Thin Solid Films 542 (2013) 38–44

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Growth and characterization of titanium oxide by plasma enhanced atomic layer deposition

Chao Zhao *, M.N. Hedhili, Jingqi Li, Qingxiao Wang, Yang Yang, Long Chen, Liang Li

Advanced Nanofabrication, Imaging and Characterization Core Lab, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

ARTICLE INFO

Article history:
Received 16 September 2012
Received in revised form 31 May 2013
Accepted 7 June 2013
Available online 14 June 2013

Keywords:
Atomic layer deposition
TiO_2 film
Raman spectroscopy
X-ray diffraction
Ellipsometer
Atomic force microscopy

ABSTRACT

The growth of TiO_2 films by plasma enhanced atomic layer deposition using Star-Ti as a precursor has been systematically studied. The conversion from amorphous to crystalline TiO_2 was observed either during high temperature growth or annealing process of the films. The refractive index and bandgap of TiO_2 films changed with the growth and annealing temperatures. The optimization of the annealing conditions for TiO_2 films was also done by morphology and density studies.

1. Introduction

The application of metal oxides has a long history in human society. They have been attracting growing attention nowadays because of the exploration of their function in areas such as transparent conductive oxide (TCO) electrode, high-k dielectric, and oxide-based semiconductors. Among these metal oxides, TiO_2 has been studied a lot in the fields of diluted magnetic semiconductors, photocatalyst materials, and electrode materials for electrochromic devices [1]. Janisch et al. discussed the origins of ferromagnetism in Co-doped TiO_2 [2]; Fujishima et al. reviewed the research progress on TiO_2 and discussed the reaction mechanisms of TiO_2 used as a photocatalyst [3]; TiO_2 also found applications in the photovoltaic field as electrode materials [4]. Furthermore, TiO_2 can also be used as a component of ternary high-k, TCO electrode and other multicomponent materials [5,6].

TiO_2 films can be fabricated in many different ways, such as physical vapor deposition [7], chemical vapor deposition (CVD) [8] and spin coating [9]. Among these growth methods, atomic layer deposition (ALD) shows the advantage of conformal growth and precise control of the film thickness, which are very important to the fabrication of future microelectronic devices [10]. The basis for ALD is supplying different precursors into the growth chamber in a sequential way. Most reports on ALD involve the reaction of the precursor and H_2O, which is called thermal ALD. There is another growth mode using O_2 plasma instead of H_2O, which is plasma ALD [11]. The plasma mode makes it possible to deposit films at lower temperatures and higher growth rates with low contamination concentration and high density of the film compared to the thermal mode [12]. Moreover, TiO_2 grown by ALD usually involves the use of titanium tetrakis(isopropoxide), tetrakis(dimethylamino) titanium, etc. as the precursor for Ti in the past [13]. Those precursors have a narrow process window, which restricts their future application.

Star-Ti [(pentamethylcyclopentadienyl)trimethoxy-titanium, $(CpMe_5)Ti(OMe)_3$] [5] is well known for its good thermal stability. There are a few reports on the growth of TiO_2 using Star-Ti. Katamreddy et al. discussed the growth of TiO_2 using Star-Ti and O_3. They also evaluated the characteristics of other precursors such as tetrakis(diethylamino) titanium and tetrakis(ethylmethylamino) titanium [13]. Langereis et al. reported the growth of $SrTiO_3$ film using Star-Ti as a precursor. They found that the optical dielectric function reflected the composition and microstructure of the films [5]. However, the study of the growth of TiO_2 by Star-Ti is still insufficient, and the growth in plasma mode and the impact of the growth conditions on the film properties are still not clear. There is a need to understand the properties of the TiO_2 film under various deposition conditions in order to control the growth in future applications. In this paper, we focus on the growth of TiO_2 by the plasma enhanced ALD using Star-Ti as the precursor. The influence of the growth temperature, Star-Ti dose time, O_2 plasma time and other experimental conditions on the properties of the deposited film have been discussed. It was found that the deposition has a wide process window, and the material properties and the refractive index of the film vary with the growth temperatures and post annealing temperatures. The optimization of the annealing conditions for TiO_2 films was also done by morphology and density studies.

* Corresponding author. Tel.: +966 2 808 2346.
E-mail address: chao.zhao@kaust.edu.sa (C. Zhao).

0040-6090/$ – see front matter.
http://dx.doi.org/10.1016/j.tsf.2013.06.010

2. Experimental details

All the TiO_2 films were deposited on 3 in. p-doped Si(100) substrates in the FlexAL ALD reactor from Oxford Instruments. For these ALD processes, Star-Ti (Air Liquide) was used as the precursor in combination with remote O_2 plasma as the oxidizer, which avoids the potential ion bombardment damaging to the film surface [14]. The precursor was kept at 110 °C in the bubbler and delivered into the chamber by argon flow, while the delivery line was kept at 130 °C to assure the delivery process. The ALD chamber walls were heated to 150 °C to prevent precursor condensation. Argon was also used as a purge gas for the precursor and O_2 plasma. In an ALD cycle, the first step is to bring Star-Ti vapor to the surface of a Si substrate; the excess unreacted precursor is then purged away by argon for 5 s at a pressure of 3.33 Pa. O_2 plasma is then brought to the surface to react with the precursor. The excess unreacted plasma is also purged away by argon for 3 s at a pressure of 10.67 Pa. This process is repeated for several cycles to reach the expected film thickness. The precursor dose time, plasma time and growth temperature have been changed to study their influence on the growth of TiO_2 films. The morphology of the films was characterized by Agilent 5500 tapping mode atomic force microscopy (AFM) using Si tips. X-ray diffraction (XRD) θ–2θ scan was used to analyze the phase and structure of the films by using a Bruker D8 diffractometer with Cu Kα radiation (40 kV × 40 mA). The density of the films was estimated by fitting X-ray reflectivity (XRR) results obtained from the Bruker D8 diffractometer. The thickness and refractive index of the samples were measured *ex situ* using an Uvisel spectroscopic ellipsometer from Horiba Jobin Yvon in the wavelength range of 245 to 825 nm at a 70° incident angle. The thicknesses of the films were also measured by XRR and cross section transmission electron microscopy (TEM). The TEM specimens were prepared by a focused ion beam lift out technique. TEM images were recorded on a FEI Titan Super Twin TEM using an accelerating voltage of 300 kV. A post-growth annealing was performed for a sample grown at 250 °C in a rapid-thermal-annealing system at different temperatures ranging from 450 °C to 850 °C for 1 min in a forming gas (N_2/H_2 mixture) atmosphere. Raman measurements were carried out on a Horiba Jobin Yvon confocal micro-Raman HR 800 system. A 100× objective lens with numerical aperture of 0.90 was used to focus the laser beam and collect scattered light in the backscattering geometry. A 532 nm laser was used as the excitation source. The diameter of the laser spot was about 0.7 μm and the laser power at the sample surface was about 0.6 mW. The chemical composition of the films was also analyzed by X-ray photoelectron spectroscopy (XPS) using an Axis Ultra DLD spectrometer (Kratos Analytical, UK), equipped with a monochromatic Al Kα X-ray source ($h\nu = 1486.6$ eV) operating at 150 W. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. Samples were mounted in floating mode in order to avoid differential charging. Binding energies were referenced to the C 1s binding energy of adventitious carbon, which was taken to be 284.8 eV.

3. Results and discussion

The thickness of the TiO_2 layer was measured by ellipsometry. A 1.4 nm thick natural SiO_2 layer between TiO_2 and Si was determined by cross section TEM. The SiO_2 layer was also included in the model when fitting the ellipsometric data to determine the TiO_2 layer thickness. The deposition rate was defined as the film thickness per ALD cycle. The precursor dose time, plasma time and growth temperature were changed, only one parameter at a time, while the other two were kept constant. The self-limiting nature of the remote plasma ALD TiO_2 process was demonstrated from measurements of the deposition rate for different growth conditions [15].

The effect of precursor dose time and plasma time on the growth rate of TiO_2 was presented. Fig. 1a shows the growth rate of TiO_2 films at 250 °C as a function of the precursor dose time at two different plasma times of 3 s and 10 s. The growth rate increased with the precursor dose time, and self-limiting kinetics was observed by the saturation of the growth rate when the dose time reached 4.5 s in both conditions; a further increase of the precursor dose time led to an abrupt grow rate increase, which was a sign of the CVD growth in this condition. Due to the limited purge time after dosing, the residue precursor in the chamber caused a reaction with O_2 plasma which results in an increase of the growth rate. A longer purge time might be able to eliminate this CVD behavior [16]. The plasma time of 3 s had a lower growth rate compared to that of 10 s, which indicates an unsaturated ALD reaction. The effect of the plasma time was also studied as shown in Fig. 1b. The growth rate seems to be higher with a precursor dose time of 4.5 s but their tendency looked very similar. In both cases, it reached a plateau region at plasma time of 4.5 s. However, below the plasma time of 4.5 s, growth rate reached a maximum at 1 s as shown in Fig. 1b, which could be attributed to initial nucleation. It was also found that the ALD growth of TiO_2 has a very wide temperature window from 150 °C up to 400 °C, at which the growth rate of TiO_2 with Star-Ti remained stable as shown in Fig. 1c. This window ranged from the minimum temperature to get enough precursor vapors to the maximum temperature of the system heater and did not change with the dose time. The only difference was that the dose time of 2.5 s had a lower growth rate because it did not reach the saturated dose amount. The growth per completed TiO_2 cycle was found stable at 0.55 Å/cycle, similar to the reported value of 0.54 Å/cycle obtained using a Star-Ti precursor and O_2 plasma [5], but higher than the rate reported for Star-Ti and O_3 because the O_2 plasma is a stronger oxidizer [17]. The growth rate was also higher than that using other precursors and/or thermal ALD as reported previously, which was 0.3–0.5 Å/cycle [18,19,20,21]. It's clear that the growth per completed TiO_2 cycle is saturated at a Star-Ti dosing time of 4.5 s and O_2 plasma exposure of 10 s, showing the self-limiting nature of the reactions. Fig. 1d shows the linear relationship of the film thickness with the number of TiO_2 cycles at 4.5 s dose time and 10 s plasma time at 250 °C. The extrapolation of the curve to zero suggests that there was almost no nucleation delay on the substrates at the initial stage of the reaction [5,22].

Fig. 2 shows the influence of the growth temperatures and annealing temperatures on the crystalline structure of the TiO_2 films. Samples grown below 250 °C showed the XRD results of an amorphous phase; at 250 °C it only showed a very weak (101) peak at 25.28° corresponding to the anatase phase, the intensity of the peak increased dramatically for temperatures above 250 °C (Fig. 2a). This indicated that the growth temperature had a great impact on the crystallinity of the films. The conversion of amorphous to crystalline material happened at high growth temperatures. Rapid-thermal-annealing is usually used to improve the quality of the as-deposited TiO_2 films. The effect of post-deposition annealing temperature was studied for samples deposited at 250 °C. The (101) orientation of the anatase phase was observed as shown in Fig. 2a in all cases. The intensity of the (101) peak at high temperatures were stronger than that at the low temperatures, which also indicated the improvement of the crystallinity of the films by post-annealing [23]. The same samples were also characterized by Raman spectroscopy. The peaks at around 144 and 198 cm^{-1} were assigned to E_g modes. The one at 395 cm^{-1} was assigned to $B1_g$ mode, which was attributed to the O–Ti–O bending vibrations. The peak at 638 cm^{-1} was assigned to E_g mode that was attributed to the Ti–O bond stretching vibrations, as shown in Fig. 2b. The peak at around 519 cm^{-1} for $A1_g + B1_g$ modes was covered by the strong peak from the substrate [24,25]. These peaks corresponding to a TiO_2 anatase phase were only observed for the films deposited at or above 250 °C and the samples annealed from 450 to 850 °C, which agreed with the XRD results. The crystallographic structure obtained from XRD and Raman results showed that the TiO_2 film only had an anatase phase. Its higher density of localized states compared to rutile TiO_2 led to the potential application as a photocatalyst [26].