Materials Science in Semiconductor Processing 87 (2018) 44–53

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Ultra-thin TiO_2 films by atomic layer deposition and surface functionalization with Au nanodots for sensing applications

Oleg Lupan[a,b,*], Vasile Postica[b], Nicolai Ababii[b], Tim Reimer[c,d], Sindu Shree[a], Mathias Hoppe[a], Oleksandr Polonskyi[e], Victor Sontea[b], Steffen Chemnitz[d], Franz Faupel[e], Rainer Adelung[a]

[a] Institute for Materials Science, Faculty of Engineering, Chair for Functional Nanomaterials, Kiel University, Kaiserstr. 2, D-24143 Kiel, Germany
[b] Department of Microelectronics and Biomedical Engineering, Technical University of Moldova, 168 Stefan cel Mare Av., MD-2004 Chisinau, Republic of Moldova
[c] Fraunhofer Institute for Silicon Technologies, (ISIT), Fraunhoferstr. 1, D-25524 Itzehoe, Germany
[d] Institute of Electrical Engineering and Information Technology, Faculty of Engineering, Kiel University, Kaiserstr. 2, D-24143 Kiel, Germany
[e] Chair for Multicomponent Materials, Institute for Materials Science, Faculty of Engineering, Kiel University, Kaiserstr. 2, D-24143 Kiel, Germany

ARTICLE INFO

Keywords:
TiO_2
Ultra-thin films
Atomic layer deposition
Gas sensor
UV photodetector

ABSTRACT

The massive application requests for high-performance sensors indicate on the importance of precise controlling of the semiconducting oxide characteristics. The sensor longevity needed for the remote areas in harsh environments is mandatory and can benefit greatly from self-cleaning abilities. To serve this demand, we present in our work ultra-thin TiO_2 films deposited with different thicknesses down to 15 nm on glass substrates using atomic layer deposition (ALD). The morphological, chemical, topographic, electronic and chemical properties of the fabricated films were investigated in detail, showing the presence of the anatase phase. As it is known by the literature, the UV and gas sensing properties are highly dependent on the thickness of the films, however fully reversible and capable of long term detection. Thinner films (15 nm) showed higher UV and gas sensing performances than thicker films (45 nm), which was related to the film thickness comparable to the Debye length. Further improvement in the UV sensing properties was achieved by surface functionalization of TiO_2 films with Au nanoparticles. The UV response increased by about one order of magnitude after the surface functionalization with Au nanoclusters/nanoparticles. All TiO_2 ultra-thin films demonstrated good selectivity to hydrogen gas, independent of the thickness. The samples with 15 nm thickness showed a response of ~ 600% to 100 ppm of H_2 at 250 °C operating temperature. The presented study demonstrates the importance of the film thickness and surface functionalization with noble metals nanoclusters for sensing applications of ultra-thin TiO_2 layers. Such ultra-thin films could be used for the development of a series of integrated detectors and chemical field effect transistors (chemFETs) directly on highly complex chips.

1. Introduction

A wide range of metal oxides thin films grown by atomic layer deposition (ALD), as well as core-shell structures are used for sensing applications, including UV and gas sensing [1,2]. Uniform layers made by ALD were reported to improve the photo-electrochemical properties of sensing devices [3,4], sensors [5] and act as a scaffold for sensors [6], etc. It is an enabling technology for the manipulation of the high surface area of TiO_2 nanotubes and its physical interaction with the main sensor material [5]. ALD is an attractive and powerful technique due to the possibility to precisely control the thickness of the films down to values comparable to the Debye length (from sub-nanometer to a few or to several tens of nanometers) and to cover various shapes of substrates [1]. In this case the sensing properties are maximized due to the involvement of the entire active region of material in the sensing process and more precise control of current flow through it, which is very beneficial for UV and gas sensing applications [1,7,8]. For example, Du and George observed for SnO_2 ALD films, that the gas response to CO gas is maximized for a film thickness comparable to the Debye length (2.62 nm) [8]. Also, in this case the local modification of the electron depletion layer on film surface can be easily performed by surface engineering [1,7,9], which can greatly improve the sensing properties [10,11]. The utilization of ultrathin ALD films for gas sensing was also reported earlier [12,13].

In this context, the functionalization with noble metal nanoparticles (e.g. Ag, Au, etc) of ultra-thin TiO_2 films produced by ALD for sensing applications were less reported [1,14]. Although, TiO_2 as a wide bandgap *n*-type semiconductor has been extensively studied in many

* Corresponding author at: Institute for Materials Science, Kiel University, Germany.
E-mail addresses: ollu@tf.uni-kiel.de, oleg.lupan@mib.utm.md (O. Lupan).

https://doi.org/10.1016/j.mssp.2018.06.031
Received 30 January 2018; Received in revised form 26 June 2018; Accepted 29 June 2018

fields, such as UV photodetectors and gas sensors, especially TiO_2 nanotubes [15], in particular Au-functionalized TiO_2 films as sensors were not reported in literature to the best of our knowledge. For example, Kim et al. reported the synthesis of ultrasensitive chemiresistors based on highly ordered TiO_2 nanotubes [16]. TiO_2 nanotubes and films are generally known to be the highly selective hydrogen gas sensors with high sensitivity [17–19]. A H_2 selective sensor based on individual TiO_2 nanotubes able to operate at room temperature was reported earlier [20]. Lee et al. reported a template-assisted approach coupled with ALD for the synthesis of TiO_2 nanotubes for selective detection of hydrogen gas [17]. Kumar et al. reported hydrogen gas sensing at room temperature using a Pd-nanoparticles (NPs)-decorated TiO_2 film with a thickness of ~ 5 nm deposited by the ALD technique [21]. Kim et al. have grown thin films of brookite TiO_2 with 80 nm thickness on a yttria-stabilized zirconia substrate by ALD for room temperature H_2 gas sensing [22].

Semiconducting oxides, in particular TiO_2, functionalized with dispersed Au nanodots are of great interest due to their extraordinary high activity for catalytic combustion, reduction of nitrogen oxides and their increase of photocatalytic performances especially under UV irradiation [23,24]. It was reported previously that the catalytic performances of small Au particles strongly depends on the support and the preparation procedure, as well as its sizes [23,25,26]. Besides, Au - TiO_2 interactions may affect the activity of such nanoparticles as catalysts [26]. It is therefore a stringent necessity to further investigate and understand the sensor behavior of Au-functionalized TiO_2 ultra-thin film based devices, since it can be further extended to highly complex shaped substrates or structures.

In this work, the anatase TiO_2 ultra-thin films with a thickness of only 15 nm were grown using ALD. Au-functionalization of the ultra-thin films allows tailoring of the microstructural, electrical and sensing performances. The morphological, micro-Raman, AFM, and electronic-chemical properties were investigated, as well as UV and gas sensing properties revealing that thinner films have higher sensing characteristics due to a thickness comparable with the Debye length.

2. Experimental part

TiO_2 ultra-thin films with different thicknesses were deposited via an atomic layer deposition in a Picosun R-200 series atomic layer deposition reactor [27]. Standard microscope glass slides (76 mm × 26 mm, Thermo Scientific) were used as substrates, which were pre-cleaned by wiping them carefully with acetone and a lint-free paper towel. The ALD chamber was maintained at a temperature of 300 °C. After pumping to a pressure of ~ 0.1 hPa, the ALD reactor chamber was allowed to re-heat to 300 °C. The TiO_2 films were deposited by alternating pulses of $TiCl_4$ and H_2O, with equal pulse lengths of 0.2 s, and purge times of 5 s for $TiCl_4$ and 7 s for H_2O [27]. The lines were purged with N_2 flow. The total deposition time for one cycle sums up to 12.4 s. The growth per cycle was calculated to be ~ 0.045 nm. In this study the film thicknesses were varied from 15 nm (340 cycles) to 45 nm (1020 cycles).

After TiO_2 ALD deposition, the ultra-thin coated samples were processed by thermal annealing (TA) at 450, 600 and 625 °C for 2 h in normal atmosphere and were denoted as TA450, TA600 and TA625, respectively. The functionalization with Au dots was performed using a custom built gas flow sputter machine. The Au sputter target was bought from EvoChem (diameter: 2 in., purity: 4 N). The pressure after sample lock in was in the range of $1 \cdot 10^{-6}$ mbar. During the deposition, the Argon gas (6 N) flow was set to 15 sccm leading to a chamber pressure of $2.5 \cdot 10^{-3}$ mbar. The deposition time was 1 s, the DC Magnetron Power was set to 50 W. The chamber and sample were at room temperature at all times, neither additional heating nor cooling was used.

The morphological characterization were performed with SEM at 5 kV as was described previously [28]. As well as, the topographic properties of the thin films were studied under AFM. An AFM analysis in tapping mode (cantilever description: spring constant 2 N/m and resonance frequency ~ 70 kHz) of this Au-functionalized TiO_2 films was performed on a 2 μm × 2 μm area. X-ray photoelectron spectroscopy (XPS) characterizations were performed on the thin films as was described previously [28]. Micro-Raman spectra were recorded at 20 °C on a Raman WITec Alpha300 RA spectrometer in a backscattering configuration, with a triple grating spectrometer (600 gr/mm) and interfaced with a digital photometer and data acquisition monitor processor. A 532 nm line from Nd-YAG laser was used for off-resonance excitation with maximum power was 52 mW. The instrument was calibrated to the same accuracy using a silicon standard. The electrical resistivity, UV and gas sensing properties were performed as described in previous papers [28,29]. Vapors of ethanol, ammonia and methanol as well as hydrogen gas were used as target gases to investigate the gas sensing capabilities of the newly developed devices. The concentration of the target gasses ranged from 100 to 1000 ppm and was calculated based on the volume fraction of the test chamber and the densities of the liquid reagents [30,31]. For the sensing studies the sensors were mounted in a test chamber at the required operating temperature for 30 min before exposition to the designated gases to stabilize the electrical baseline. By monitoring the output voltage across the ultra-thin film-based sensor, the conductance was measured in air and under the test gas atmosphere by using a Keithley 2400. The sensor response and recovery times are calculated as the time to reach and recover 90% of the total values, respectively.

3. Results and discussions

3.1. Morphology

Fig. 1a and b show the SEM images at low and high magnification of a TiO_2 film annealed at 450 °C, respectively. The uniformly 15 nm thick film completely and continuously covers the glass substrate without the formation of agglomerations. Also the homogeneous granular surface is visible. The grains correspond to small aggregates of nano-microcrystalites depicted by SEM. The grain size was measured to be in the range of 20–200 nm (see Fig. S1a). No evident differences between films annealed TA at 450 °C and treated by rapid thermal annealing (RTA) at 450 °C for 120 s were observed (see Fig. S2a–b, Fig. 1b versus Fig. S2c). The SEM images of Au-functionalized TiO_2 films is presented in Fig. 1c–d and S2d. The Au NPs are well dispersed on the surface of the TiO_2 grains, the diameter of such nanoparticles is in the range of 5–11 nm (see Fig. S1b). Fig. S3a–b shows the SEM images of TiO_2 films produced by ALD with a thickness of 30 nm thermally annealed at 450 °C, at low magnification and at high magnification, respectively. It can be seen that the 30 nm thick films completely cover the glass substrate, is quite uniformly deposited, but formed grains, which is highly beneficial for sensor applications [31,32]. SEM images of TiO_2 films produced by ALD with a thickness of 45 nm thermally annealed at 450 °C for pristine and Au-functionalized samples are depicted in Fig. S3c–d, respectively. It can be concluded that the films are more densely packed in this case.

The AFM analysis of the Au-functionalized 30 nm TiO_2 film in Fig. 2 shows the uniform granular structure of the TiO_2 layer. The grain size is in the range of 20–200 nm and the average surface roughness was calculated to be ~ 3.11 nm.

3.2. XPS investigations

The electronic chemical composition of the Au-functionalized TiO_2 films (with 15 nm thickness) was determined using XPS analysis. Charge correction of the obtained spectra was done using aliphatic carbon at 285.0 eV as a reference. Fig. 3a shows the survey XPS spectrum of an Au-functionalized TiO_2 ultra-thin film. The spectrum indicates on the presence of only titanium (19.8%), oxygen (47.2%), gold