Nanostructured TiO_2 films deposited by MOCVD on Si-substrates

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INTRODUCTION

Titanium dioxide is a material with applications in many fields. It is used as catalyst, as photocatalyst, as gas sensor, as pigment, in electrical, optical and optoelectrical applications, etc. Often nanostructured materials have superior properties as compared to bulk. Chemical vapour deposition (CVD) has been found to be a versatile method for depositing thin films. In the deposition of TiO_2 many different precursors has been used, for instance $TiCl_4$ and titanium alkoxides. The alkoxides has been preferred as the deposition process can be carried out at lower temperatures and no chlorine contamination is incorporated. Titanium tetraisopropoxide, TTIP ($Ti(OC_3H_7)_4$) has been used in many studies. It has been shown that using TTIP no extra oxygen is needed to acquire a stoichiometric TiO_2 film (1).

EXPERIMENTAL

TiO_2 films and particles were prepared in a chemical vapour synthesis reaction using titanium tetraisopropoxide, TTIP, $Ti(OC_3H_7)_4$ (99.999%, Aldrich Chemical co.) as precursor. The decomposition of TTIP took place in a flow reactor.

The precursor was delivered to the furnace by bubbling nitrogen gas through the liquid. In order to increase the vapour pressure the bubbler was immersed in a thermal bath held at 60°C. The tube from the bubbler to the furnace was heated with heating tape to 120°C to prevent the precursor vapour from condensing. The temperature of the furnace was set to 700°C.

TiO_2 was deposited on Si-substrates at different locations both in and downstream of the furnace. Prior to the deposition the substrates were washed with ethanol.

The morphology and the thickness of the deposited TiO_2 films were analysed using a Leo Gemini 982 Scanning Electron Microscope (SEM). Analysis of the size and the shape of the particles exiting the reactor was done using a Philips CM-200 Transmission Electron Microscope (TEM). The SEM samples were analysed as-deposited.

RESULTS

Close to the inlet, at 20 cm, the deposit has a leaf-like structure. At 30 cm and 45 cm from the inlet the deposits consists of particles and CVD deposited TiO_2. These deposits are deposited by particle-aided chemical vapour deposition.

At distances of 60 and 90 cm from the inlet of the reactor the TTIP vapour is already consumed and particles have formed. The particles deposit via diffusion. However, as the wall is still warmer than the gas, thermophoresis drives the particles away from the wall and only particles with a high enough diffusion velocity will deposit. This makes the particles deposited nearly monodisperse. A SEM image of the deposit at 90 cm from the inlet of the furnace is presented in figure 1. We can see that the deposit consisted of separate nearly monodisperse particles. Size analysis of the deposited particles was done using the Digital Micrograph software. The mean diameter of the deposited particles was 14.4 nm.

Downstream of the furnace TiO_2 particles were deposited via thermophoresis. The deposit consisted of agglomerated particles, with a primary particle size of about 20 nm in diameter. From the TEM image it was seen that the particles are agglomerated with a primary particle size of 15-20 nm.

CONCLUSIONS

With the presented experimental set-up very diverse deposits were prepared depending on the deposition conditions. Closer to the inlet of the furnace the deposit was fairly dense and closer to the outlet a monolayer of nearly monodisperse 15 nm particles was deposited. Downstream of the reactor the deposit consists of loosely attached agglomerated particles with a primary particle size of 15-20 nm. The primary particle size can be modified by varying the amount of TTIP vapour and the furnace temperature.

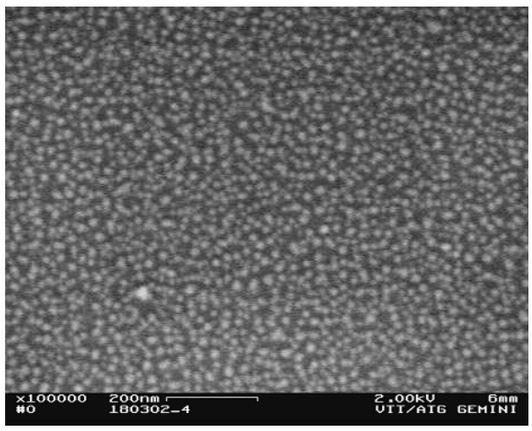

Figure 1: SEM image of deposit at 90 cm from the inlet of the reactor.

REFERENCES

1. P. Babelon, A.S. Dequiedt, H. Mostéfa-Sba, S. Bourgeois, P. Sibillot and M. Sacilotti, *Thin Solid Films,* **322**, 63 (1998)