Applied Surface Science 255 (2009) 5240–5244

Contents lists available at ScienceDirect

Applied Surface Science

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

RHEED study of titanium dioxide with pulsed laser deposition

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ARTICLE INFO

Article history:
Available online 26 September 2008

Keywords:
RHEED
PLD
TiO_2

ABSTRACT

Reflection high-energy electron diffraction (RHEED) operated at high pressure has been used to monitor the growth of thin films of titanium dioxide (TiO_2) on (1 0 0) magnesium oxide (MgO) substrates by pulsed laser deposition (PLD). The deposition is performed with a synthetic rutile TiO_2 target at low fluence. The topography and structure of the deposited layers are characterized using *in situ* high pressure RHEED and atomic force microscope (AFM). Based on these observations the growth mode of the films is discussed. The results will be compared to earlier results obtained for the growth of TiN films on (1 0 0) MgO.

1. Introduction

Titanium dioxide has been studied considerably due to both physical and chemical properties of the material. The material has a wide range of technological application possibilities owing to its dielectric, electrochemical, photocatalytic and optical properties [1]. The three TiO_2 phases; anatase, rutile and brookite, also give a scientific interest, since they exhibit different properties, stabilities and growth modes [2].

Investigations of TiO_2 growth modes by combined RHEED and PLD setups have been conducted prior to this work [3,4], but with substrates other than MgO, i.e. with $SrTiO_3$ and TiO_2 substrates. Other groups have studied deposition of TiO_2 on MgO [5,6], but not by the combined use of PLD and RHEED. To our knowledge no previous RHEED investigations of the TiO_2 growth mode on MgO deposited by PLD have been conducted so far.

Another titanium compound, titanium nitride (TiN), is often utilized as industrial tribological coatings for improving the cutting performance and wear resistance of tools. This industrialized deployment of TiN is due to the very high hardness and chemical stability of the material [7]. The present growth study of TiO_2 is part of a work, which is investigating the possibility of an optically monitoring system consisting of tribological TiN on top of an optical TiO_2 layer. TiO_2 is usually not utilized as a tribological coating, but the refractive index is significantly different from that of TiN. This means that the thickness of a thin, residual layer of tribological TiN (on top of an optical TiO_2 layer) exposed to a wear process can be determined optically, if the refractive index of all materials is known in advance [8].

The lattice mismatch of *a*-axis constants between MgO and rutile or anatase TiO_2 is considerable. The mismatch between rutile and anatase TiO_2 and the substrate is 9.2 and 9.9%, respectively. The lattice mismatch between brookite and MgO is 119%. This does not make TiO_2 and MgO a good match regarding film growth. Our previous studies of TiN on MgO [9] and our optical monitoring system with TiN and TiO_2 [8] lead us, nevertheless, to choose MgO as a substrate in this TiO_2 study.

Here we present a study of the initial growth stages of TiO_2 on single crystal MgO deposited by PLD from a TiO_2 target. The change in surface structure during the complete growth process was monitored with *in situ* high pressure RHEED [10].

2. Experimental

Thin films of TiO_2 have been deposited in the large-area PLD facility at Risø National Laboratory for Sustainable Energy [11]. The films were grown in an ultra high vacuum chamber with a base pressure of 10^{-7} Pa. A disc-shaped synthetic rutile TiO_2 target from Williams Advanced Materials was irradiated with 20 ns laser pulses from a KrF excimer laser at 248 nm with a fluence of 0.5–1 J/cm^2 and a frequency of 1 Hz. The films were grown on disc-shaped substrates ($\varnothing$ = 25.4 mm) of single crystal periclase (1 0 0) MgO. Prior to the film growth the substrates were annealed at 1050 °C for 5 h with a ramp of 100 °C/h from 0 to 900 °C followed by a ramp of 50 °C/h from 900 to 1050 °C [12]. The crystals were subsequently cooled down reversely with the same temperature ramp. The substrates were thermally annealed in a 100% oxygen atmosphere during the complete process. The material ablated from the TiO_2 target was collected on the substrate, which was kept at a constant

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doi:10.1016/j.apsusc.2008.09.041

temperature level of 700 °C and located 88 mm from the target. An oxygen background pressure of 10 Pa was introduced in the vacuum chamber during the deposition.

A high pressure RHEED system was applied to observe the film growth *in situ*. Typical parameters for the RHEED system were electron energy of 35 keV and a beam current of 1 μA. The diffracted RHEED patterns were collected on a fluorescent screen and observed with a CCD camera. The recorded movies were subsequently analyzed by the use of the commercial software KSA 400. A combination of SEM and the program CASINO [13] was used to estimate the film thickness. The energy dispersive X-ray (EDX) signals from Ti in the deposited film and Mg of the substrate were measured and compared with Monte Carlo simulations of electron trajectories from CASINO in both the film and substrate, such that a layer thickness could be obtained, and thereby the film growth rate. The morphology and surface structure of the deposited films were investigated with a DIVIE SPM atomic force microscope after film deposition. Analysis of the AFM images gave additional information on the height and roughness of the film surfaces.

3. Results

A RHEED pattern from an MgO (1 0 0) single-crystalline substrate recorded prior to film deposition (see Fig. 1a) is slightly asymmetric and shows long vertical streaks, which is characteristics of a smooth surface. The corresponding AFM scan from the MgO (1 0 0) substrate surface is shown in Fig. 1b, where the substrate sample prior to deposition and AFM measurement was thermally annealed and directly measured afterwards. The root mean square deviation roughness (RMS) of the substrate surface was found by the DualScope (tm) software to be ~7 nm, which is higher than expected, although we have used an identical heat treatment procedure as described in [12]. The relative high surface roughness could be due to the comparatively short annealing time, e.g. see [9]. This means that the surface as observed by AFM is not as smooth, as we would have expected from the observation of the RHEED image (Fig. 1a), which indicates a smooth surface.

A series of *in situ* RHEED patterns taken from the film surface at different times (a) 300 s, (b) 400 s, (c) 500 s and (d) 600 s is shown in Fig. 2a–d. The vertical sharp streaky pattern from the substrate observed in the RHEED image (Fig. 1a) disappeared gradually until the average film thickness exceeds around 0.03 nm (after 300 s). After 300 s the diffraction streaks from the substrate shift into an elongated spotty-shaped appearance (see Fig. 2a–b). New spots also started appearing after ~450 s and turned clearly visible after 600 s (Fig. 2d). The appearance of these diffraction spots are round and almost but not regular streaks.

A gradual transformation from the streaky patterns into elongated spotty-shaped patterns is seen within the first few hundred seconds of deposition. This indicates that the film growth proceeds through a three-dimensional island-like growth mode with a relatively rough surface. It is well known that a 2D growth regime is associated with streaky RHEED patterns, due to reflection diffraction on a smooth surface. A 3D growth is characterized by spotty patterns, due to transmission diffraction through 3D islands [14]. A transition from 2D to 3D growth could, nevertheless, not be observed from the intensity of the specular spot. An analysis of the recorded RHEED pattern showed an overall decrease in the intensity of the specular spot (see Fig. 2e). The decrease is occurring fast during the first 100 s. This is followed by almost stagnation during the subsequent 500 s, after which a more rapid decrease is seen. The intensity of the specular spot shows no sign of oscillations associated with layer-by-layer (2D) growth. The deposition of a 0.1 nm film (1200 s) gave rise to the RHEED diffraction pattern presented in Fig. 3a, where the appearance is similar to that of Fig. 2d (600 s). The pattern possesses typical 3D diffraction features indicating the growth of 3D islands. The interpretation given in the RHEED schematics (Fig. 3b) for a TiO_2 film corresponds to the following orientation relationships: rutile TiO_2(1 0 0) || MgO(1 0 0).

The topography of the film surfaces has been investigated with AFM for different deposition times (see Fig. 1b and 4). These images correspond to the thin films leading to the RHEED patterns of Fig. 2d and 3a. The AFM images of Fig. 4 have been obtained after (a) 600 s and (b) 1200 s. The images give the impression of an almost uniform film growth, where valleys and gorges of the substrate are filled during the PLD, since the MgO substrate contour (Fig. 1b) is seen to get more blurred for longer deposition periods and since the surfaces (Fig. 4) appear to get smoother for longer deposition periods. The surface height (see Fig. 5a) has been evaluated directly from the AFM images (Fig. 1b and 4), i.e. at the initial stage of the deposition (0 s, blue diamonds) and after 600 s (red triangles) and 1200 s (green squares). The roughness of the surface is changing during the deposition. The evaluated surface is initially rather rough (0 s), then smoothing out (600 s) and finally getting slightly rougher again after 1200 s. It should be noted that the surface after 1200 s of deposition is not even as rough or structured as the naked MgO substrate.

A combination of the program CASINO and measured EDX signals from both film and substrate has been used to deduce the layer thickness of a film deposited for 7200 s with a 40 Hz repetition rate of the laser. The EDX signals were obtained during 120 s of measuring at 15 different positions across the film surface to get good statistics on the film thickness evaluation. The average film thickness was estimated to be ~25 nm. This leads to a fairly

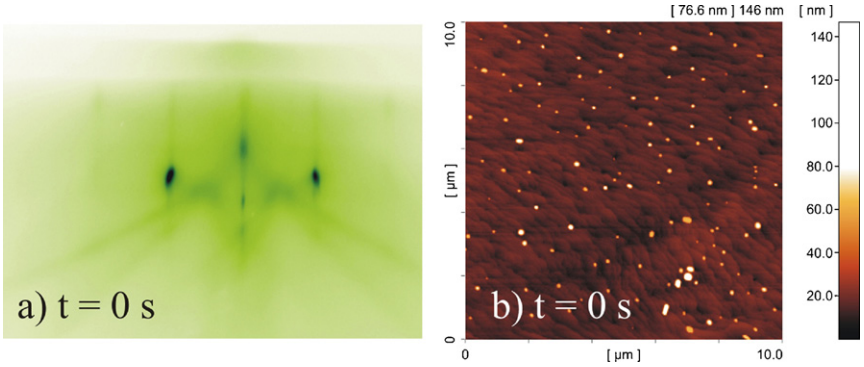

Fig. 1. The surface of the thermally annealed MgO substrate prior to film deposition as seen by the (a) RHEED system and (b) AFM.