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Compositional and structural evolution of the titanium dioxide formation by thermal oxidation

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Titanium oxide films were prepared by annealing DC magnetron sputtered titanium films in an oxygen ambient. X-ray diffraction (XRD), Auger electron spectroscopy (AES) sputter profiling, MCs^+-mode secondary ion mass spectrometry (MCs^+-SIMS) and atomic force microscopy (AFM) were employed, respectively, for the structural, compositional and morphological characterization of the obtained films. For temperatures below 875 K, titanium films could not be fully oxidized within one hour. Above that temperature, the completely oxidized films were found to be rutile in structure. Detailed studies on the oxidation process at 925 K were carried out for the understanding of the underlying mechanism of titanium dioxide (TiO_2) formation by thermal oxidation. It was demonstrated that the formation of crystalline TiO_2 could be divided into a short oxidation stage, followed by crystal forming stage. Relevance of this recognition was further discussed.

Keywords: thermal oxidation, titanium oxide, compositional and structural evolution
PACC: 6000, 8115, 6170A

1. Introduction

Titanium dioxide thin films have received great attention due to their attractive properties. Among the three different allotropes of TiO_2, rutile, the thermodynamically most stable structure, is promising for applications such as optical coatings[1] and high dielectric capacitors in dynamic-random-access-memory[2] because of its high refractive index, excellent optical transmittance and high dielectric constant; on the other hand, anatase is interesting for self-cleaning windows, anti-fogging glasses,[3] environmental protection devices because of its hydrophilic and photocatalytic properties.[4] For a special application, thus, control of the structure formation during film fabrication appears to be of great importance. During the last years, a variety of technical approaches, such as sol–gel processing,[5] reactive magnetron sputtering,[6,7] chemical vapour deposition,[8,9] and ion beam assisted deposition,[10] were established for the preparation of TiO_2 films. Generally, the as-deposited films are amorphous, exhibiting occasionally admixtures of small amounts of anatase TiO_2. After being annealed in oxygen or atmosphere ambient, pure anatase, pure rutile or mixture of the both can be obtained at different temperature ranges.

Pure rutile TiO_2 forms quite often at temperatures above 1170 K through an anatase-to-rutile transition. Such high temperature often causes oxygen deficiency in the obtained films, which could be a reason for the degradation of film properties.[11] Recently, thermal oxidation of the DC sputtered titanium films was reported to be a simple and convenient technique to prepare rutile TiO_2,[12−14] where pure rutile structured films could be fabricated at temperatures down to 825 K without an anatase-to-rutile transition. Furthermore, unlike the reactive sputtering, where a low deposition rate resulting from target poisoning seems to be inevitable, sputter deposition of titanium metal film in argon ambient ensures a high deposition rate. Oxidation and crystalline structure formation being now a process independent from the film deposition, this method should provide more possibilities during parameter optimization so as to obtain a crystal structure optimized for specific applications. To our knowledge, however, reports up to date excluded the anatase formation during thermal oxidation.[12,14] Owing to in sufficient experimental results reported, the under-

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standing of the formation mechanism of TiO_2 is as yet very limited. Especially, a detailed study of the composition evolution during thermal oxidation of sputtered Ti films is to our knowledge still missing.

For a deeper insight into the underlying mechanism, this paper reports a detailed study on the compositional and structural evolution in the films during thermal oxidation of DC magnetron sputtered titanium metal layers on Si substrates in an oxygen ambient for the temperature range between 625 K and 1375 K. Special attention was paid on the initial process during thermal oxidation. X-ray diffraction (XRD), Auger electron spectroscopy (AES) sputter profiling, MCs^+-mode secondary ion mass spectrometry (MCs^+-SIMS)[15] and atomic force microscopy (AFM) were employed, respectively, for a thorough investigation of the films' structural, compositional and morphological properties. For oxidation temperatures above 875 K, the obtained TiO_2 films are all rutile structured. Oxidation time dependent analysis has shown that the formation of the crystalline TiO_2 at 925 K could be divided into two stages: full oxidation with little crystalline generation, which lasts only a little longer than 5 min in our case, and crystallite formation during the following annealing stage.

2. Experiment

Titanium thin films were deposited on silicon substrates in a home-made DC magnetron sputtering system. A titanium disc (99.5% pure) of 85 mm diameter and 5 mm thickness was used as the target. The target and the substrate are in a 45 degree configuration with a distance of about 18 cm between the both centres. The substrate holder was rotating during deposition, which ensured the thickness homogeneity of obtained films. The system was first evacuated with a turbomolecular pump to a base pressure in the low 10^{-4} Pa region. High purity argon (99.99%) was then backfilled to a pressure of 2 Pa for film deposition. The DC power for target sputtering was kept at about 100 W. Prior to each deposition, the target was pre-sputtered for 15 min, so as to remove the oxidized surface layer. During film deposition, the substrates were not externally heated. The deposition took mostly 15 min, resulting in films about 200 nm thick. The as-deposited titanium films were annealed at temperatures between 625 K and 1375 K in oxygen under ambient pressure for different time duration.

The crystal structure of the various films prepared was determined by XRD (X' Pert PRO) measurements in a $\theta/2\theta$ geometry using Cu K_α irradiation (λ=0.154 nm). The film composition was analysed by AES sputter profiling (Perkin–Elmer SAM 660) and MCs^+-SIMS (Cameca IMS-4f). During AES measurement, a 2-keV Ar^+ ion beam was used for sputtering and the O KLL and Ti LMM Auger transitions excited by 5-keV electrons were monitored. In MCs^+-SIMS analysis, the samples were sputtered with a 5.5-keV Cs^+ primary ion beam (20–50 nA current) by raster-scanning across a surface area of $\sim(125\,\mu m)^2$ at an incidence angle of $\sim$42° and positive secondary ions (Cs^+ and MCs^+) were detected from a circular area with a diameter of 33 μm or 60 μm. Contact mode AFM (NT-MDT Solver P47) was employed to probe the surface morphology of the films.

3. Results

3.1. Annealing at different temperatures

The as-deposited Ti films were first annealed at temperatures ranging from 625 K to 1375 K. Fig.1 displays the XRD patterns of an as-deposited film and three films annealed at 775 K, 825 K and 925 K for one hour, respectively. Different from previous reports, where as-deposited Ti films are α-Ti, the XRD pattern of the 200 nm thick Ti-film has only one peak due to (100) reflection. XRD patterns taken on Ti-films thicker than 500 nm, however, show double-peak feature of α-Ti. As thicker films crack often or even flake off from the substrates when being annealed at temperatures above 975 K, similar to previous observations,[14] 200 nm thick films were used in this study. In the spectrum of the film annealed at 775 K, the Ti peak remains with reduced intensity, and the most pronounced peak at 37.3° can be attributed to TiO. Since there exists a series of daughter structures of nonstoichiometric titania, an exact identification of the small peaks of the spectrum seems to be difficult. Most possible assignments of these peaks are also suggested according to the JCPDS files. XRD pattern indicates that this film is not fully oxidized. The peaks in the spectrum of the film annealed at 925 K can all be attributed to the rutile form TiO_2 with the two dominant peaks from the (110) planes at 27.4° (which will be abbreviated as $R(110)$ in the following text, and similarly for the other peaks) and $R(101)$ at 36.1°. The spectrum of the 825 K annealed

film is characterized by a low signal intensity with tiny peaks at the position of $R(110)$ and $R(101)$, indicating a mainly amorphous structured film. In all of the films annealed at temperatures above 875 K, only the rutile structure of TiO_2 was detected.

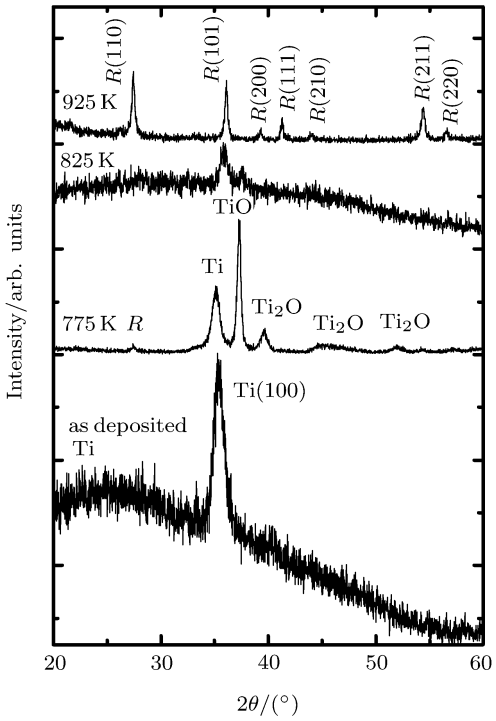


Fig.1. XRD spectra of an as-deposited Ti film and three TiO_x films oxidized for one hour at 775 K, 825 K and 975 K, respectively.

Figure 2 displays the AES sputter profile of the film oxidized at 825 K for 1 h. As indicated by the dashed lines, the profile of TiO_x can be divided into two parts. The first part shows the stoichiometry of the TiO_2, while the second part displays a c_O/c_{Ti} value smaller than 2, demonstrating an insufficient oxidation.

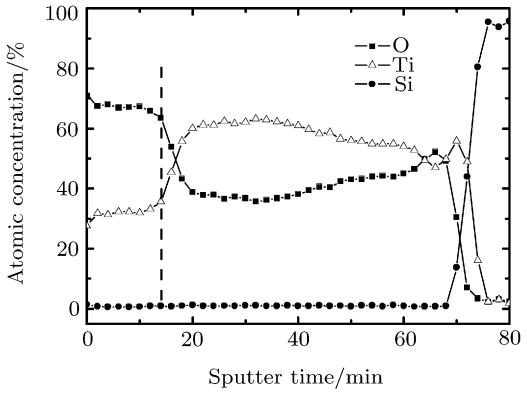


Fig.2. AES sputter profile of a film oxidized at 825 K for one hour. The dashed line indicates the interface between the fully and partially oxidized regions.

3.2. Time dependent evolution

Oxidation of the metal Ti films was further carried out at 925 K for 5, 15 and 30 min, respectively, to find out the detailed compositional and structural evolution in the films with increasing oxidation time, especially that in the initial stage. Fig.3 shows the XRD spectra of these films. For comparison, the spectrum of an as-deposited Ti-film is shown again. The Ti peak vanished after only 5 min oxidation. Instead, tiny peaks of rutile TiO_2 appears with the $R(110)$ peak as the most obvious one. When oxidation time is increased, the already existing peaks become more and more pronounced and additional rutile peaks, such as $R(111)$ at 41.5° and $R(211)$ at 54.6°, appear. The peak width obtained from a Lorentz fit decreases with increasing oxidation time. For instance, the FWHM of the $R(110)$ peak decreases from 0.32° at 5 min oxidation to 0.29° at 15 min, and 0.25° at 30 min. This suggests an increasing grain size in the obtained films with increasing oxidation time.

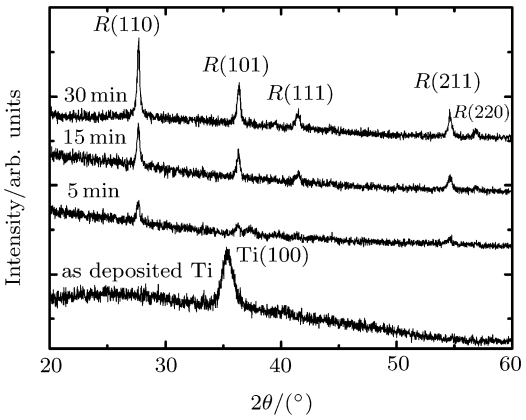


Fig.3. XRD spectra of films oxidized at 925 K for 5, 15 and 30 min, respectively. Also shown is that of an as-deposited Ti film.

Concentration profiles of the two films oxidized for 5 and 15 min taken with MCs^+-SIMS are presented in Fig.4. The profile region of interest for the film oxidized for 5 min can be divided into three parts, as indicated by the dashed lines: (1) a fully oxidized region, (2) an incompletely oxidized Ti-rich region, and (3) a diffusion region at the film-substrate interface. The fully oxidized region is characterized by a constant concentration ratio of O to Ti (c_O/c_{Ti}) of 2.26±0.05. The slight deviation of this value from 2 should be a result of our calibration to determine the relative sensitivity factors for the quantification of SIMS results.[16] In the Ti-rich region, the c_O/c_{Ti} values are smaller than 2 and decreases with the increasing sputtering

time. The interface diffusion region is, however, characterized by a high Si concentration (around 40%) and a low oxygen concentration. This profile shows that the time needed to oxidize completely our sample at 925 K is only slightly longer than 5 min. In the spectrum of the sample oxidized for 15 min, the Ti-rich region disappears while the interface diffusion region remains. In the interface diffusion region of the both profiles, the atomic concentration of Si and Ti do not vary monotonically with the sputter time. This should be a result of the strong dependence of the relative sensitivity factors on the oxygen concentration.[16]

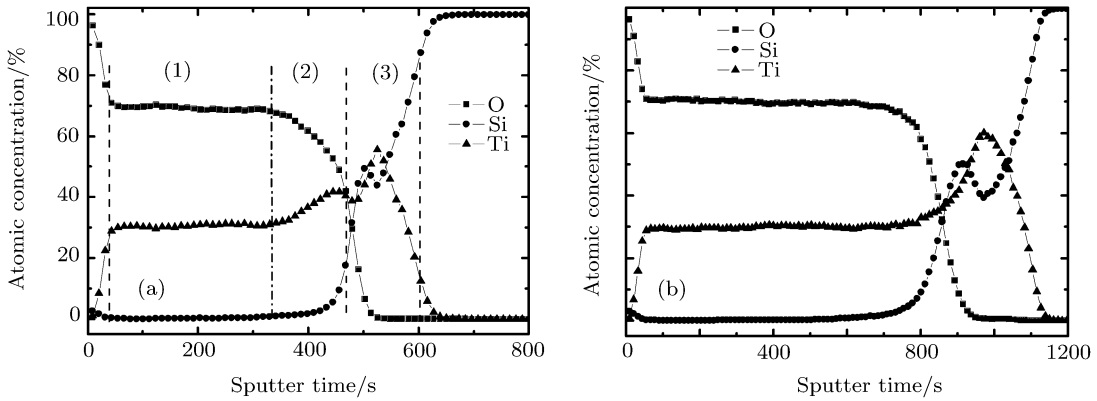


Fig.4. MCs^+-SIMS sputter profiles of films oxidized at 925 K for 5 min a) and for 15 min b). The dashed lines indicate different regions of the sputter profile.

Figure 5 shows the AFM images of the films oxidized at 925 K for 5, 15 and 30 min respectively. The topography of the three samples looks quite similar. From 5 min to 15 min oxidation time, the AFM images show an increase in grain size. This trend is, however, not to be seen between 15 min and 30 min. As the XRD measurements demonstrate larger grain sizes for longer oxidation times, the AFM results suggest that such a crystal growth takes place in the direction of film depth.

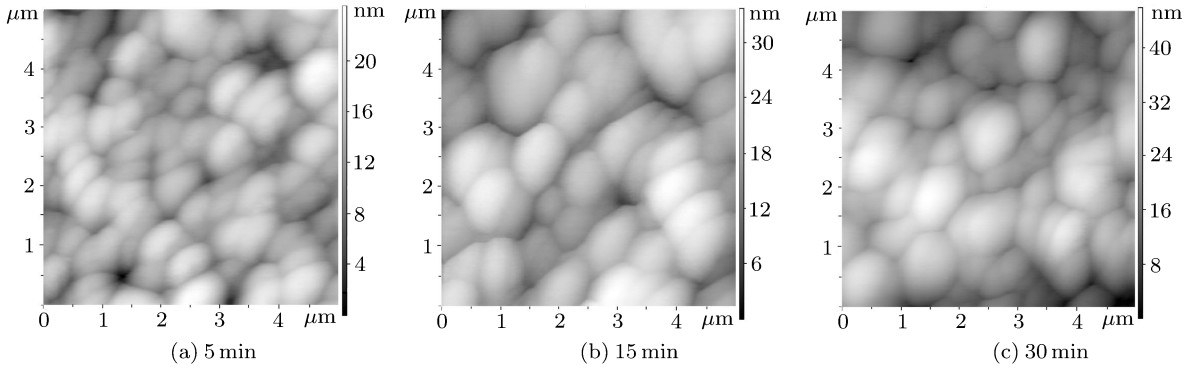


Fig.5. AFM images of the three films after 5, 15 and 30 min oxidation at 925 K.

4. Discussion

In the present study, only the rutile structure of TiO_2 has been detected in films prepared at temperatures above 875 K. As shown above, oxidation time slightly above 5 min is already sufficient to fully oxidize the whole film at 925 K (Fig.4), while 1 h is still not enough for a full oxidation at 825 K (Fig.2(a)). One further difference worth noting is that the incompletely oxidized titania, such as TiO, which are the main products of oxidation at 775 K for 1 h (Fig.1), are not detected for oxidation at 925 K. From this finding it can be concluded that the partially oxidized titania are more stable in the lower temperature region.

Unlike in the film oxidized at 925 K (as shown in Fig.4), no interfacial diffusion region is observed in the AES sputter profile of the film oxidized at 825 K (see Fig.2). Such difference is not due to different analysis methods used here, since in a comparative analysis carried out on a film oxidized at 925 K for

1 h (results are not presented here), both AES and SIMS profile show similar interface diffusion region as displayed in Fig.4. Noteworthy is that no diffraction peaks from Ti–Si intermetallic compounds[14] are found in the XRD patterns shown in Fig.3. Absence of oxygen in the Ti–Si diffusion layer supports the assumption that such diffraction peaks should originate from Ti_5Si_4 or Ti_5Si_3.[14]

At this point it is still unclear when the amorphization of the Ti crystal takes place, and what is the reason for this process. One possibility is that it occurs gradually during the diffusion of the oxygen into the metallic Ti. The other possibility is that this happens suddenly as a result of stress accumulation. It has been reported that thick films flake-off from the substrates during oxidation.[14] This suggests that a huge stress is generated during the oxidation. Such stress could also be the reason for the amorphization.[17,18] To clarify this issue, investigations with a more detailed control of the oxidation process, such as XRD measurement on films oxidized for a shorter time, would be favourable, and a simultaneous stress monitoring would be further helpful.

Annealing of reactively sputtered amorphous TiO_x films at temperatures between 573 K and 973 K in atmosphere or an oxygen ambient leads usually to the formation of anatase TiO_2. One may also expect the formation of anatase TiO_2 by further annealing a sample like that already oxidized for 5 min at 925 K at an appropriate temperature. We got, however, still only rutile TiO_2 by annealing this sample at 875 K for 1 h. This result confirms that the structure formation during thermal annealing of mainly amorphous TiO_2 films deposited by reactive sputtering depends on the initial crystallographic state.[19]

5. Conclusions

Rutile TiO_2 has been prepared by thermal oxidation of DC magnetron sputtered Ti films in oxygen ambient at temperatures $\geq$875 K. For lower oxidation temperatures, the resulting film contains mainly incompletely oxidized titania. A Ti-Si diffusion layer containing no oxygen is observed at the interface of the film oxidized at 925 K but not that at 825 K. Detailed structural and compositional analysis demonstrates that the whole TiO_2 formation process at 925 K can be divided into two stages: a short oxidation stage followed by a crystal growth stage. In this respect, thermal oxidation should provide further possibilities for much better control of the process parameters to obtain the desired crystalline state of TiO_2. For a more detailed understanding on the growth mechanism, further investigation on the early stage of oxidation, especially the rutile TiO_2 formation at the very beginning, should be carried out.

Acknowledgments

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