สำนักงานวิทยทรัพยากร จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER II

LITERATURE REVIEW

This chapter is devoted for not only review of some previous representative reports about methods of preparing transparent ZnO thin films, but also survey of information for improving photoinduced hydrophilic property of TiO_2 and ZnO thin films.

2.1 Methods of preparing transparent ZnO thin films

Gao et al. (2007) developed a novel solution method for the deposition of transparent ZnO film from aqueous solution, integrating the ultrasonic irradiation with the stepwise chemical deposition at relatively high temperature (>100°C). ZnO films exhibited high crystallinity, highly preferential orientation alone the *c*-axis, smooth and compact morphology. The transmittance spectra of ZnO films on glass substrate deposited with ultrasonic irradiation exhibit high transmittance (>80%) in the wavelength band of 200-800 nm.

GÜMÜŞ et al. (2006) studied polycrystalline ZnO thin films deposited on a glass substrate by a spray pyrolysis technique using solution of zine acetate and air as the carrier gas at 400°C. The films were found to exhibit high transmittance (>90%), low absorbance and low reflectance in the visible regions. The energy band gap, and the thickness of the films were evaluated as 3.27 eV and 0.31-0.52 μm respectively. The films were polycrystalline in nature with preferred (002) orientation perpendicular to substrate surface and the grain size estimated to be 40 nm.

Berber et al. (2005) synthesized dispersions of zinc oxide nanoparticles synthesized by the electrochemical deposition under oxidizing conditions process with organic surfactants were spin coated on glass substrates. After sintering, the microstructure, surface morphology, and electro-optical properties of the transparent

หอสมุดกลาง สำนักงานวิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

nanocrystalline zinc oxide films have been investigated for different coating thickness and organic solvents.

Li et al. (2005) found that ZnO films with preferred orientation along the (002) plane fabricated by the sol-gel method using a spin coating technique. The films were dried at 300°C and then postheated at 600°C shown the preferred (002) orientation of ZnO and high transmittance above 80% in the visible range. Also, SEM images of the films shown microstructure consisting of many round shaped particles for the films heated at 400°C and 500°C and hexagonal particles as the temperature increased to 600°C.

Armelao et al. (2001) studied semiconductor nanoclusters in thin coatings of transparent and homogeneous silica glasses for the development of optical devices. To achieve a good control over film composition and morphology the sol-gel route of ZnO nanocrystals embedded in silica has been faced by the study of gel-derived binary system $ZnO-SiO_2$. The dip coating procedure from alcoholic solutions containing tetraethoxysilane and zinc acetate was adopted. The synthesis of ZnO nanoclusters starting from solutions were not containing many additives to yield stable sols and to obtain homogeneous layers.

Ohyama, Kozaka and Yoko (1997) studied ZnO films with preferred orientation along the (002) plane fabricated by the sol-gel method using Zn $(CH_3COO)_2.2H_2O$ as starting material. A homogeneous and stable solution was prepared by dissolving the zinc acetate in a solution of 2-methoxyethanol and monoethanolamine. ZnO films highly oriented along the (002) plane were obtained by preheating the dip coating films at temperatures from 200-500°C for 10 min after each coating and postheating at temperatures from 500-800°C for 1h. The result was found that ZnO films prepared by repeating the dip coating (WS=3.5 cm/min) and preheat-treatment at 300°C three times and postheating at 500, 600 and 800°C, respectively. In all case the films were found to be transparent (above 70%) in the visible range with a shape absorption edge at wavelength of about 380 nm which is very close to the intrinsic band gap of ZnO (3.2eV).

2.2 Photoinduced hydrophilic property of TiO_2 and ZnO thin films

Fijishima, Rao and Tryk (1999) studied photocatalytic and superhydrophilic properties of TiO_2 semiconductor which it has a band gap energy about 3.2 eV. TiO_2 can be excited pairs of electrons and holes to discover superhydrophlic property after UV illumination. They described the electrons tend to reduce Ti (IV) cations to Ti (III) state and holes oxidize the O_2^- anions. In the process, oxygen atoms are ejected and created oxygen vacancies. Then the water molecules can occupy these oxygen vacancies and producing adsorbed OH groups which tend to the surface hydrophilic and show to the smaller contact angle of water approach zero.

Watanabe et al. (1999) studied photoinduced hydrophilic conversion evaluated on the different crystal faces of rutile single crystal and also polycrystalline anatase titanium dioxide. Contact angle measurements were performed to examine the surface wettability change TiO_2 upon UV illumination which three hours are sufficient to give rise to a highly hydrophilic surface for anatase. The (110) and (001) surface of rutile single crystal were illuminated to a highly hydrophilic surface for five hours. The wettability is greatly dependent on the existence of bridging site oxygen which the reactive bridging site oxygen tends to be oxidized by a photogenerated hole to produce an oxygen vacancy to react with the hole and water, resulting in a hydrophilic surface. However, the hydroxyl group generated on the surface is not stable and then this wettability results in slower hydrophilic conversion upon UV illumination and faster hydrophobic conversion.

Liu et al. (2002) prepared SnO_2-TiO_2 composite thin films that were fabricated on soda-lime glass with sol-gel technology. XRD spectra for powder and films of pure TiO_2 and composite are all of anatase that the average diameter of the composite is smaller than that of the latter. They studied the composite film with 1-5 mol% SnO_2 doping and heat-treatment temperature at 450°C improved the hydrophilicity with the contact angle of water as zero degree. And they can see that the contact angle decreased with the increasing in the film thickness.

Guan, Lu and Yin (2003) investigated the effect and the amount of SiO_2 addition on the photo-generated hydrophilicity of TiO_2 films. They found that addition of 40 mol% SiO_2 to TiO_2 is most effective for reducing the contact of water from 10° to 3° within 1 h UV irradiation. And the film can maintain in the dark for 24 h which the contact angle of the film increase very slowly.

Sharma et al. (2006) prepared pure and nickel doped TiO_2 thin films on soda glass substrates by sol-gel dip coating process. The films were annealed at 500°C for 1 h and observed crystalline peaks correspond to anatase TiO_2 phase. Both films are uniformity and exhibit spherical shape which the pure film has a particle of 40-50 nm, while TiO_2 thin film with 10 mol% Ni ions added has crystal whose particle size is 20-30 nm. The undoped films could be entirely wetted by water after 1 h UV illumination and the doped films become entired wetted after 20 min UV illumination.

Kontos et al. (2007) prepared nanocrystalline titania thin films by deposition and annealing of titania sol-gel precursor, both non-hydrate solutions and hydrosols. The sol gels were immobilized on glass substrates applying doctor blade and dip-coating techniques. The substrates coated with TiO_2 gels were calcined at 450°C for 60 min. Hydrosol with dip coating presents the best photoinduced superhydrophilicity and the water contact angle drops from about 14° to 4° within 180 min UV irradiation.

Sun et al. (2001) investigated the photoinduced surface wettability conversion reactions of ZnO and TiO_2 thin films preparing with spray pyrolysis method. Before ultraviolet illumination, ZnO and TiO_2 films exhibited water contact angles of ~109 and ~54°, respectively. UV illumination turned surface to highly hydrophilic with water contact angle was 5° after UV illumination for 1 h. Storage in the dark reconverted the highly hydrophilic films to their original states. Moreover, the surface wettability conversion reactions are dependent not only on illumination time but also on the light intensity. Both ZnO and TiO_2 are photosensitive oxide semiconductor with band gap energies of ~3.2 and ~3.0 eV, despite their different crystal structures (hexagonal wurtzite structure for ZnO and tetragonal structure for TiO_2).

Feng et al. (2003) synthesized the aligned ZnO nanorods via a two step solution. The wettability was evaluated by the water contact angle of 161.2±1.3°. Upon UV obtained from a 500 W Hg lamp with a filter centered at 365 nm irradiation for 2 h, the water contact angle of about 0°. After the UV irradiated films were placed in the dark for 7 days, the super-hydrophobicity of the nanorad films obtained again. This process has been repeated several times and good reversibility of the surface wettability.

Liu et al. (2004) studied reversible between superhyphobicity and superhydrophilicity of ZnO film that was fabricated by Au-catalyzed by chemical vapor deposition method. The surface of film exhibits hierarchical structure with nanostructures on sub-microstructures. The contact angle of water was 164.3° turning into superhydrophilic surface (CA < 5°) after UV illumination within 13 h.

Guo, Diao and Cai (2007) reported that a surface modification-induced hydrophilicity to superhydrophobicity transition on well-aligned single crystalline ZnO nanorod array films (ZnO-NAFs) that were prepared from solution by a hydrothermal method. The surface of transparent ZnO-NAFs was highly hydrophilic with a water contact angle of 9.6±0.8°. However, after being exposed to octadecanethiol solution, the surface of the ZnO-NAFs became superhydrophobic with a water contact angle of 156.2±1.8°.