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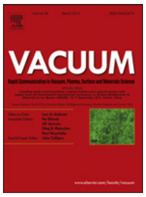

Synthesis and properties of crystalline TiO_2 films deposited by a HIPIMS+ technique

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ABSTRACT

Crystalline TiO_2 thin films were synthesized on the Si and glass substrates by reactive sputtering in a HIPIMS+ coating system. The films with a bit oxygen deficiency were deposited on the Si and glass substrates at oxygen flux rate of 10 sccm. The phase structure of the films changed with varying the parameters the MPP power pulse, the bias voltage, and working gas pressure. Anatase-dominant, anatase–rutile, and rutile films can be obtained by controlling the deposition parameters. The anatase-dominant and anatase–rutile TiO_2 films possess good photoinduced hydrophilicity and photocatalytic properties. The rutile films exhibited high dielectric constant. The related mechanism and potential application was discussed.

1. Introduction

Due to its ability of photocatalysis and photo-induced super-hydrophilicity, TiO_2 was paid significant attentions in recent years. Under the irradiation of ultraviolet lights, the organic pollutants can be degraded into water and small inorganic molecules [1–4]. The potential application utilizing the photo-active properties of TiO_2 films include self-cleaning glasses for automotives and architectural glasses [5]. Also, due to the high dielectric constant of TiO_2 ($\varepsilon = 20–60$ and 89–173 for anatase and rutile phase, respectively), the TiO_2 film is potential as the dielectric layer in the capacitors for future ultra-large-scale dynamic random access memory (DRAM) [6]. A high dielectric material will be necessary to replace the conventionally used silicon oxide–nitride–oxide (ONO) triple layers, since the reduction of thickness will reach its physical limits [6].

There are three different crystalline phases of TiO_2, namely anatase, rutile, and brookite [7]. In addition, amorphous TiO_2 films are often observed when deposition temperature is low. Depending on the phase structure, the TiO_2 films can be tailored for different applications. A variety of deposition methods have been used to produce TiO_2 films, such as electron-beam evaporation [8], sol-gel methods [9], chemical vapor deposition [10], and DC or RF magnetron sputtering [11–13], etc. However, in most cases, the photoactive anatase or anatase–rutile mixture necessitates substrate temperature above 400 °C during film deposition or post-deposition thermal treatment [14, 15], which limits the wider utilizations, such as application on the technologically interesting polymer foils.

By increasing the energy of the incoming particles involved during film deposition, it is possible to reduce the substrate temperature while obtaining the desirable phase structure. In Ref. [16], the correlation between phase composition of TiO_2 films and deposition temperature/energy was given. Crystalline anatase, rutile–anatase or even rutile phase can be deposited at low temperatures by increasing the energy of the incoming particles. Film of high-temperature rutile phase has been deposited by filtered arc deposition on (111) conducting silicon substrates at a bias voltage of −100 V or lower [17].

High power impulse magnetron sputtering (HIPIMS) is an emerging technology that utilizing extremely high power densities of the order of kW/cm^2 in short pulses at low duty cycle (on/off time ratio less than 10%). In the HIPIMS technique, a strong ionization (higher than 30%) is obtained, which opens new

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perspectives for thin film deposition because of energetic condensation. As deposited species are ions, it is possible to calibrate metal ions energy by biasing the substrate. HIPIMS technique has been shown to enable the deposition of dense and smooth metallic and compound films, allowing phase tailoring [18]. TiO_2 films with anatase or rutile phase have been also deposited by HIPIMS technique by controlling the peak power and bias voltage [19].

As a variation of high power impulse magnetron sputtering (HIPIMS) technique, HIPIMS+ technology is utilizing Modulated Pulse Power (MPP) supplies on the cathode [19–21]. The characteristics of HIPIMS+ differing from the HIPIMS is the longer (500–3000 μs vs 100–500 μs), milder (0.5–1.5 kW/cm^2 vs 1–3 kW/cm^2) and programmable power pulses [21]. By this kind of method, some metallic and nitride coatings have been synthesized [20,22]. Due to the similar high ionization rate as HIPIMS, it is reasonable to believe that HIPIMS+ can be also tailored to deposit high-quality crystalline TiO_2 films. However, it seems that there is no report on the deposition of TiO_2 films by HIPIMS+ technique.

In this study, TiO_2 films were deposited at room temperature using a HIPIMS+ sputtering in an Ar/O_2 gas mixture. The phase structure and some properties of the films were investigated.

2. Experimental details

The TiO_2 thin films were deposited on single crystalline (100) Si wafers and microscope glass slides by a HIPIMS+ coating system. A HIPIMS+ package produced by Hauzer Techno Coating BV including an Modulated Pulse Power (MPP) generator for sputtering target and a constant DC bias voltage power supply with arc suppression was installed in the HIPIMS+ coating system. Ti target with diameter of 80 mm and thickness of 6 mm was sintered from the Ti (99.5% purity, 10 μm) powders using a spark plasma sintering technique. The sintering temperature was 900 °C. The Si and glass substrates were cleaned in an ultrasonic cleaner using acetone and alcohol for 30 min, dried by nitrogen gas, and then loaded into the coating chamber. A turbo pump based vacuum system was used to achieve a base vacuum below 4×10^{-3} Pa. Pre-sputtering the Ti target was conducted for 5 min in an Ar atmosphere of 0.7 Pa in order to remove its oxide surface layer before the coating process. The substrates were further cleaned by an Ar ion bombardment at a bias voltage of −600 V for 5 min. Then the deposition process began. During the deposition process, MPP pulses with length of 1500 ms were used for providing the power of sputtering cathode. The average power of the cathode was fixed at 1 kW. The parameters of the power pulse (peak voltage, peak current, peak power, and repetition frequency, etc.) can be adjusted by setting some charge voltage values in the MPP power supply. The pulse parameters are also influenced by the status of the cathode (metallic or oxide mode, will be described in the results and discussion). The Ar gas was injected near the Ti target while the O_2 gas near the substrate. The substrate was fixed facing the sputtering target with a target–substrate distance of about 10 cm. The deposition time was 2 h. All the depositions are conducted without any additional heating on the substrate. However, due to the plasma heating from the cathode, the substrate temperature increased to about 70 °C during deposition. In some depositions, additional negative bias voltage was applied on the substrates.

The film thickness was measured using an α-step stylus instrument. X-ray diffractometer (XRD; D8, ADVANCE) was used to characterize the phase structure of the TiO_2 films. The Cu $K\alpha$ radiation was operated at 40 kV and 40 mA with a scanning speed of 3° per minute at 2θ step of 0.02°. X-ray photoelectron spectroscopy (XPS, VG Scientifics ESCALAB250) was used to analyze the chemical bonding status of the TiO_2 films. The XPS spectra were obtained after removing the surface contamination layer of the sample by in situ sputtering with Ar^+ ions (3 keV) for 30 s, and were calibrated by carbon peak C 1*s* at 284.6 eV. The optical characteristics of the obtained films were analyzed using a double-beam ultraviolet–visible light (UV–vis) spectrophotometer. The photo-induced hydrophilicity of the films was investigated by measuring the contact angle of water (Kruss contact angle measurement) after irradiation with ultraviolet light. To apply reproducible uniform volume drops of de-ionized water, calibrated micropipettes were used. The volume of the water drop was in the range of 20–100 μl. Drop shape was recorded with a high speed framing camera, images were then processed by a programmed computer. The photo-catalytic assessment of the film was evaluated by measuring the consumption of methylene blue (MB) in water (0.134 μmol/l, the absorbance measured using an Ocean Optics spectrometer (HR 4000)) due to ultraviolet light irradiating the specimen in the MB solution. The dielectric constants of the films were measured with a C–V analyzer (Keithley 590) at a frequency of 1 MHz. All the obtained data were average values of ten measurements.

3. Results and discussion

During reactive sputtering from a metallic target, the working status of the cathode can be affected significantly by the partial pressure of the reactive gas. Fig. 1(a) outlines the specific machine parameters (peak voltage, peak current and peak power) influenced by the flux rate of oxygen (oxygen partial pressure). An apparent decrease in peak voltage and increase in peak current and peak power can be seen with an increase in the oxygen partial pressure. This phenomenon is different from that observed in reactive sputtering TiO_2 films by conventional DC or pulsed DC power, in which increase of cathode voltage and corresponding decrease of cathode current is always encountered with increase of oxygen pressure [23,24]. Magnus et al. [25] observed similar phenomenon when they deposited TiN films by a HIPIMS technique. They attributed the reason to the self-sputtering in HIPIMS discharge. HIPIMS differs significantly from conventional DC magnetron sputtering due to the fact that self-sputtering quickly becomes dominant and the working gas ions are depleted from the area in front of the target. The plasma ions are supplied by the target and not the working gas. The ion induced electron emission (ISEE) coefficient of TiN is larger than that of the Ti metal. Therefore, in a HIPIMS discharge, the current will increase when a nitride is formed on the target, opposite to what is seen in the DC sputtering. The HIPIMS+ discharge in this study is also a self-sputtering dominant discharge. The ISEE coefficient of Ti oxide is also larger than that of the Ti metal. Therefore, we observed the apparent decrease in peak voltage and increase in peak current and peak power as increasing the oxygen gas pressure in this study.

In Fig. 1b, the deposition rate decreased abruptly when the oxygen flux rate increased from 0 sccm to 5 sccm, which is corresponding to the fast increase of peak current and peak power in Fig. 1a. Further increase of oxygen flux rate resulted in no significant change. As confirmed by the inset photos of the specimens in Fig. 1b, the films deposited at oxygen flow rate less than 5 sccm (transition deposition mode) exhibited metallic characteristics (no transparency) while the films deposited at higher oxygen flow rate (oxide deposition mode) exhibited TiO_2 characteristics (transparency). The film deposition at oxygen flux rate of 10 sccm is in the stable oxide deposition status. Therefore, we choose this value for our subsequent experiment.

Fig. 2a and b shows the Ti 2*p* and O 1*s* core level XPS spectra recorded from the TiO_2 film deposited at oxygen flux rate of 10 sccm. The Ti $2p_{3/2}$ spectra could be resolved into two spin–orbit