# 論 文 内 容 の 要 旨

Metal oxide gas sensors have been widely applied in various fields. Among the different types of metal oxide gas sensors, metal oxide thin-film gas sensors have attracted considerable interest, as they readily facilitate integration and miniaturization in structure. In addition, such thin-film gas sensors have higher sensitivity and shorter response time than thick film-type metal oxide gas sensors.

Recently, titanium dioxide ($TiO_2$) thin films have been investigated as a promising sensing material for application in various thin-film reducing gas sensors due to their outstanding sensing properties, chemical stability and electrical properties.

$TiO_2$ naturally crystallizes in three phases, which were known as rutile, anatase and brookite. The thermal stability of brookite phase $TiO_2$ is poorer than anatase phase and rutile phase $TiO_2$, which limits the application of brookite phase $TiO_2$. In addition, brookite is the most difficult $TiO_2$ phase to fabricate in thin-film form. Compared with rutile phase $TiO_2$ films, anatase phase $TiO_2$ has greater sensitivity to $H_2$ and volatile organic compound gases than rutile phase $TiO_2$.

Hitherto, anatase phase $TiO_2$ thin films have been synthesized by various techniques, including magnetron sputtering, high-vacuum chemical vapor deposition, atomic layer deposition, electron beam evaporation, and sol-gel method. However, it is still strict issue to obtain pure anatase phase $TiO_2$ with good uniformity, high thermal stability and high crystallinity using current synthesis methods. Firstly, the $TiO_2$ thin films obtained by these methods are mostly a mixture of anatase and rutile phase $TiO_2$. Although there are some reports on fabricating pure anatase phase $TiO_2$ films, their thermal stability is poor due to the presence of (112) surface in anatase phase $TiO_2$, which limits the application of anatase phase $TiO_2$ films as sensing material. Particularly, it is difficult to fabricate anatase phase $TiO_2$ thin films with good crystallinity by spray pyrolysis, conventional chemical vapor deposition, atomic layer deposition or high vacuum chemical vapor deposition. When these methods are applied with a low deposition temperature (not higher than 350 ˚C), the deposition of anatase phased $TiO_2$ film is kinetically controlled, which means the growth of anatase phased $TiO_2$ film is limited by low decomposition rate of precursor. As a result, the crystallinity of obtained $TiO_2$ film is poor. When deposition temperature is increased, the deposition will become controlled by mass transport, and the growth of anatase phased $TiO_2$ film is limited by the lack of precursor, resulting in a poor thickness uniformity of deposited $TiO_2$ film.

In order to fabricate pure anatase phase $TiO_2$ film with good uniformity and high crystallinity, it is necessary to develop a novel synthesis method. According to our previous research experience, we found the mist chemical vapor deposition is a suitable method to synthesize metal oxide thin film, by which the growth orientation, uniformity and grain size of thin film could be precisely controlled. Therefore, mist chemical vapor deposition is expected to an alternative method to synthesize pure anatase phase $TiO_2$ thin films.

In this thesis, a mist chemical vapor deposition system with novel designed reaction chamber was applied to deposit pure anatase phase $TiO_2$ thin films. In order to enhance the surface area of $TiO_2$, $TiO_2$ films were coated onto ZnO nanorods to fabricate ZnO/$TiO_2$ core-shell nanostructures.

Until now, there are still strict issues on anatase phase $TiO_2$ based thin-film gas sensors:

**(1)** The fabricated $TiO_2$ is mostly a mixture of rutile phase and anatase phase. The fabrication of pure anatase phase $TiO_2$ is difficult.

**(2)** The properties of anatase phase $TiO_2$ (including uniformity, surface area and crystallinity) are still low, which limited the performance of gas sensor.

**(3)** Due to the high surface energy, the {001} facets of anatase phase $TiO_2$ could significantly enhanced the gas sensitivity. However, it was difficult to enhance the growth of {001} facets.

**(4)** The working temperatures of gas sensors are still high (over 200 °C).

**(5)** The response time and recovery time of gas sensors are too long.

**(6)** The cost of some methods for gas sensors fabrication is relatively high, such as RF sputtering and ALD method.

**(7)** The thermal stability of anatase phase $TiO_2$ based thin-film gas sensors are poor.

**(8)** The sensitivity to some gases ($H_2$, methanol) are still low.

In my research, some of the above issues were solved. The detail was shown as following:

**(1)** Pure anatase phase $TiO_2$ was successfully fabricated by mist chemical vapor deposition method.

**(2)** The obtained pure anatase phase $TiO_2$ showed excellent uniformity, high crystallinity and relative high surface area.

**(3)** The growth of the anatase phase $TiO_2$ {001} facets was significantly enhanced by using a methanol system.

**(4)** Pure anatase phase $TiO_2$ based gas sensor could be fabricated by mist chemical vapor deposition with a low cost.

**(5)** The obtained anatase phase $TiO_2$ showed an ultra-high thermal stability.

**Academic novelty or originality of the research**

**(1)** Pure anatase phase $TiO_2$ films were fabricated by mist CVD method for the first time.

**(2)** The mechanism of fabricating anatase phase $TiO_2$ films from TTIP by mist CVD was investigated for the first time. Base on the calculation and investigation, the fabricating mechanism of $TiO_2$ films deposited from 300 °C to 400 °C was confirmed as the pyrolysis of TTIP.

**(3)** The methanol system was found to be a new method to effectively enhance the growth of {001} facets of pure anatase phase $TiO_2$.

The main work will be discussed in terms of fabrication of anatase phase $TiO_2$ thin films with ethanol system, fabrication of anatase phase $TiO_2$ thin films with methanol system, and fabrication of ZnO nanorods and ZnO/$TiO_2$ core-shell nanorods.

## 1. Fabrication of anatase phase $TiO_2$ thin films with ethanol system

$TiO_2$ thin film has attracted considerable interest as a promising sensing material with potential applicability for various thin-film gas sensors due to its outstanding sensing properties, chemical stability and electrical properties. In this part, pure anatase phase $TiO_2$ films were fabricated with ethanol system by mist chemical vapor deposition. The effects of deposition temperature, concentration of titanium tetraisopropoxide, film thickness and substrate on the properties of $TiO_2$ films were investigated.

The crystallinities of $TiO_2$ films were significantly improved by increasing deposition temperature. Pure anatase phase $TiO_2$ films with good uniformity were obtained from 300 °C to 400 °C. The roughnesses of all $TiO_2$ films were less than 7 nm and showed a variation tendency of increase as the deposition temperature increased from 200 °C to 400 °C.

When the titanium tetraisopropoxide concentration increased from 0.05 mol/L to 0.40 mol/L, the aspect ratio of $TiO_2$ nanosheets first increased then decreased. The highest aspect ratio of $TiO_2$ nanosheets was obtained at a titanium tetraisopropoxide concentration of 0.20 mol/L. The deposition rate of $TiO_2$ films had the same variation tendency with aspect ratio. The roughnesses of all $TiO_2$ films were less than 10 nm regardless of titanium tetraisopropoxide concentration variation. The crystallinity of $TiO_2$ films showed a variation tendency of increase as the titanium tetraisopropoxide concentration increased from 0.05 mol/L to 0.40 mol/L. The best crystallinity was obtained under the titanium tetraisopropoxide concentration of 0.05 mol/L. From the XPS results, the highest binding energies of $TiO_2$ films were also obtained at a titanium tetraisopropoxide concentration of 0.05 mol/L.

The crystallinity of $TiO_2$ films increases with the increasing of film thickness. The transmittance of all $TiO_2$ films is more than 75% in the visible region and almost independent of film thicknesses. The surface of obtained $TiO_2$ films with different thickness are uniform. With the thickness increasing, the roughness of $TiO_2$ film shows tendency of increase.

The $TiO_2$ films deposited on all substrates showed the same dominant (101) growth orientation. The crystallinity of $TiO_2$ films grown on different substrates increased in an order of glass, quartz glass, p-type silicon and gallium oxide doped ZnO. It was confirmed by Raman spectroscopy that $TiO_2$ films deposited on four kinds of substrates were pure anatase phase, which was in a good agreement with the GIXRD result. The $TiO_2$ thin film deposited on p-type silicon showed the highest percentage of exposed {001} facets. The $TiO_2$ films with good uniformity were obtained on all of the substrates. The surface area of $TiO_2$ films deposited on p-type silicon substrate was larger than that of $TiO_2$ films deposited on quartz glass, glass and gallium oxide doped ZnO substrates. The precise control of the growth orientation, uniformity and grain size of thin film were achieved. The transmittance of $TiO_2$ films on quartz glass, glass and gallium oxide doped ZnO substrates was higher than 75% in the visible region. The $TiO_2$ film deposited on p-type silicon is expected to have higher gas sensitivity and be applicable to thin film gas sensors.

## 2. Fabrication of anatase phase $TiO_2$ thin films with methanol system

Compared with ethanol, methanol is much easier to atomize ultrasonically. The deposition rate of $TiO_2$ thin films will be more controllable by using methanol as solvent. However, the titanium tetraisopropoxide is not stable in pure methanol. Recently, we obtained a stable mixture of titanium tetraisopropoxide and methanol by adding acetylacetone as stabilizer.

Until now, the growth of preferred {001} facets could be controlled by only a few methods. Among these approaches, the $F^-$ ion methods were mostly used to enhance the growth of {001} facets because $F^-$ could be strongly absorbed on {001} facets. However, $F^-$ is a dangerous ion which is corrosive to the fabrication equipment and harmful to human skin. Compared with the use of $F^-$, we found that changing the water-to-methanol ratio is a safer method to control the growth of {001} facets.

In this part, pure anatase phase $TiO_2$ films were fabricated on aluminum oxide doped ZnO and glass substrates with methanol system by mist chemical vapor deposition. The effects of film thickness and water-to-methanol ratio on the properties of $TiO_2$ films were investigated.

Uniform $TiO_2$ films with different thickness were obtained. With the thickness increasing, the roughness and crystallinity of $TiO_2$ film showed tendency of increase. The of $TiO_2$ films increases with the increasing of film thickness. With the thickness increasing, the transmittance of $TiO_2$ films decreased from around 80 % to around 65 % gradually.

During the deposition, the growth of {001} facets and surface area were significantly influenced by the water-to-methanol ratio. By decreasing the water-to-methanol ratio, the growth of {001} facets was enhanced, while the growth of {101} facets was suppressed. The surface roughness and surface area of $TiO_2$ films showed the same trend of increasing with a decrease of the water-to-methanol ratio. The highest surface roughness and maximized surface area was obtained with a water-to-methanol of 0 %. The transmittance of all $TiO_2$ films was higher than 70 % in the visible region. The photocatalytic efficiency of TiO2 film showed an increasing trend with the decrease of the water-to-methanol ratio. The TiO2 film deposited with a water-to-methanol of 0 % showed the highest photocatalytic efficiency due to a maximum number of {001} facets and an optimum surface area, which has high potential for photocatalyst applications.

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### 3. Fabrication of ZnO nanorods and ZnO/$TiO_2$ core-shell nanorods.

In this part, well-arrayed ZnO nanorods and well-arrayed ZnO/$TiO_2$ core-shell nanorods were fabricated on conductive aluminum oxide doped ZnO films. The effects of solution concentration and deposition time on the properties of ZnO nanorods were investigated. The effects of $TiO_2$ film coating time on the properties of ZnO/$TiO_2$ core-shell nanorods were investigated.

The solution concentration had a significant influence on the morphological, structural, and optical properties of ZnO nanorods. It was found that well-arrayed ZnO nanorods with hexagonal structure were obtained with solution concentration from 100 % to 40 %. With the decreasing of solution concentration, the crystallinity of ZnO nanorods showed a tendency of decrease, and the transmittance of ZnO nanorods increased gradually in visible range. Oxygen vacancies and oxygen interstitials of ZnO nanorods was confirmed by the PL measurement.

The morphological, structural and optical properties of ZnO nanorods were significantly influenced by the deposition time. Well-arrayed ZnO nanorods with hexagonal structure were obtained with with deposition time of 5 hours and 10 hours. With the deposition time increasing from 5 hours to 10 hours, the crystallinity of ZnO nanorods increased significantly, and the transmittance of ZnO nanorods in the visible region decreased from around 75 % to around 35 %.

The $TiO_2$ shells on ZnO nanorods were confirmed as pure anatase phase, which will contribute to high chemical stability as photoanodes. The surface area of ZnO nanorods was significantly increased with increase in $TiO_2$ coating time. The transmittance of ZnO nanorods decreased from 75 % to 65 % after 15 minutes coating $TiO_2$. The well-arrayed ZnO/$TiO_2$ core-shell nanorods will contribute to a high transmittance (around 70 %), a higher electron transfer, an excellent chemical stability, and relatively large surface area for dye absorption, which are expected to applied as sensing material to improve the performance of gas sensors.