طرق تحضير الأغشية الرقيقة (الافلام الرقيقة) لجزيئات النانو لثاني أكسيد التيتانيوم

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Methods of preparation nanoparticles TiO_2 Thin Film

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الملخص :

ظهرت الأغشية الرقيقة لجزيئات النانو لثاني أكسيد التيتانيوم العديد من الخصائص المثيرة للاهتمام والتي يمكن استغلالها في العديد من التطبيقات مثل المحفزات الضوئية, والخلية الشمسية الحساسة للأصبغة, وأجهزة استشعار الغار, والأجهزة الإلكترونية والطبقة العازلة في مستشعر مقياس الضغط الكهربائي, وهو أمر مهم جداً لتحقيق ودراسة خصائص كثافة التيار ثاني أكسيد التيتانيوم.

تناقش هذه الدراسة تطبيقات ثاني أكسيد التيتانيوم وتوضح طرق التحضير التي تسمح بالتحكم في الحجم والشكل ومعالجة السطح .

Abstract

Nanoparticles thin films of the titanium dioxide (TiO_2) exhibit many interesting properties that can be exploited in a variety of applications such as such as a Photocatalysts, Dye-sensitized solar cell, Gas sensors, Electronic devices and an insulator (buffer layer) in the dielectric bolometer sensor, which are very important to investigate and study the properties of its current density. This review discusses the applications and syntheses of titanium dioxide (TiO2) and outlines methods of preparation that allow control over the size, morphology, surface treatment.

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1 Introduction

1.1 TiO_2 nano-particles

Currently, TiO_2 nano-particles have created a new approach for remarkable applications as an attractive multi-functional material. TiO_2 nano-particles have unique properties such as higher stability, long lasting, safe and broad-spectrum anti-biosis. TiO_2 nano-particles have been especially the center of attention for their photo-catalytic activities. This makes TiO_2 nano-particles applicable in many fields such as self-cleaning, anti-bacterial agent, UV protecting agent, environmental purification, water and air purifier, gas sensors, and high efficient solar cell. The photo-activity property is strongly related to the structure, micro-structure and the powder purification (Weibel, et al 2013) .

Three famous crystalline structures for TiO_2 have been known as anatase (tetragonal, a = 0.3785 nm, c = 0.9514 nm, band gap = 3.2 eV which is equivalent to a wavelength of 388 nm), rutile (tetragonal, a = 0.4593 nm, c = 0.2959 nm, band gap = 3.02 eV) and brookite (orthorhombic, a = 0.9182 nm, b = 0.5456 nm, c = 0.5143 nm, band gap = 2.96 eV).

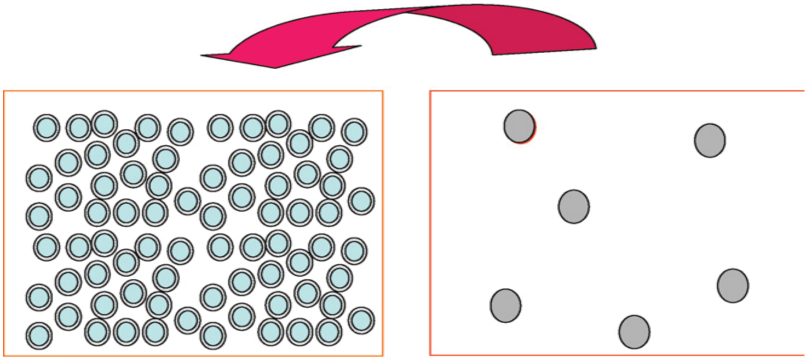

Fig. 1. Increasing the available nano-silver particles via surface coating of nanosilver on titanium dioxide (Dastjerdiet al 2008)

Titanium dioxide nano-particles have been used to achieve antibacterial, self-cleaning, UV-protection, hydrophilic or ultra-hydrophobic properties, dye degradation in textile effluent and as a nano-catalyst for cross-linking cellulose with poly carboxylic acids (Dastjerdi et.al.2008).

1.2 Titanium dioxide (TiO_2) Thin Film

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula TiO_2. When used as a pigment, it is called titanium white, Pigment White 6, or CI 77891. It is noteworthy for its wide range of applications, from paint to sunscreen to food colouring . Titanium dioxide (TiO_2) has been known for quite some time to afford oxidation of organic substances under illumination. This is due to the high oxidation potential of its valence band holes. Therefore, TiO_2 has become an interesting candidate as a catalyst for photochemical water (and air) purification. Other applications are in electronic and optical devices due to its electronic and optical properties. (Bokhimi et .al 2001)

Titanium dioxide (TiO_2) thin film is an n-type semiconductor, a very interesting applied material that has many useful electrical and optical properties, such as high refractive index, high dielectric permittivity, semiconductivity, and excellent transmittance of visible light, etc. These properties make them useful in many fields, as they are used for microelectronics, optical cells, solar energy con-version, highly efficient catalysts, microorganism photolysis, antifogging and self-cleaning coat, gratings. (Mmackenzie et al 2013).

Nanoparticle thin films of the titanium dioxide (TiO_2) have attracted growing interest due to their unique structure and properties. Many works recently have concentrated on the TiO_2 thin films due to their important applications in photo catalyst, dye-sensitized solar cell, gas sensor, and so on. Another applications, such as a dielectric material for electronic devices [4] and an insulator in dielectric bolometer sensor, which are very important to investigate and study the properties of its current density The Crystal structures of TiO2 Thin Films. (Efil et al 2009)

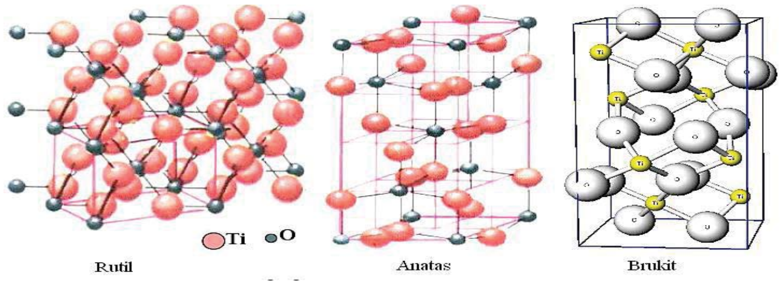

Fig.2 Crystal Structure of TiO_2

2. Applications Titanium dioxide (TiO_2)

2.1 Pigment

Titanium dioxide is the most widely used white pigment because of its brightness and very high refractive index (n = 2.7), in which it is surpassed only by a few other materials. Approximately 4 million tons of pigmentary TiO_2 are consumed annually worldwide. When deposited as a thin film, its refractive index and colour make it an excellent reflective optical coating for dielectric mirrors and some gemstones like "mystic fire topaz". TiO_2 is also an effective opacifier in powder form, where it is employed as a pigment to provide whiteness and opacity to products such as paints, coatings, plastics, papers, inks, foods, medicines (i.e. pills and tablets) as well as most toothpastes. In paint, it is often referred to offhandedly as "the perfect white", "the whitest white", or other similar terms. Opacity is improved by optimal sizing of the titanium dioxide particles. Used as a white food colouring, it has E number E171. Titanium dioxide is often used to whiten skimmed milk; this has been shown statistically to increase skimmed milk's palatability. (Hsing et.al 2010)

In cosmetic and skin care products, titanium dioxide is used as a pigment, sunscreen and a thickener. It is also used as a tattoo pigment and in styptic pencils. Titanium dioxide is produced in varying particle sizes, oil and water dispersable, and with varying coatings for the cosmetic industry. This pigment is used extensively in plastics and other applications for its UV resistant properties where it acts as a UV absorber, efficiently transforming destructive UV light energy into heat. In ceramic glazes titanium dioxide acts as an opacifier and seeds crystal formation. (Carp et.al 2007)

Titanium dioxide is found in almost every sunscreen with a physical blocker because of its high refractive index, its strong UV light absorbing capabilities and its resistance to discolouration under ultraviolet light. This advantage enhances its stability and ability to protect the skin from ultraviolet light. Sunscreens designed for infants or people with sensitive skin are often based on titanium dioxide and/or zinc oxide, as these mineral UV blockers are believed to cause less skin irritation than chemical UV absorber ingredients. The titanium dioxide particles used in sunscreens have to be coated with silica or alumina, because titanium dioxide creates radicals in the photocatalytic reaction. These radicals are carcinogenic, and could damage the skin. (Fu,G et.al 2015)

Titanium dioxide is used to mark the white lines on the tennis courts of the All England Lawn Tennis and Croquet Club, best known as the venue for the annual grand slam tennis tournament The Championships, Wimbledon.[18] The exterior of the Saturn V rocket was painted with titanium dioxide; this later allowed astronomers to determine that J002E3 was the S-IVB stage from Apollo 12 and not an asteroid. (Kime et al 2010)

2.2 Sunscreen and UV Absorber

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2.3 Photocatalyst

Titanium dioxide, particularly in the anatase form, is a photocatalyst under ultraviolet (UV) light. Recently it has been found that titanium dioxide, when spiked with nitrogen ions or doped with metal oxide like tungsten trioxide, is also a photocatalyst under either visible or UV light. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly. Titanium dioxide is thus added to paints, cements, windows, tiles, or other products for its sterilizing, deodorizing and anti-fouling properties and is used as a hydrolysis catalyst. It is also used in the Graetzel cell, a type of chemical solar cell. **(** Nasonova et al .2010)

The photocatalytic properties of titanium dioxide were discovered by Akira Fujishima in 1967and published in 1972. The process on the surface of the titanium dioxide was called the Honda-Fujishima effect. Titanium dioxide has potential for use in energy production: as a photocatalyst, it can

- Carry out hydrolysis; i.e., break water into hydrogen and oxygen. Were the hydrogen collected, it could be used as a fuel. The efficiency of this process can be greatly improved by doping the oxide with carbon.
- Titanium dioxide can also produce electricity when in nanoparticle form. Research suggests that by using these nanoparticles to form the pixels of a screen, they generate electricity when transparent and under

the influence of light. If subjected to electricity on the other hand, the nanoparticles blacken, forming the basic characteristics of a LCD screen. According to creator Zoran Radivojevic, Nokia has already built a functional 200-by-200-pixel monochromatic screen which is energetically self-sufficient.

In 1995 Fujishima and his group discovered the superhydrophilicity phenomenon for titanium dioxide coated glass exposed to sun light. This resulted in the development of self-cleaning glass and anti-fogging coatings. TiO_2 incorporated into outdoor building materials, such as paving stones in noxer blocks or paints, can substantially reduce concentrations of airborne pollutants such as volatile organic compounds and nitrogen oxides.

Aphotocatalytic cement that uses titanium dioxide as a primary component, produced by Italcementi Group, was included in Time's Top 50 Inventions of 2008.[23] TiO_2 offers great potential as an industrial technology for detoxification or remediation of wastewater due to several factors.

(a) The process occurs under ambient conditions very slowly; direct UV light exposure increases the rate of reaction.
(b) The formation of photocyclized intermediate products, unlike direct photolysis techniques, is avoided.
(c) Oxidation of the substrates to CO_2 is complete.
(d) The photocatalyst is inexpensive and has a high turnover.
(e) TiO_2 can be supported on suitable reactor substrates.

2.4 Other applications

It is also used in resistance-type lambda probes (a type of oxygen sensor). Titanium dioxide is what allows osseointegration between an artificial medical implant and bone. Titanium dioxide in solution or suspension can be used to cleave protein that contains the amino acid proline at the site where proline is present. This breakthrough in cost-effective protein splitting took place at Arizona State University in 2006.

Titanium dioxide on silica is being developed as a form of odor control in cat litter. The photocatalyst is vastly cheaper than silica beads per usage and effectively eliminates odor for longer. Titanium dioxide is also used as a material in the memristor, a new electronic circuit element. It can be employed for solar energy conversion based on dye, polymer, or quantum dot sensitized nanocrystalline TiO_2 solar cells using conjugated polymers as solid electrolytes.[26] It has also been recently incorporated as a photocatalyst into dental bleaching products. It allows the use of decreased concentrations of hydrogen peroxide in the bleaching agent, thus claimed to achieve similar bleaching effects with fewer side effects (e.g. transient sensitivity, change in tooth surface topography, etc.) It is also used by film and television companies as a substitute for snow when filming scenes which require a winter setting. Synthetic single crystals and films of TiO_2 are used as a semiconductor, and also in Bragg-stack style dielectric mirrors due to the high refractive index of TiO_2 (2.5 – 2.9).

3 The Preparation Techniques of NPs TiO_2 Thin Films

TiO_2 can be prepared in the form of powder, crystals, or thin films. Both powders and films can be built upfrom crystallites ranging from a few nanometers to several micrometers. It should be noted that nanosized crystallites tend to agglomerate. If separate nanosized particles are desired, often a deagglomeration step is necessary. Many novel methods lead to nanoparticles without an additional deagglomeration step.

Natural polymorphs of TiO_2 are known to exist as tetragonal rutile, anatase, and brookite. For small particle size (<35nm) anatase is more stable than brookite. The preparation technique of the NPs is also of crucial importance. TiO_2 thin films could be fabricated with several methods, including sol-gel technique, Electron Beam Evaporation, Plasma Chemical Vapor Deposition (PCVD), and DC Magnetron Sputtering. (Efil Yusrianto et al).

3.1 Preparation TiO_2 Thin Films by using Sol-Gel Spin Coating Methods

Sol–gel methods. These methods are used for the synthesis of thin films, powders, and membranes. Two types are known: the non-alkoxide and the alkoxide route. Depending on the synthetic approach used, oxides with different physical and chemical properties may be obtained. The sol–gel method has many advantages over other fabrication techniques such as. (MacKenzie, J.D 2003) purity, homogeneity, felicity, and flexibility in introducing dopants in large concentrations, stoichiometry control, ease of processing, control over the composition, and the ability to coat large and complex areas. In addition the process is simple and good homogeneity, the possibility of producing large surface and complex geometry and low processing temperature and low equipment cost. (X. Bokhimi et al 2010)

Experimental Procedures

P-type silicon (Si) substrates (12 mm x 20 mm x 1.2 mm) were used as the support substrates. It was carefully cleaned by ultrasonic clearer with acetone, methanol and distilled-water. Silicon dioxide and ruthenium (IV) oxide were deposited by electron-gun evaporation with thickness of 1500 Ǻ and 1000 Ǻ, respectively. SiO_2 thin films has been prepared onto Si substrate and used as an insulator to prevent charges injection from Si substrate to the bottom electrode (RuO_2). After that, TiO_2 thin films were prepared onto $RuO_2/SiO_2/Si$ substrate. Fig. 2. Shows the flow chart of the TiO_2 thin films preparation process. The sol-gel process consists of a precursor organometallic or suspension followed by hydrolysis and a condensation reaction resulting in the final spin coating. In this work we used titanium butoxide to make either amorphous, nanocrystalline or polycrystalline titanium dioxide films.

The hydrolysis and condensation of titanium butoxides proceeds according to the following scheme:

$$Ti(OC_4H_9)_4 + H_2O \rightarrow Ti(OC_4H_9)_3OH + C_4H_9OH \ : \text{Hydrolysis}$$

$$Ti(OC_4H_9)_4 + Ti(OC_4H_9)_3OH \rightarrow Ti_2O(OC_4H_9)_6 + C_4H_9OH \ : \text{Condensation}$$

$$Ti(OC_4H_9)_3OH + Ti(OC_4H_9)_3OHO \rightarrow TiO_2(OC_4H_9)_6 + H_2O \ : \text{Condensation of water}$$

Hydrolysis and condensation reaction for nanoparticle obtainable could be:

$$Ti(OC_4H_9)_4 + 4H_2O \xrightarrow{H^+} Ti(OH)_4 + 4C_4H_9OH$$

$$Ti(OH)_4 + Ti(OH)_4 \rightarrow Ti_2O(OH)_6 + H_2O$$

$$Ti_2O(OH)_6 \rightarrow 2TiO_2 + 3H_2O$$

Titanium butoxide (1.001 ml) was dissolved in ethanol (5.076 ml). After stirring vigorously for 6 hours at room temperature, the ion-free water (0.300 ml) and hydrochloric acid (0.432 ml) was added to the above solution during constant stirring. After that, the solution was vigorously stirred for an hour at room temperature. The obtained solution was transparent at room temperature. The chemical composition of starting but oxide solution was $Ti(OC_4H_9)_4$: C_2H_5OH: H_2O: Hal = 1:26.5:1:1 in molar ratio. Using a spin coater at 2500 rpm for 30 seconds, the solution was transferred onto substrates. The TiO_2 solution was transferred onto $RuO_2/SiO_2/Si$ for characterisation polymorphs, grain size, thickness and current density. All of the films were dried at 323 K in air for an hour to evaporate the solvent and the films were annealed at the temperature range of 573 to 823K with increasing temperature rate of 278 K/min for 30 minutes in furnace. X-ray diffraction was used for crystal phase identification and field emission scanning electron microscope (FE-SEM) was used to measure the grain size and thickness of the TiO_2 thin films. Before the measurement of the current density, aluminium (1000 Ǻ) layer which acts as a top electrode were deposited onto the samples by electron-gun evaporation. These give us the capacitor with configurations of $Al/TiO_2/RuO_2/SiO_2/Si$ (Fig. 2). Electrometer Model Keighley 2602 System SourceMeter was used to measure current density of the TiO_2 thin films, respectively.

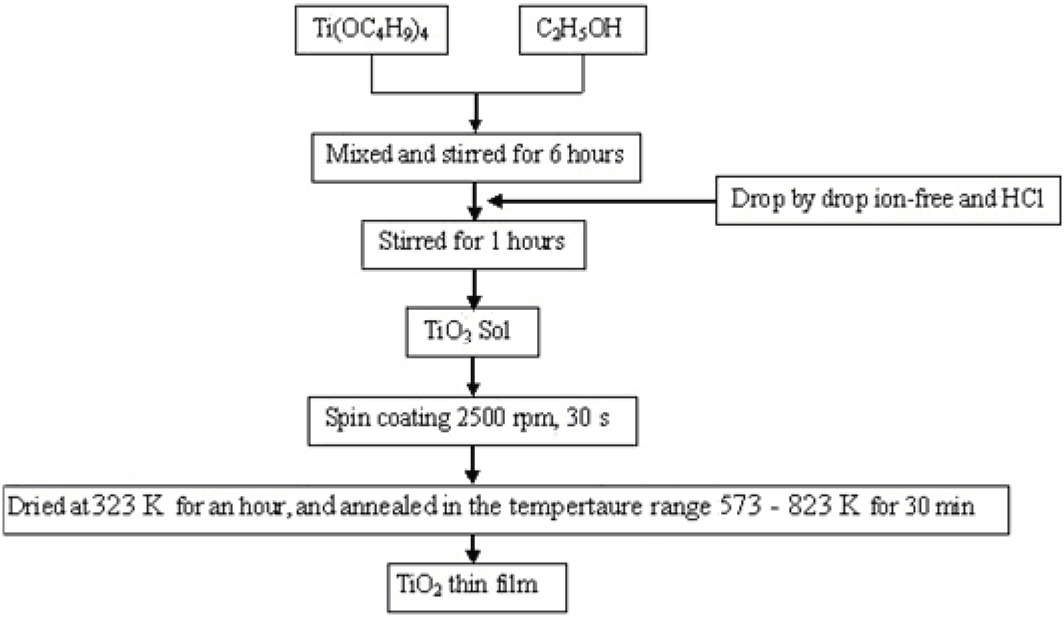

Fig. 2.1.1 the process of fabrication of nanoparticle TiO_2 thin films

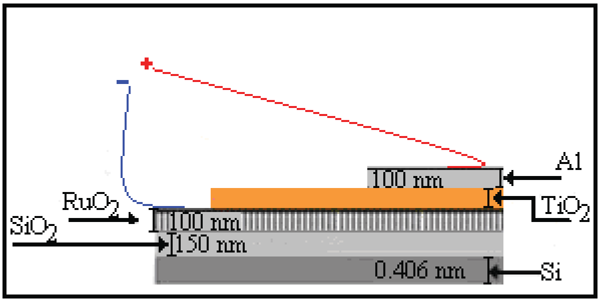

Fig. 2 The thin film capacitor structure

The sol-gel method was introduced in this study along with a summary of its inherent advantages. The fundamental chemical reactions in the sol-gel process were performed. The mechanisms of hydrolysis and condensation, and the factors that bias the structure toward linear or branched structures are the most critical issues of sol-gel science and technology.

The sol-gel method of anatase TiO_2 fabrication is simple, and low cost. It can yield high uniformity and fine particle size of the catalyst. This method can be operated at room temperature and is easy to control (Efil et al.2009) (-Hsing et al. 2010).

3.2 Preparation of TiO_2 Thin Film by using Electron Beam Evaporation

Electron Beam Evaporation has alto of advances such as the deposition rate in this process can be as low as 1 nm per minute to as high as few micrometers per minute. The material utilization efficiency is high relative to other methods and the process offers structural and morphological control of films. Due to the very high deposition rate, this process has potential industrial application for wear resistant and thermal barrier coatings in aerospace industries, hard coatings for cutting and tool industries, and electronic and optical films for semiconductor industries.

Another unusual technique is dynamic ion beam mixing, which uses high-energy O_2 and/or O+ beams and Ti vapour to deposit TiO_2 films with high speed and control over the composition. Although these methods have the merit to control the film growth and the feasibility to obtain pure materials, they are energy intensive and involve high temperatures.

Thus, techniques for film processing should also be developed in view of economical aspects.

Experimental Procedures

The TiO_2 films under study were prepared in the electron-beam evaporation system assembled by Branchy Vacuum Technology Co., Ltd (Toayuan, Taiwan). A schematic diagram of the system is shown in Fig. 2. The distance between the rotating substrate holder and the electron-beam evaporation source was 550 mm. The chamber was evacuated by a mechanical pump (ALCATEL-2033SD) and a cryopump (CTI-Cryo-Torr8_). The films were deposited in oxygen atmosphere using rutile TiO_2 (99.99%) as a source material. The base pressure is $4.0 * 10^{-6}$ Torr ($5.3 \cdot *10^{-4}$ Pa), and the working pressure is increased to $0.5–2.0 * 10-^{4}$ Torr various flow rates is supplied to the chamber at a constant pumping speed. The series of the films are assigned to A, B, C, D, and E samples corresponding to the O_2 pressure at 0 (without O2 sup- ply), $0.5 *10^{-4}$, $1.0 * 10^{-4}$, $1.5 * ^{-4}$ and $2.0 \cdot 10^{-4}$ Torr, respectively. The substrates used are polished Si (100) or quartz wafers, which were sputteretched with argon ions (Ar) for 5 min prior to the deposition to remove any residual pollutants on the surface. The substrate temperature was maintained at 250^{o}C by quartz lamp. The deposition rate was adjusted to 0.2nms^{-1} by quartz crystal monitor to deposit a thickness about 1.2 lm for all of the films (Yang et al 2004).

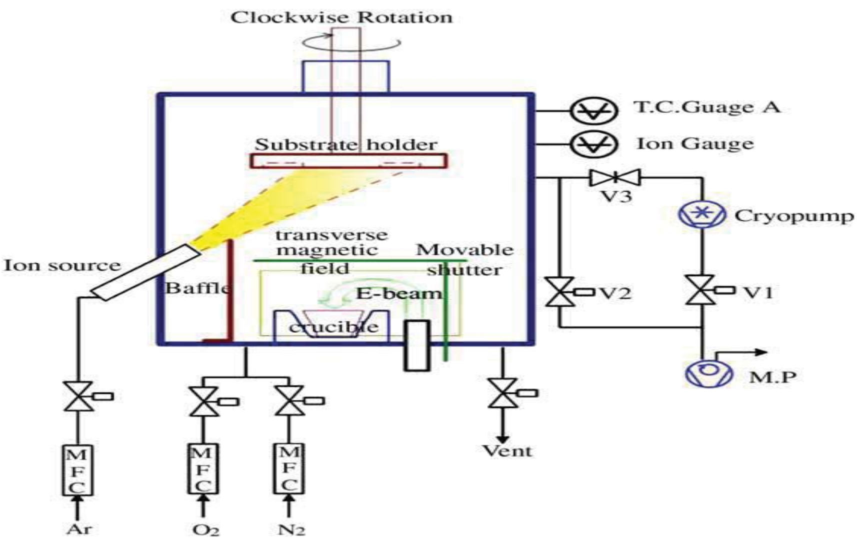

Fig. 2.2. Schematic diagram of the e-beam evaporation system (Tien-Syh Yang et al ,2004)

3.3 Preparation TiO_2 Thin Films by using Plasma Chemical Vapor Deposition

Plasma Chemical Vapor Deposition (PCVD) reactor has been widely used to prepare uniform thin films for semiconductor fabrication and can also is used to coat thin films on particles uniformly. Also PCVD has several advantages, such as easy scaleup , high throughput, relatively low cost, and short process time. Chemical vapour deposition (CVD) is a widely used versatile technique to coat large surface areas in a short span of time. In industry, this technique is often employed in a continuous process to produce ceramic and semiconductor films. The family of CVD is extensive and split out according to differences in activation method, pressure, and precursors. Compounds, ranging from metals to composite oxides, are formed from a chemical reaction or decomposition of a precursor in the gas phase. (Nasonova et al .2010)

Experimental

TiO_2 thin films were coated on glass beads of 3 mm diameter by using a rotating cylindrical PCVD reactor as shown in Fig. 2.3. The inner diameter and the length of the cylindrical quartz reactor are 55 mm and 280 mm, respectively. A mechanical rotary vane pump was used for evacuation of the gas stream from the reactor. We used an ultrasonic nebulizer to supply TTIP (Aldrich, 97%) as a source of Ti into the plasma reactor. TTIP mists were made by the ultrasonic nebulizer at 40 ^oC and were supplied into the plasma reactor with N_2 carrier gas during deposition onto the particles. To calculate the flow rate of TTIP, we measured the weight difference of TTIP between before turn-on and after turn-off of the ultrasonic nebulizer by electronic balance with 0.01 g readability. The flow rate of TTIP was controlled by changing the power of the ultrasonic nebulizer. The feed line for TTIP was heated to help the evaporation of TTIP droplets and also to prevent condensation of TTIP. O_2 was supplied to the reactor separately from TTIP to prevent reaction between O_2 and TTIP in the feed line. The flow rates of all gases were controlled by mass flow controllers (MFC). A water-cooled spiralshape coil electrode is located outside the cylindrical reactor to rotate the plasma reactor independently. RF power of 13.56 MHz frequency was applied to the electrode to generate inductively coupled plasmas in the cylindrical reactor. The volume of plasmas in the cylindrical plasma reactor is 2661 cm^3 and, for the maximum applied power of 30 W, the power density in the reactor is calculated to be 0.01 W/cm3. The precursors for the TiO2 thin films were generated from TTIP by plasma reactions in the gas phase. The rotation speed of the cylindrical quartz reactor was controlled by a DC motor.

The precursors of the TiO_2 thin films deposited on the glass beads contain some carbon and hydrogen compounds. After coating the glass beads with TiO_2 thin films for various process conditions, we heated the glass beads at 500°C for 1 h to remove the carbon and hydrogen compounds. Dastjerdi, et al 2010)[4]

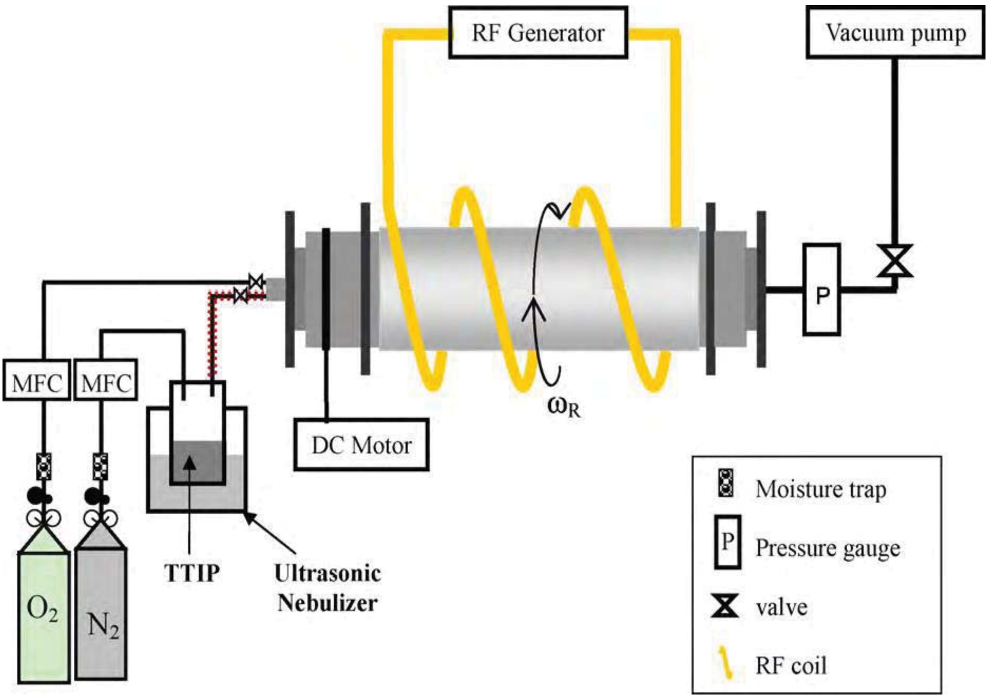

Fig. 2.3. Schematic diagram of experiment talsetupforcoatingof TiO_2 thin films on glass beads by PCVD process

3.4 Preparation TiO_2 Thin Films by using DC Magnetron Sputtering

NPs are synthesized by making use of reactive direct-current (DC) magnetron sputtering. This well-known deposition technique is currently applied in industry for the elaboration of titanium dioxide (TiO_2) thin films and does not suffer of the limitations of the other methods. In fact, when associated with appropriate process control, as for example, a closed loop control system for high speed adjustment of a reactive gas, reactive DC magnetron sputtering is very interesting for industrial applications because metal targets are used, the stoichiometry is controllable, the environment is respected and large scale production is possible. Weibel., et al 2013[12]

Experiment

The TiO_2 NPs were deposited on carbon-coated copper transmission electron microscopy grids (C grids) by reactive DC magnetron sputtering with the substrate at ground potential. The distance between the target and substrate was 15 cm and the temperature of the substrate was maintained around 400°C throughout the deposition process. The base pressure in the plasma chamber was 10−4 Pa, maintained by a 300 l/min turbo pump (vessel size: 0.05m3). The titanium target (99.9 %, diameter 5 cm) was sputtered with plasma (14 W/cm2) of argon (99.99%, flow rate=0.18 slpm) at 10 Pa. Reactive oxygen (99.99%) was introduced between the plasma and the substrate. It is well known that a poisoning effect occurs with DC plasma, resulting in a hysteresis effect as a function of the oxygen flow. Without reactive gas, the system remains in metallic mode and only Ti atoms are deposited on the substrate. When the oxygen flow is higher than a critical value, the poisoning effect is established and the Ti target is covered by an oxide layer. As a consequence, the deposition rate drastically decreases while the target voltage increases. As is well known, the compound deposited is titanium dioxide when the oxygen flow rate is higher than this critical value. For our TiO_2 layers, the plasma was stabilized between these two modes at the end of the transition region by regulating the oxygen flow at 3 10−3 slpm with a feedback at the cathode voltage (O_2/Ar partial pressure ratio: 1.7% assuming the same pumping speed for both gases).

With the aforementioned process parameters, the deposition rate, inferred by masking half of a glass cover slip and measuring the deposited step for 120 min deposition duration, was estimated by profilometry at (6±1) nm/min. The samples discussed here were produced at two deposition times: 40 s and 210 s. Yang, et al 2004[13]

4. Conclusion

Substantial progress has been made in the synthesis of TiO_2 thin films for applications in nanotechnology and biotechnology. Methods have been developed that offer control over the size, size distribution, shape, crystal structure, defect distribution and surface structure. Among the methods reviewed, continuous supercritical sol-gel technique synthesis probably offers the most promise for process control and scalability. Furthermore, this method is environmentally benign and does not involve the use of toxic solvents or surfactants. Surface treatment of nanoparticles, however, will require additional steps in this method. A major challenge for all methods is the design of magnetic nanoparticles with effective surface coatings that provide optimum performance in vitro and in vivo biological applications. Additional challenges include scale-up, toxicity, and safety of large-scale particle production processes. Substantial progress has been made in the synthesis TiO_2 thin films.

REFERENCES

Bokhimi, X.A., Morales, M., Aguilar, J.A. & Antonio, F. 2001.Pedraza, Local order in titania polymorphs, *International Journal of Hydrogen Energy* **26**:1279–1287.

Carp,O., Huisman,C.L & Reller, A. 2007. Photoinduced reactivity of titanium dioxide. *Progress in Solid State Chemistry* **32**: 33–177.

Dastjerdi,R .& Montazer, M. 2010. A review on the application of inorganic nano-structured materials in the modification of textiles: Focus on anti-microbial properties. *Colloids and Surfaces B: Biointerfaces* **79**: 5–18.

Dastjerdi,R., Mojtahedi,M.R .& Shoshtari, A.M.2010. Investigating the effect of various blend ratios of prepared masterbatch containing Ag/TiO2 nanocomposite on the properties of bioactive continuous filament yarns, *Fibers and Polymers* **9**: 727–734.

Efil, Y., Noor Baa'yah, I., Zahari, I. 2009. Characterizations of TiO_2 Thin Films Nanoparticles Prepared by Sol-Gel Spin Coating Methods, *Proceedings ASEAN-INDIA Workshop and Annual Meeting on Surface Engineering II – 2009,* (CD), Bandung, Indonesia.

Fu, G., Vary, P& Lin,C.T . 2015. Anatase TiO2 nanocomposites for antimicrobial coatings, *Journal of Physical Chemistry* **109**: 8889–8898.

Hsing Lin,C., Lee, J., Chang,C., Chang,Y., Lee,Y.& Hwa,M. **2010 .**Novel TiO2 thin films/glass fiber photocatalytic reactors in the removal of bioaerosols. *Surface & Coatings Technology*.

Kim,D.J., Kang,J.Y .& Kim,K.S.2010. Preparation of TiO_2 thin films on glass beads by a rotating plasma reactor . *Advanced Powder Technology* **21**: 136-140.

MacKenzie, J.D.2013. Sol-gel research – achievements since 1981 and prospects for the Future. *J. Sol Gel Sci. Techn* **26:**23–27.

Masudaa,Y., Sugiyamaa,T., Linb,H., W. Seoa,W.S .& Koumotoa,K. 2010 Selective deposition and micropatterning of titanium dioxide thin film on self-assembled monolayers .*Thin Solid Films* **38**:153_157.

Nasonova,A., Pham,H.C., Kim, D. J .& Kim,K.X.2010. NO and SO_2 removal in non-thermal plasma reactor packed with glass beads-TiO_2 thin film coated by PCVD process . *Chemical Engineering Journal* **156**: 557-561.

Weibel,A., Bouchet,R .& Knauth,P.2013. Electrical properties and defect chemistry of anatase (TiO_2). *Solid State Ionics* **177**: 229–236.

Yang, T. Shiu,C .& Wong.C. 2004. Structure and hydrophilicity of titanium oxide films prepared by electron beam evaporation. *Surface Science* **548**:75–82.