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Structural and mechanical properties of annealed thin films of pure and carbon doped titania

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ABSTRACT

This study investigated the annealing effects on structural and mechanical properties of pure (pure TiO_2) and carbon doped titania (C-TiO_2) thin films. The amorphous films of pure TiO_2 and C-TiO_2 were deposited on the substrates of Si wafer (100) at 100 °C by reactive magnetron sputtering. Through annealing at different temperatures, times and atmospheres, the crystallinity and defect density of the films could be varied. Under H_2 annealing, oxygen vacancies are generated in the films which facilitate the phase transformation from amorphous to anatase at a lower onset temperature than those under air annealing. The onset temperature of crystallization for C-TiO_2 is higher than that for pureTiO_2 due to the existence of carbon atoms which impairs the diffusion of Ti and O atoms for crystallization. The hardness of the films by nano-indentation test ranges from ~7 GPa for the amorphous to ~12 GPa for the crystallized films and is affected by the phase, degree of crystallinity, grain size and defect density. When the amorphous titania film fully transforms to a crystalline phase of small grains at temperatures ranging from 300 to 500 °C, its hardness will reach a maximum. However, at temperatures over 400 to 500 °C, the film hardness declines conversely with increasing temperatures or extending annealing time due to increase in grain size and change in defect density.

1. Introduction

Titania or titanium dioxide (TiO_2) and related materials are among the most explored oxides in science and industries owing to their versatile, outstanding, beneficial and functional properties [1–4]. They are mechanically hard, optically transparent and chemically inert and stable and possess many useful functional properties for promising applications in areas ranging from optical, photovoltaic and photocatalysis to photo/electrochromics and sensors. With the advent of nanotechnology, nanostructured titanium dioxide has found even greater applications, of which examples include dye-sensitized solar cells, hydrogen production and storage, sensors, rechargeable batteries, self-cleaning and antibacterial surfaces, electrocatalysis and photocatalytic cancer treatment.

Titania exists in amorphous and crystalline phase, and the common crystalline phases in nature are anatase, rutile and brookite. The crystal structures of both anatase and rutile belong to tetragonal system, but they possess different physical and chemical properties and thus, different applications. Anatase is metastable at low temperatures, while rutile is stable at high temperatures. Phase transformation to crystalline titania occurs under a wide range of temperatures, depending on stoichiometry, crystallinity and impurity of the starting materials and the processing methods and conditions. Our past research [5–7] indicated that sub-stoichiometric titania or titania annealed in oxygen-deficient environment facilitates the formation of oxygen vacancies which favors the phase transformation to rutile at a lower onset temperature, while under oxygen sufficient environment anatase can be stable at temperatures as high as over 800 °C.

Carbon containing titania (C-TiO_2) films with high anatase crystallinity and proper amount of carbon-doping exhibit outstanding photocatalytical performance under a visible light [8,9]. The films could transform to rutile at lower temperatures in oxygen-deficient atmosphere, resulting in the red-shift of absorption edge toward the visible light. Carbon in C-TiO_2, can exist in many possible ways including replacement of oxygen and forming a Ti – C bond, substitution of Ti atom and forming C – O bond, and interstitial position and free carbon on surfaces or interfaces [8,9]. The analysis of our sputtered C-TiO_2 films shows that the carbon is present both in the form of substituted Ti – C bonds and free graphitic carbon on the grain boundaries. However, the influence of carbon incorporation in titania films on the film mechanical properties hasn't been well-studied.

Thin films of titania are usually deposited on various substrates like glass, Si, metals, etc. as an indispensible part of a functional system for most applications [10]. The thin films on substrates are likely to be subjected to mechanical stresses and localized contacts during service. Thus, studies on the mechanical properties of titania in relation with processing and structure are necessary for the design of reliable coatings. The mechanical properties of titania films have been studied [10–17], which indicate that the rutile phase is harder and has a higher

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elastic modulus compared to anatase or amorphous phases. Depending on the preparation and processing conditions, the reported values of titania vary largely, between 1.5 GPa and 21 GPa for hardness, and between 85 GPa and 260 GPa for elastic modulus.

This study is to investigate the mechanical properties, particularly the hardness and modulus of the TiO_2 and C-TiO_2 films deposited on Si substrates by reactive magnetron sputtering technique, and followed by post thermal treatment. Through annealing at different temperatures, times and atmospheres, the crystallinity and defect density of the films could be varied, which allow the structural control of the films, thus permitting different film structures in relationship to mechanical properties to be investigated.

2. Experimental

Pure TiO_2 and C-TiO_2 films were deposited on the substrates of Si wafer (100) at 100 °C using a reactive magnetron sputtering system of three targets in the DC mode. The films were prepared in argon and oxygen plasma by sputtering two Ti targets with a power of 250 W for pure TiO_2, and one Ti target and one graphite target with a power of 300 W for C-TiO_2. The base pressure is better than 1.3×10^{-5} Pa, and the flow rate of oxygen and argon are 7 sccm and 40 sccm, respectively. The working pressure is 0.4 Pa. Before the film deposition, sputter etching the substrate with argon plasma is carried out to remove any residual pollutant on the substrate surface, and then pre-sputtering the targets is done to remove the oxide layer on the target surface. The rotational speed of the substrate holder is 5 rpm without substrate bias. The deposition time is 60 min, and the film thicknesses of pure TiO_2 and C-TiO_2 are about 422 and 334 nm, respectively. The atomic percent of carbon in C-TiO_2 is about 5 atomic%.

The as-deposited films are all amorphous. Then the films are annealed isochronally and isothermally in different atmosphere in a rapid thermal annealing (RTA) furnace (Mila300, Ulvac Company, Tokyo, Japan). The annealed samples are classified into five series and each sample is denoted with an ID representing the film type, annealing atmosphere and temperature as listed in Table 1. (e.g., PA300 represents pure TiO_2 annealed in air at 300 °C; CH500 represents C-TiO_2 annealed in hydrogen at 500 °C) Series one to four are pure TiO_2 and C-TiO_2 films annealed isochronally in air and in hydrogen, respectively, at 300–800 °C for 1 h. Series five is pure TiO_2 films annealed isothermally in air at 300 °C for 1–12 h. The film structure is analyzed by an X-ray diffractometer (XRD, Rigaku D/MAX-2500) using Cu-Kα which operates at 40 kV with an emission current of 100 mA. The surface morphology is observed by a field emission scanning electron microscope (FE-SEM, JEOL JSM-6500F). The composition and the binding of the film are characterized by an X-ray Photoelectron Spectrometer (XPS, Thermo K-Alpha) using Al-Kα X-ray (1486.6 eV) at 15 kV and 100 W, and choosing C1s at 284.8 eV as a standard for calibration. Surface roughnesses are about 1–5 nm which are measured by AFM. The film thickness was obtained by measuring the step height using a profilometer (Veeco, Dektak 150).

The hardness of the films is measured by the nanoindentation tests using a computer-controlled nanoindentor (MTS, Nanoindentor XP) equipped with a Berkovich diamond indenter by employing the continuous stiffness measurement mode and applying Oliver–Pharr theory [18–21]. The measurement method is to take a 4 × 3 matrix on the sample, and the distance between each point in the matrix is 25 μm to avoid the effect of plastic deformation of the other indents in the film. The maximum indentation depth is set to 300 nm.

3. Results and discussion

The XRD patterns of the as-deposited and the annealed films of pure TiO_2 and C-TiO_2 on (100) Si wafer were reported in reference 7. The films were annealed isochronally in air and in H_2 at different temperatures from 300 °C to 800 °C for one hour. The intensities and the width of the strongest (101) XRD peak of anatase for all the annealed samples are listed in Table 1. Fig. 1 is the XRD pattern of the pure TiO_2 films isochronally annealed in air, which represents the typical structural evolution of the films due to the annealing effect. No XRD diffraction peaks are observed for the as-deposited film, indicating an amorphous structure. The films transform from amorphous to crystalline anatase phase with (101) preferred orientation after annealing. At 300 °C the air-annealed film just begins to crystallize, so its diffraction peak is relatively weak. After annealing at 400 °C, the XRD peak intensities become stronger than those of the 300 °C air-annealed film, but the peak intensities remain about the same for the films annealed at temperatures above 400 °C. This indicates that the films annealed above ~400 °C have transformed completely into anatase phase. At the same annealing temperatures, the pure TiO_2 films annealed in H_2 exhibit stronger anatase XRD peak intensities than those annealed in air.

Table 1
The structural and mechanical properties for pure TiO_2 and C-TiO_2 films isochronally annealed for 1 h at various temperatures under different atmosphere.

Sample ID	Annealing atmosphere, Temp. (°C)	XRD A(101) FWHM	XRD A(101) intensity (a.u.)	Hardness (GPa)	Modulus (GPa)
P-as	–	–	–	7.7	159.7
PA300	Air, 300	0.30	60	8.3	164.8
PA400	Air, 400	0.28	317	11.8	188.8
PA500	Air, 500	0.31	282	11.4	183.5
PA600	Air, 600	0.29	316	11.2	181.0
PA700	Air, 700	0.31	298	10.8	184.6
PA800	Air, 800	0.28	322	10.2	176.8
PH300	H_2, 300	0.27	280	10.8	177.4
PH400	H_2, 400	0.27	407	10.9	168.0
PH500	H_2, 500	0.26	356	10.5	170.8
PH600	H_2, 600	0.25	307	9.4	157.1
PH700	H_2, 700	0.28	340	9.4	156.6
PH800	H_2, 800	0.26	468	9.0	164.3
C-as	–	–	–	6.7	143.6
CA300	Air, 300	–	–	7.5	150.1
CA400	Air, 400	–	–	7.5	147.8
CA500	Air, 500	0.29	322	10.2	164.8
CA600	Air, 600	.026	304	10.1	156.4
CA700	Air, 700	0.28	386	9.4	160.1
CA800	Air, 800	0.29	334	9.1	154.0
CH300	H_2, 300	–	–	7.4	145.3
CH400	H_2, 400	–	–	7.3	145.9
CH500	H_2, 500	0.25	448	10.1	164.8
CH600	H_2, 600	0.25	404	8.9	152.3
CH700	H_2, 700	0.26	313	8.3	146.7
CH800	H_2, 800	0.28	333	6.9	143.5

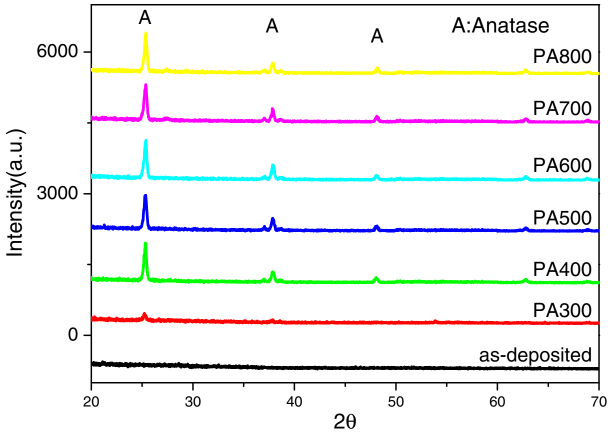

Fig. 1. The XRD patterns of the isochronally annealed pure TiO_2 in air.