous thin films calcinated at various temperatures. It can be seen that the porous structure was not formed in the thin film calcinated at 200 °C. At this temperature, the organic components did not burn completely, and Si-O bonding was incomplete. Therefore, the nano-porous structure was not form. Fig. 2 shows that a nano-porous structure formed in the silica thin film calcinated at 300 °C. Nano- pores with sizes between 30 and 80 nm are clearly observed in the thin film calcinated at this temperature. These nano-pores were formed during the burning of PDDA and PAA organic components in the calcination process. Accordant to the FE-SEM images, it may be seen that the pore sizes and silica nano-particles in the thin films increased with an increase in the calcination temperature. When the calcination temperature approached the transtion temperature of the soda lime glass substrate, the morphology of the thin film changed and porous structure vanished. These conditions affect the hydrophilic properties of the thin film which is discussed in the following.

AFM was used to characterize the surface roughness of the bare glass and glass coated silica nanoporous thin film. Fig. 3 shows AFM images of the bare glass and glass coated silica nanoporous thin film calcinated at 300 and 500 °C, respectively. The root mean square roughness values (Rrms) of the bare glass and glass coated silica nanoporous thin film calcinated at 300 and 500 °C are 2.52, 18.87 and 19.97 nm, respectively. Thus, deposition of silica nanoporous thin film on the glass substrate significantly increased the surface roughness. The surface roughness is believed to affect the wettability of the coatings. The effect of the surface roughness on the surface wettability of
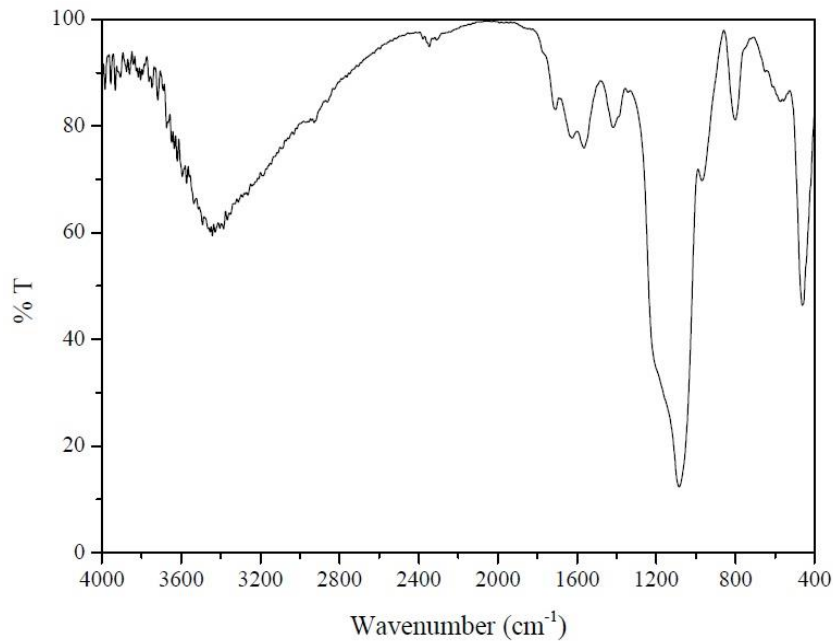
Fig. 1. FTIR-ATR spectra of the silica nanoporous thin film

the coating is discussed below in detail.

Fig. 4 shows the wide XPS scan spectra of the silica nano-porous thin film. The X-ray photoelectron spectra were referenced to the C1s peaks (Eb = 285 eV) resulting from the adventitious hydrocarbon (i.e. from the XPS instrument itself) present on the sample surface. Fig. 4 shows the high resolution XPS scan spectra of the Si 2s, Si 2p, C1s and O1s peaks. According to Fig. 4, the XPS Si peaks centered at about 155 eV (Si 2s) and 104 eV (Si 2p), C1s peak centered at about 285 eV and the O1s XPS signal centered at a binding energy of 533 eV. The Si2p spectra indicated the chemical state of Si and in to be Si^{+4}. Therefore, the XPS spectrum confirms that the film contains the silicon dioxide (SiO_2) structure [14[.

Fig. 5 display the results of the water contact angle measurements on the glass and glass coated silica nano-porous film surfaces calcinated at various temperatures. According to Fig. 5, it can be seen that that the water contact angle is decreased by increasing the calcination temperatures to 300 °C, but at higher temperatures, is increased. In other words, silica nanoporous thin film calcinated at 300 °C (with contact angle 3°) can act as a superhydrophilic thin film for glass substrate. That is, the water has completely spread over the surface and the surface shows superhydrophilicity.

Therefore, the effect of calcination temperatures on the hydrophilicity of glass coated silica nano-porous thin films can be contributed to three major factors:

The first major factor is surface roughness. In the glass coated silica nanoporous thin film, nanoporous increased the surface roughness as shown by AFM. Surface roughness has an intense effect on the hydrophilicity. The principle relationship between surface roughness and contact angle was developed by Wenzel and is given below [15-17]:

$$Cos\ \theta^* = r\ Cos\ \theta \qquad (1)$$

where r is the roughness parameter, θ^* is the apparent water contact angle on a rough surface and θ is the young contact angle induced only by chemical surface interaction, i.e., which would be measured on an ideally flat surface. From this equation, it appears that the roughness enhances the surface wetting behavior, i.e., $\theta^* < \theta$, of a naturally hydrophilic surface ($\theta < \pi/2$). These results showed that glass coated silica nanoporous thin film possess hydrophilicity and as a consequence a high content of hydroxyl groups are present on the surface which are absolutely necessary for the successful adsorption of water on the surface. This can be explained by the rough surface of the film with the combined effect of various pore channels and cracks or small ditches, which may provide enough capillary force to suck water into the film [16].
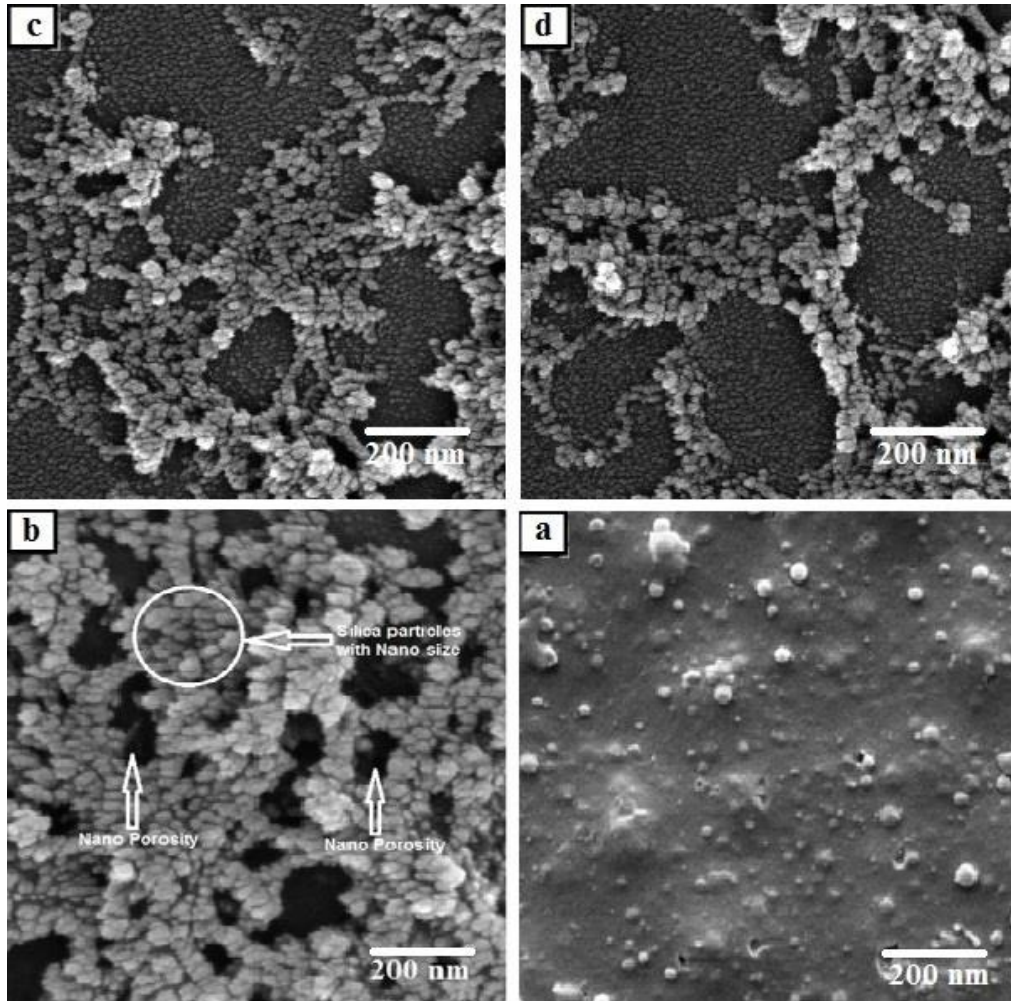
Fig. 2. FE-SEM images of the thin films calcinated:a-200, b-300, c-400 and d-500 °C [16].

Therefore, based on the equation 1, it is expected that thin film calcinated at 500 °C due to higher surface roughness shows lower contact angle in comparison to silica thin film calcinated at 300 °C while Fig. 4 displays reveres results. It is necessary to mention that roughness shape has an important key on the surface wettability. As shown by Bico and Marzolin, [21] the main parameter that determines the contact angle of a drop on a hydrophobic rough surface is the fraction of solid actually in contact with the liquid (eqs. (2) and (3)), and not only the surface roughness.

$$\cos \theta^* = -1 + \phi_s (\cos \theta + 1) \qquad (2)$$

$$\cos \theta^* = -1 + \phi_B (\cos \theta + 1)^2 \qquad (3)$$

Where the ϕ_B is the ratio of the surfaces of the spike bases over the total solid surface [18].

Because there are some very rough surfaces which has been found to be high hydrophobic. Thus, it is not necessary to deal with fractal surfaces to get water-repellent surfaces: Interestingly a flat surface with a low roughness (r = 1:3) decorated with spikes was shown to be highly hydrophobic. This surface behaves like a fakir carpet for the drop, which is in contact only with the top of the spikes. In this situation, the water drop mainly sits on trapped air between the spikes which make the drop nearly spherical.

Fig. 5 shows the relation between calcination temperature and contact angle (hydrophilicity). Calcination at 200 °C would burn the redundant polymers but not all of them and the needed textured rough surface would not be formed yet. However the contact angle (35°) will be lower than the contact angle for bare glass (67°)

130

RMS= 2.52 nm **(a)**

RMS= 18.87 nm **(b)**

μm/div
0.006

1.0 μm/div

1.0 μm/div

RMS=19.97 nm **(c)**

μm/div
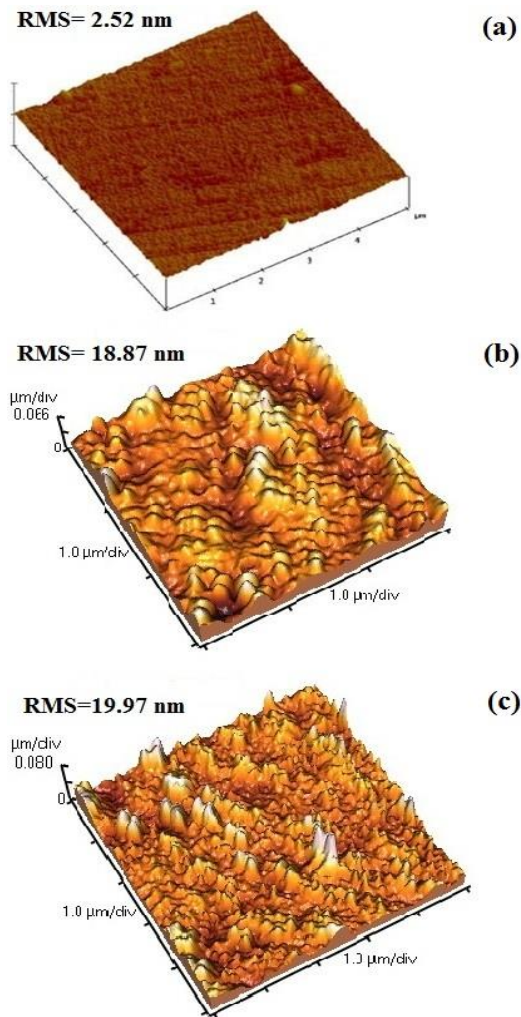0.080

1.0 μm/div

1.0 μm/div

Fig. 3. AFM images of (a) glass (b) film calcinated at 300 and (c) film calcinated at 500 °C.

thanks to the retained hydrophilic polymers which have been used to build the film layers. As the calcination temperature increases to 300 °C, all the redundant polymers will burn and take out of the system and the nano-porous texture will occur. A rough surface with the optimum fraction of solid contacting the liquid and the minimum of trapped air. In this situation the roughness of the surface, the solid fraction and the capillary effect all together helps the contact angle to reduce to 3° which has made the surface superhydrophilic. When the temperature increases to 400 and 500 °C the surface texture will dramatically change and the surface structure of soda-lime glass (substrate) would be damaged [18]. Higher temperature makes the cavities larger and the spikes thinner

which would result in a lower solid fraction contacting to liquid and higher amounts of trapped air between the spikes that make the contact angle increase to 18° and 25°. As can be seen from Fig. 3, it is clear that silica thin film calcinated at 300 and 500 °C shows different configurations. These configurations can trap some air under valleys and cavities which reduce solid fraction, and then prevent water spreading completely [19]. This is the reason why thin film calcinated at higher temperatures (500 °C) despite the higher surface roughness indicated higher water contact angle with respect to thin film calcinated at 300 °C.

The second factor is nano-porosity. Nano-porosity in the thin films is another key factor for the excellent hydrophilicity. The nano-pores in the thin film surface simplify the water spreading by wicking effect [20-21]. Wicking is the spontaneous absorption of liquid in a pore where the driving force that attracts the liquid into the medium is the capillary suction force. This suction force occurs due to wetting of pore surfaces in a porous thin film by the mobile liquid-front [12]. Therefore, nano-porous structure increased the hydrophilicity of the film because of water nanowicking into the network of capillaries existent in the thin film [22-23]. By this we mean: if we design the surface with a texture like spikes which has the minimum fraction of solid in contact with liquid and the maximum contact of trapped air between spikes to liquid the contact angle will increase and the surface would become hydrophobic. Conversely, if we design the rough surface with a texture with the maximum fraction of solid contacting the liquid and the minimum of trapped air between the spikes, the contact angle will reduce and the capillary effect would occur. The liquid will be sucked into the holes and it will reduce the contact angle.

According to Fig. 2, it can be seen that thin film calcinated at various temperatures has different surface morphologies which affect the surface wettability. In other words, increasing water contact angle by increasing calcination temperature can be attributed to the low transition temperature of glass substrate. By increasing the calcination temperature, the temperatures come close to the transition temperature of the glass substrate, and this leads to softening of the glass. This phenomenon can change the surface morphology of the coatings and cause a change in the pore structure and the arrangement of
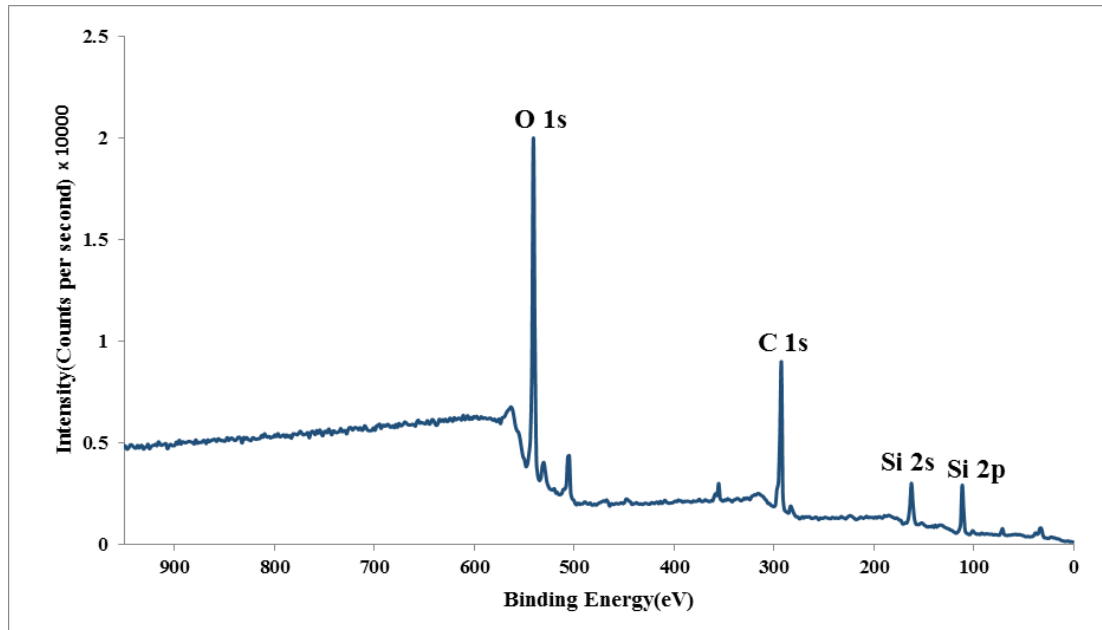
Fig. 4 XPS wide-scan spectra of the silica nano-porous thin film calcinated at 300 °C.
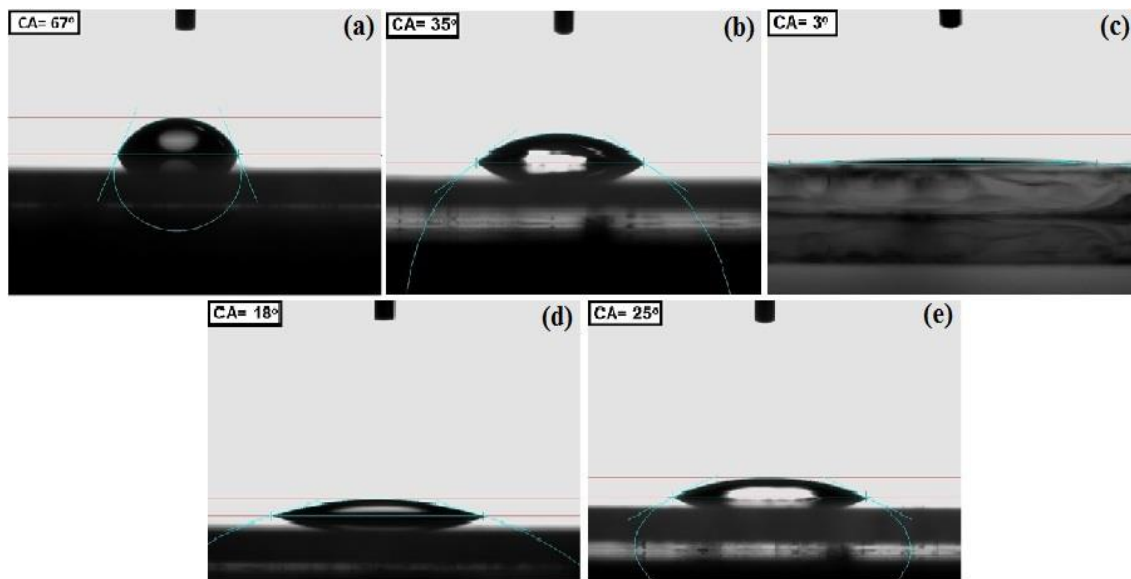

Fig. 5. Water contact angle on (a) glass and films calcinated at: b-200, c-300, d-400, e-500 °C.

silica nanoparticles in the thin film (see Fig. 2). In other words, by changing the surface morphology, the pore sizes in the thin films increase and possibly vanish during calcination which leads to non-wicking effect [27]. In addition, silica thin film calcinated at 200 °C revealed higher water contact angle than films calcinated at 300 °C. At this temperature, the organic components did not burn completely and nano-porous structures were

not formed. Thus, this film has a dense structure and could not decrease the contact angle in comparison to the nano-porous thin film obtained at 300 °C.

Indeed, silica thin film calcinated at 200 °C due to hydrophilic nature of organic component in the films showed lower contact angle in comparison of silica thin film calcinated at higher temperatures.

The three factors are silica nanoparticles. Silica

nano-particles with large surface area can adsorb water molecules and then hydroxyl groups on the film surfaces. These hydroxyl groups attract water molecules with hydrogen bonding and contribute to the rapid spreading [21]. By increasing calcination temperature, the silica nano-particle sizes increase and surface area decrease which has adverse effect on the hydrophilicity.

So, we can understand the reasons for the obtained different hydrophilicity in the glass coated silica nano-porous thin film calcinated at various temperatures.

In conclusion, the silica nanoporous thin film duo to its superhydrophilic and antireflection properties can be used as a transparent self-cleaning coating for solar cell and optical devises.

CONCLUSIONS

In this research, the effect of calcination temperatures on the hydrophilic properties of silica nano-porous thin films deposited on glass substrates was investigated. The results indicated:

1- Calcination temperature first decreased water contact angle of the glass coated silica nanoporous thin film and then increased it as the calcination temperature was increased.

2- The minimum water contact angle was obtained in the silica nano-porous thin film calcinated at 300 °C.

3- Silica nano-porous thin film calcinated at 300 °C can be act as a superhydrophilic and the antifogging thin film for glass substrates.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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