Review article

44Ti self-diffusion in nanocrystalline thin TiO2 films produced by a low temperature wet chemical process

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ARTICLE INFO

ABSTRACT

Grain boundary self-diffusion of titanium in nanocrystalline TiO2 films is investigated in an extended temperature interval by the radiotracer technique applying the 44Ti isotope. The diffusion annealing treatments are performed at low and high oxygen partial pressures. At low oxygen partial pressure Ti grain boundary self-diffusion follows an Arrhenius type temperature dependence with the pre-exponential factor of 7.25×10^{-12} m^2/s and the activation enthalpy of 74.7 kJ mol^{-1}. At high oxygen partial pressure Ti diffusion follows an Arrhenius type temperature dependence below 773 K and changes drastically the behavior above 773 K indicating a possible grain boundary structure transition.

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Titanium dioxide TiO2 is a well-known photo catalyst and is widely used in the production of self-cleaning materials, hydrogen generation by water splitting [1–4] and in water purification [1,5,6] due to its corrosion resistance in aqueous environments. Recently, research has been focused on various nanocrystalline and nanostructured TiO2 materials [7,8]. Doping is widely used to modify the chemical composition and the properties of TiO2. A deviation from the non-stoichiometric composition of TiO2 and a related defect disorder change the electronic structure and, therefore, the catalytic properties and energy absorption parameters [9,10]. The doping procedures frequently include the diffusion of atoms into TiO2. Therefore, the knowledge of diffusion coefficients, especially in nanocrystalline TiO2 is important for the processing of well-defined TiO2-based materials.

Hoshino et al. [11] studied the self-diffusion of 44Ti in single crystalline TiO2. Unfortunately, grain boundary diffusion of Ti in TiO2 was not measured so far, which prohibits any estimates of Ti diffusion in nanocrystalline TiO2. This task is the main goal of the present investigation.

It is important to underline that the radiotracer technique using the 44Ti isotope is the only way to measure Ti self-diffusion in view of the absence of any suitable stable Ti isotope which could be used in combination with a secondary ion mass-spectrometry.

In the present study, nanocrystalline thin TiO2 films were deposited using a novel "liquid ceramic" method. This method has been developed by the research team of Prof. A.A. Myatiev (NATU MISiS, Moscow, Russia) for the manufacturing of nanocrystalline powders and for the deposition of single- and multi-component oxide films through pyrolytic decomposition from organic precursors containing salts of metals and carbon acids, such as the butanoic acid [12–15]. Via this approach, the films can be deposited on various substrates. The deposited films are dense, non-porous, nanostructured, uniform, and non-textured. The chemical components in multicomponent films are distributed uniformly [16,17]. This technology is extremely flexible. It allows synthesizing oxides of various compositions, particularly nanograined oxides containing a high amount of grain boundaries what is preferable for solid oxide catalysts [18].

The nanocrystalline TiO2 multilayer thin films were deposited on a polycrystalline Pt substrate. For the microstructure characterization, 20 thin TiO2 layers of the total thickness of about 600 nm were consequently deposited on the Pt substrate which was kept at 400 °C on a heating plate in air atmosphere. One specimen was annealed at 800 °C for 24 h for structure stabilization to mimic the samples used for the diffusion measurements. Another specimen was annealed first at 800 °C for 24 h and then at 200 °C for 500 h. The second specimen mimics the longest diffusion annealing treatment used in the present study and is used to follow possible changes of the TiO2 thin film microstructure.

The crystalline structure of TiO2 films was studied by X-ray diffraction (XRD) using a Siemens diffractometer D5000 with a Cu K$_{\alpha1}$

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radiation. After stabilization annealing treatment at 800 °C for 24 h, the diffraction patterns revealed only the peaks corresponding to the rutile phase of TiO$_2$ and the Pt substrate.

The microstructure was examined by transmission electron microscopy (TEM) using a Zeiss Libra 200FE field-emission microscope at the accelerating voltage of 200 kV. Cross-section samples were prepared. The Pt foil with the deposited TiO$_2$ films were glued together between two copper half-cylinders and glued into a steel tube. After that the samples were cut into discs, grinded and polished using a Gatan Dimple Grinder and ion etched with an Ar ion beam using a Gatan's Precision Ion Polishing System.

To study ^{44}Ti self-diffusion in nanocrystalline TiO$_2$, a film consisting of 100 layers was deposited onto a sapphire substrate. A total thickness of at least 3 μm was produced to keep the diffusion length of the ^{44}Ti isotopes smaller than the film thickness. The TiO$_2$ layers were deposited at 400 °C on a heating plate in air atmosphere. The samples were annealed at 800 °C for 24 h in air atmosphere that resulted in a stable nanocrystalline structure. The roughness of the produced multilayer TiO$_2$ films was investigated using an atomic force microscope and found to be <10–20 nm.

The ^{44}Ti radioactive isotope (half-live of 49 years, 68 and 78 keV γ-decays) was available as a HCl solution. The original radiotracer solution was highly dissolved in a double-distilled water. The specific radioactivity of the solution was about 700 Bq/μl. Ten microlitres of the solution were dropped on the prepared specimen surface and dried in air. Subsequently, the samples were sealed in quartz ampoules either evacuated to 1 Pa pressure (residual pressure of oxygen, p$_{O2}$, at 5×10^{-1} Pa) and filled with 3×10^4 Pa purified Ar or evacuated and then again filled with air up to 3×10^4 Pa (p$_{O2}$ at 2×10^4 Pa). Then the samples were annealed. After annealing the abundant tracer was removed from the surface by means of cleaning in acetone.

The diffusion profiles were determined by ion-beam sputtering using Ar ions. The sputter facility, for details see Ref. [19], used a beam current of 20 mA, beam voltage of 1000 V and an acceleration voltage of 200 V. The mass difference before and after the sputtering was used to calculate the section thickness and, correspondingly, the diffusion depth. The relative specific activity of each section was measured in a well-type intrinsic Ge γ-detector equipped by a multi-channel energy analyzer. The tracer concentration in a section is proportional to the area of the peak with background subtracted divided by the section mass.

Fig. 1(a) shows a dark field TEM micrograph of an as prepared nanocrystalline TiO$_2$ film. The film is dense and pore- or crack-free. The subsequently deposited individual layers, being parallel to the free surface, cannot be visually distinguished in the microstructure. This fact substantiates that the film has a uniform structure regardless of the number of deposited layers. The grains are equiaxial and have a size of 10–20 nm. The diffraction pattern shows that the film is fully crystalline, does not contain any amorphous phase and has no macro texture.

Fig. 1(b) represents a bright field TEM micrograph of the nanocrystalline TiO$_2$ film after stabilization annealing at 800 °C for 24 h. The grains are equiaxed. The obvious grain growths lead to an average grain size of 100 nm. The bright regions in the film appeared during the sample preparation for TEM (some of the grains were etched out). Fig. 1(c) shows a bright field TEM micrograph of the nanocrystalline TiO$_2$ film after stabilization at 800 °C for 24 h and subsequent annealing at 200 °C for 500 h. The second annealing, which mimics the longest diffusion annealing in the present study, documents no visible structure changes. Thus, the grain structure is stable even during the longest diffusion annealing and potential grain growth does not affect the diffusion process.

It is crucial that both, bulk and GB diffusion fluxes are generally to be taken into account to analyze the tracer distribution in a polycrystalline solid [20]. Three kinetic regimes of GB diffusion, the so-called A-, B- and C-type regimes were introduced by Harrison [21]. In the case of the A-type kinetic regime the diffusion length in the crystalline bulk, $\sqrt{D_v t}$, is significantly larger than the grain size and the diffusing particles travel along several grain boundaries and grains (here D_v is the volume diffusion coefficient and t is the diffusion time). This regime corresponds typically to high temperatures, long diffusion times and/or relatively small grain size [22]. As the analysis below will show, the B- and C-type regimes are relevant for the present experiments. In the B-type kinetic regime the volume diffusion length is smaller than the grain size, but is still significantly larger than the grain boundary width δ [20]. This regime corresponds typically to moderate temperatures and the trace leakage from grain boundaries into the crystalline bulk dominates the resulting tracer distribution. The C-type kinetic regime corresponds to the lowest temperatures and/or shortest annealing times when the bulk diffusion depth is less than the grain boundary width, thereby the resulting tracer distribution is given by the grain boundary diffusion only.

The GB diffusion kinetic conditions are defined by the value of the parameter α, which can be exactly determined in the case of self-diffusion, and is given by

$$\alpha = \frac{\delta}{2\sqrt{D_v t}} \tag{1}$$

The diffusional grain boundary width δ was measured for Ni$_2$O as $\delta = 0.5$ nm [23]. In fact, the same value is reported in the majority of direct grain boundary diffusion measurements, for a recent reference see, e.g., [24].

The values of α > 1 correspond to Harrison's C-type kinetics [25]. The tracer atoms diffuse only along the GBs. Thus the GB diffusion coefficient can be determined as

$$D_{\text{gb}} = \frac{1}{4t} \left(-\frac{\partial \ln \bar{c}}{\partial y^2} \right)^{-1} \tag{2}$$
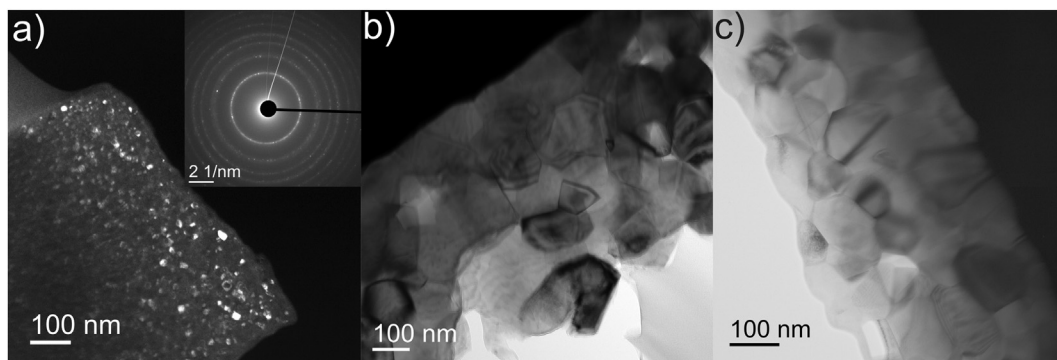

Fig. 1. Cross-section TEM micrographs of a) as prepared nanocrystalline TiO$_2$ films, b) after stabilization annealing at 800 °C for 24 h and c) after stabilization and diffusion annealing at 800 °C for 24 h + 200 °C for 500 h.