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Journal of the European Ceramic Society 26 (2006) 2753–2759
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Low-temperature crystallization of tantalum pentoxide films under elevated pressure

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Received 27 February 2005; received in revised form 28 June 2005; accepted 3 July 2005
Available online 1 September 2005

Abstract

Ta_2O_5 thin films deposited via a metal-organic decomposition method were crystallized via atmospheric pressure annealing and a high-pressure crystallization (HPC) process. Ta_2O_5 thin films started to become crystallized at 700 °C as subjected to atmospheric pressure annealing. When the HPC process was adopted and annealing at 16.5 MPa was performed, the crystallization temperature of Ta_2O_5 films was greatly dropped to as low as 350 °C. The developed HPC process considerably reduced the thermal budget and energy consumption during film processing. The crystallized Ta_2O_5 phase was found to be homogeneously distributed within the HPC-derived films. With annealing at 700 °C under atmospheric pressure, the silicon species diffused from the substrates into the Ta_2O_5 layers, thereby leading to reduced dielectric constants. The HPC process effectively suppressed the interdiffusion between the substrates and dielectric layers by lowering the required heating temperature, and also significantly increased the dielectric constants of Ta_2O_5 thin films. The HPC process was confirmed to effectively lower the crystallization temperature and improve the dielectric properties of Ta_2O_5 thin films.

Keywords: Ta_2O_5; Films; X-ray methods

1. Introduction

Recently there is a rising demand for improving the performance of dynamic random access memory (DRAM). This kind of improvement can be achieved by increasing the number of interconnected layers in integrated circuits. In light of the trend for making compact devices, the development of new materials having high dielectric constants becomes much more important.[1] Tantalum pentoxide (Ta_2O_5) has been demonstrated to be a promising dielectric material used in dynamic random access memories.[2] Ta_2O_5 films have been utilized as capacitors,[3] oxygen sensors,[4] and optical wave guides.[5,6] These applications are based on the good chemical stability, high dielectric constants, high ionic conductivity, and superior optical properties of Ta_2O_5 films.

Ta_2O_5 thin films have been deposited by various techniques, such as chemical vapor deposition, thermal oxidation,[7–9] sputtering,[10] and chemical solution deposition.[11] The crystallization temperature of Ta_2O_5 films was reported to be around 700 °C.[12] The high-temperature heating results in interdiffusion of species between dielectric layers and substrates, and the diffusion of silicon leads to a reduction in the effective dielectric constants. In order to suppress the interfacial reactions between dielectric layers and microelectronic devices, the development of novel low-temperature crystallization processes is necessary.

A new high-pressure crystallization (HPC) process was lately developed by our group to reduce the crystallization temperature of Pb(Zr, Ti)O_3 films to 350 °C.[13,14] For conventional hydrothermal methods, the solution containing the constituent ions is filled into an autoclave container, and the crystallized particles will be formed due to the nucleation and growth in high-pressure environment. On the other hand, in the HPC process, only distilled water is filled in the autoclave

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doi:10.1016/j.jeurceramsoc.2005.07.054

container and the amorphous precursor films are positioned above the water surface. The amorphous films become crystallized during the heating processes in a high vapor-pressure environment at elevated temperatures.

In this study, we applied a similar process to crystallize tantalum oxide thin films at low temperatures. The precursor films of tantalum oxide were deposited via a metal-organic deposition (MOD) method. The deposited films were annealed via two processes viz. atmospheric pressure annealing and the HPC process. The microstructural and phase evolutions during these two processes were investigated. In addition, the diffusion phenomenon and the dielectric properties of Ta_2O_5 thin films crystallized via both processes were also studied. The HPC process was confirmed to effectively lower the crystallization temperature and improve the dielectric properties of Ta_2O_5 thin films.

2. Experimental

Ta_2O_5 thin films were prepared via a metal-organic decomposition method. Tantalum ethoxide [$Ta(OC_2H_5)_5$] dissolved in toluene was used as the starting materials. The prepared precursors were spin-coated onto Pt/Ti/SiO_2/Si substrates at a spinning rate of 3000–4000 rpm. Silicon wafers were first thermally oxidized to form a SiO_2 layer with a thickness of 200 nm. Then titanium was deposited on the top of this SiO_2 layer via the electron-gun technique to form a 30 nm thick layer. Platinum was subsequently deposited on the top of the titanium layer via the same technique to form a 200 nm thick layer. The platinum layer was used as the bottom electrode, and the titanium layer served to enhance the adhesion of the platinum layer onto the silicon oxide layer. The coated films were baked on a hot plate at 150 °C for 30 min to evaporate the organic solvent, and subsequently pyrolyzed at 350 °C for 30 min. The spinning–baking–pyrolyzing cycle was repeated for three to four times to achieve proper film thickness. The 350 °C pyrolyzed films were amorphous with a thickness of around 0.20 μm.

The pyrolyzed films were annealed via two types of annealing processes. The first method was to anneal the pyrolyzed films in a furnace under atmospheric pressure (0.1 MPa) in flowing oxygen at temperatures ranging from 500 to 800 °C at a heating rate of 30 °C/s. The second method (the HPC process) was to anneal the precursor films in a closed bomb under high pressure. A sealed stainless-steel (T316-SS) bomb was used as the autoclave container. The bottom of the bomb was filled with distilled water to produce a high vapor-pressure environment at elevated temperatures. The pyrolyzed films were positioned above the water surface and the pressure in the bomb was determined by the saturated vapor-pressure. This autoclave container was surrounded by a heating system which was controlled by a programmable controller. One thermal couple was inserted into the water for measuring the temperature. The heating rate was set to 10 °C/min. Once it reached the pre-set temperature in the autoclave, the heating process was continued for 30 min to 1 h. Being sealed in a closed bomb at elevated temperature, the saturated vapor created a high-pressure environment during the heating process. When the temperature was raised to 250–350 °C, the pressure was increased to 4.0–16.5 MPa.

The formed crystalline phases of the heated films were identified via X-ray diffraction (XRD) analysis. The surface morphologies were examined via scanning electron microscopy (SEM) and also via an atomic force microscope (AFM) using a tapping mode with amplitude modulation. Secondary ion mass spectroscopy (SIMS) was conducted to determine the depth profiles of the prepared thin films. In order to analyze the distribution of phases in the crystallized thin films, grazing incident X-ray diffraction (GIXRD) was performed. The dielectric properties of tantalum oxide films were measured using an impedance analyzer. The measuring voltage was 0.1 V and the frequency was between 50 Hz and 1 MHz.

3. Results and discussion

3.1. Crystallization of Ta_2O_5 thin films annealed under atmospheric pressure

The as-deposited films pyrolyzed at 350 °C were found to be amorphous according to XRD analysis. Post-annealing was required to crystallize Ta_2O_5 thin films. Fig. 1 illustrates the XRD patterns of Ta_2O_5 thin films annealed under atmospheric pressure at various temperatures. When the annealing temperature was increased up to 650 °C, the heated films remained amorphous. With 700 °C annealing, the crystallization process began to proceed, and β-Ta_2O_5 was formed. The XRD pattern of this formed phase was consistent with the data recorded in ICDD No. 25-922.[15] With a further rise in the annealing temperature, the crystallinity of β-Ta_2O_5 was

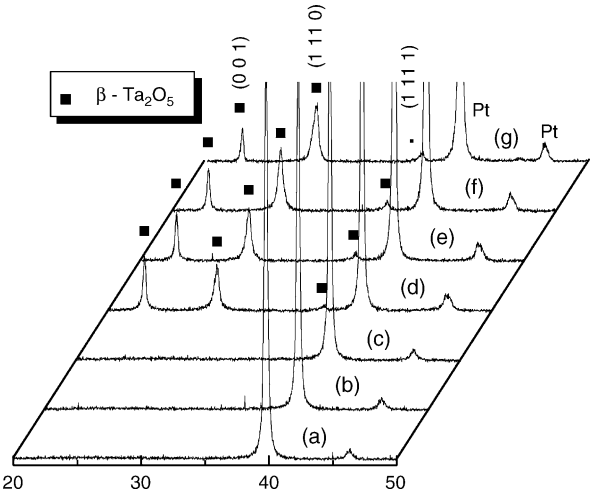

Fig. 1. X-ray diffraction patterns of (a) as-pyrolyzed Ta_2O_5 thin films and the films annealed under atmospheric pressure at (b) 600 °C, (c) 650 °C, (d) 700 °C, (e) 750 °C, (f) 800 °C, and (g) 850 °C.

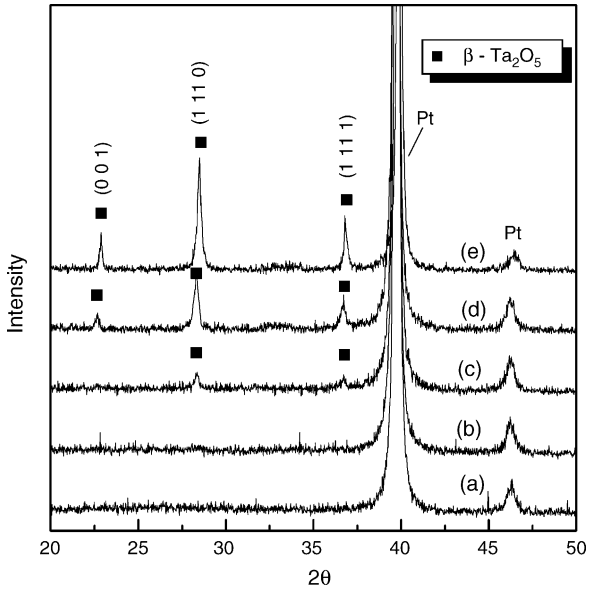

Fig. 2. X-ray diffraction patterns of (a) as-pyrolyzed Ta_2O_5 thin films and the HPC-derived Ta_2O_5 films annealed at (b) 300 °C under 8.6 MPa, (c) 320 °C under 11.3 MPa, (d) 340 °C under 14.5 MPa, and (e) 350 °C under 16.5 MPa.

enhanced. These results indicate that the crystallization temperature of Ta_2O_5 thin films needs to be as high as 700 °C, which is similar to that reported in literature.[16]

3.2. Crystallization of Ta_2O_5 thin films via the HPC process

In order to lower the crystallization temperature of Ta_2O_5 thin films, the high-pressure crystallization process was adopted. The XRD patterns of Ta_2O_5 films annealed via the HPC process are illustrated in Fig. 2. No crystallized phase was observed after annealing at 300 °C under 8.6 MPa for 1 h. As the heating temperature and process pressure increased respectively to 320 °C and 11.3 MPa, a small amount of crystallized Ta_2O_5 was formed. Well-crystallized Ta_2O_5 thin films were obtained as the heating temperature reached 340 °C under a process pressure of 14.5 MPa. The formed phase was confirmed to be β-Ta_2O_5. Fully crystallized Ta_2O_5 thin films were produced after annealing at 350 °C under 16.5 MPa, and the formed phase was confirmed to be β-Ta_2O_5. The above results indicate that the adoption of the high-pressure process successfully lowered the crystallization temperature of Ta_2O_5 thin films from 700 to 350 °C. This temperature was lower than the results reported by Lin et al.,[17] who deposited Ta_2O_5 thin films on Ru-film coated substrates and annealed the films in H_2 atmosphere to reduce the crystallization temperature of Ta_2O_5 thin films to 400 °C. The developed HPC process in this study considerably reduced the thermal budget and energy consumption during film processing.

Fig. 3 shows the SEM micrographs of Ta_2O_5 thin films crystallized via the HPC process. After annealing at 300 °C under 8.6 MPa as shown in Fig. 3(a), the films were amorphous and no specific feature was observed. Once the films began to become crystallized after annealing at 320 °C under 11.3 MPa, certain special clusters with irregular shapes were formed as demonstrated in Fig. 3(b). These clusters were nuclei of crystallized Ta_2O_5. With 340 °C annealing under 14.5 MPa, the surface of Ta_2O_5 thin film was covered with the clustered grains with a size of 0.1–0.2 μm. When the temperature and pressure were increased respectively to 350 °C and 16.5 MPa, the number of the clustered grains was further increased. By comparing the XRD data in Fig. 2 with the SEM photographs in Fig. 3, the crystallization of Ta_2O_5 was confirmed to take place after annealing at 320 °C under 11.3 MPa.

The surface morphology of Ta_2O_5 thin films prepared via the two processes was examined via AFM. Fig. 4(a) shows the AFM image of the 350 °C pyrolyzed films. The pyrolyzed film was rather smooth without any specific feature. The microstructures of Ta_2O_5 prepared via atmospheric pressure annealing at 700 °C and the HPC process at 350 °C under 16.5 MPa are shown in Fig. 4(b) and (c), respectively. Both films exhibited a particulate feature. The magnitudes of the roughness of the film prepared via atmospheric pressure annealing and the HPC process were 4.5 and 10.1 nm, respectively. The greater roughness in the films prepared via the HPC process is considered to result from the formation of clustered grains during the crystallization process.

3.3. Effects of pressure and annealing time on the formation of crystallized Ta_2O_5 during the HPC process

For investigating the influence of pressure on the formation of crystallized Ta_2O_5, various pressures were applied during the HPC process. To adjust the pressure during the HPC process, various amounts of distilled water were filled into the bomb. Saturated vapor-pressure was generated when provided with sufficient quantity of water. If the water amount was insufficient, vapor-pressure was reduced. As illustrated in Fig. 5, the films remained amorphous after heating at 340 °C under 10.3 MPa. When the pressure was increased to 11.0 MPa, a small amount of crystallized Ta_2O_5 was formed. Once the vapor-pressure was raised to 14.5 MPa and reached the saturated status at 340 °C, well-crystallized Ta_2O_5 thin films were formed. These results indicate that the crystallization process is dependent on the pressure during the HPC process.

For elucidating the effects of annealing time on the formation of crystallized Ta_2O_5, various heating durations were performed during the HPC process. Fig. 6(a)–(c) illustrate the XRD patterns of Ta_2O_5 thin films heated at 350 °C under 16.5 MPa for 15, 30, and 60 min, respectively. After heating for 15 min, a small amount of crystallized Ta_2O_5 was produced. With an increase in the heating time, the crystallization degree of Ta_2O_5 thin films was increased. After heating for 60 min, the crystallization of Ta_2O_5 thin films was nearly complete. Prolonging the heating time led to complete

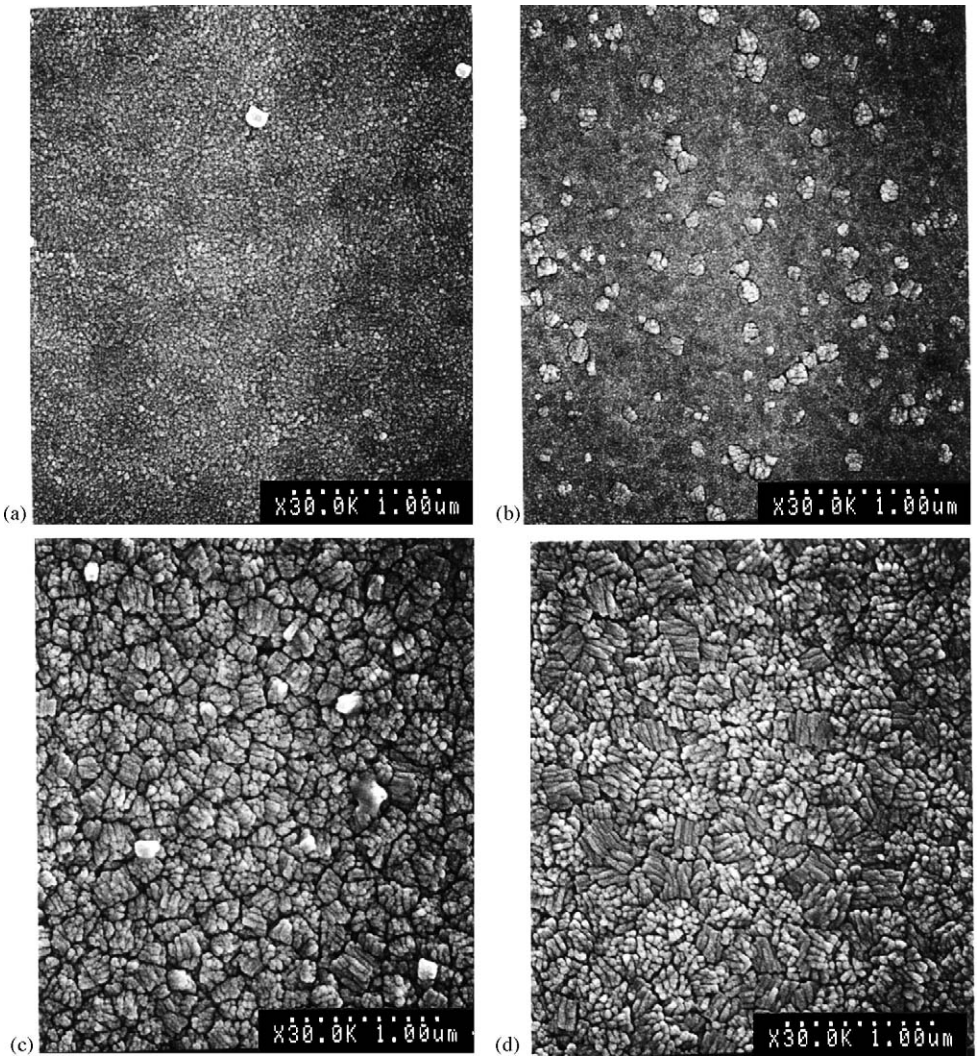

Fig. 3. Scanning electron micrographs of the HPC-derived Ta_2O_5 films annealed at (a) 300 °C under 8.6 MPa, (b) 320 °C under 11.3 MPa, (c) 340 °C under 14.5 MPa, and (d) 350 °C under 16.5 MPa.

development of crystallized Ta_2O_5. The formation of crystallized phases from amorphous films usually involves both the nucleation and growth stages. According to the classical nucleation theory, it is known that the critical nucleation energy for forming stable nuclei depends on the pressure.[18,19] The high-pressure annealing process might lead to a reduction in the critical free energy required for the formation of stable nuclei, and promotes the nucleation process at low temperatures. A possible alternative mechanism is that the high vapor-pressure developed during the process probably forms a water coating on the film surface, thereby facilitating a dissolution-precipitation process to produce the crystallized nuclei at low temperatures.[20]

In order to examine the distribution of crystallized Ta_2O_5 within the films, grazing incidence X-ray diffraction analysis was performed. Fig. 7 shows the GIXRD patterns of Ta_2O_5 thin films prepared via the two different processes at incidence angles $\alpha = 0.5°$, 1°, and 1.5°. Based on the calculation equation of penetration depth,[21] the depths that X-ray penetrated into the thin films were calculated to be 0.07, 0.14, and 0.21 μm for the above three incidence angles. As illustrated in Fig. 7(a), the crystallinity of Ta_2O_5 thin films annealed at 700 °C under atmospheric pressure was almost the same in different depths of thin films. From Fig. 7(b) and (c), similar behaviors were also observed in Ta_2O_5 thin films prepared via the HPC process. In spite of the difference in crystallization temperature, the crystallinity of Ta_2O_5 thin films was independent of the distinct position of depth. The GIXRD results corroborate that crystallized Ta_2O_5 phase was homogeneously distributed in the thin films prepared via the both processes.

The depth profiles of constituent species measured via SIMS for Ta_2O_5 thin films prepared via both processes are illustrated in Fig. 8. As shown in Fig. 8(a), the distribution of silicon and titanium expended through platinum to Ta_2O_5 layer as the thin film was annealed at 700 °C under atmospheric pressure. The SIMS analysis indicated that the high-temperature annealing inevitably caused extensive outward

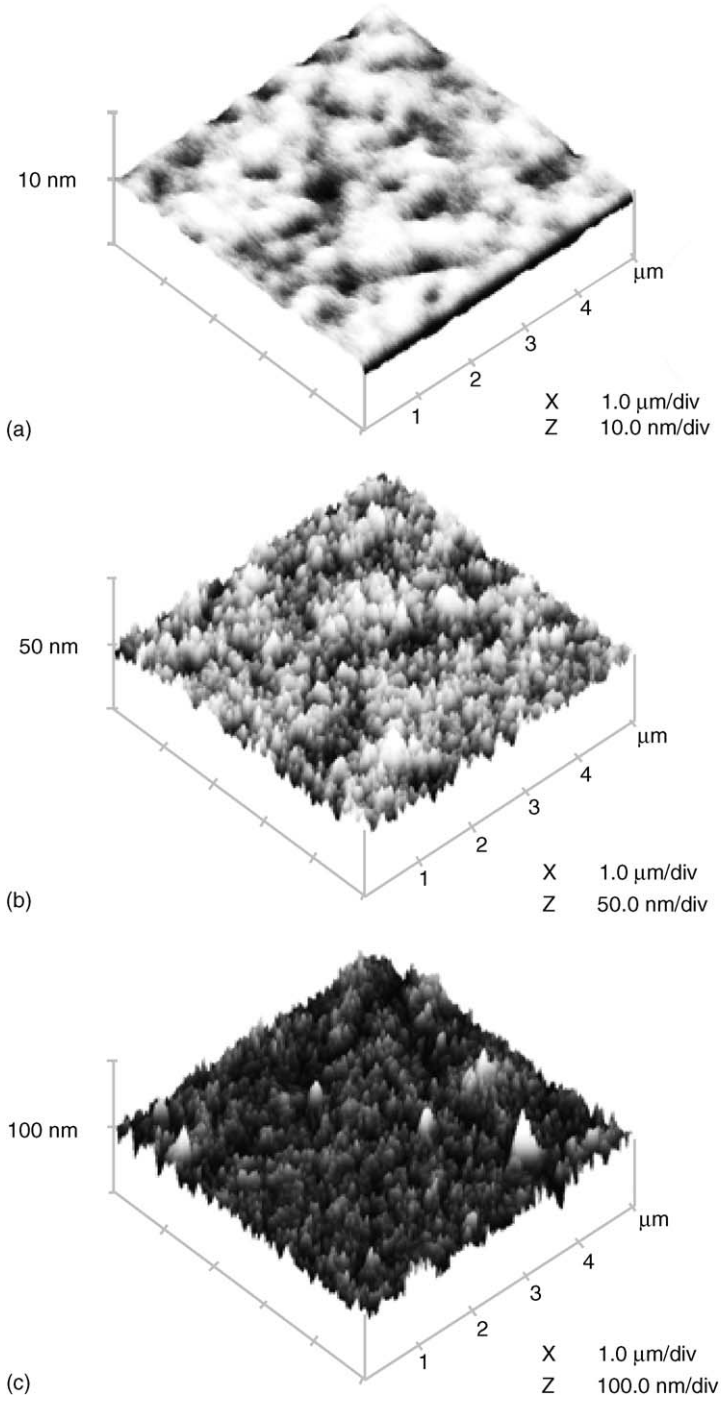

Fig. 4. Atomic force micrographs of (a) as-pyrolyzed Ta_2O_5 films, (b) Ta_2O_5 films annealed at 700 °C under atmospheric pressure, and (c) Ta_2O_5 films annealed at 350 °C under 16.5 MPa.

diffusion of silicon and titanium species from the substrates and bottom electrodes into the dielectric layers. On the other hand, when the films were annealed via the HPC process at 350 °C as illustrated in Fig. 8(b), the diffusion of titanium and silicon species was limited. The SIMS results suggest that the interdiffusion between the substrates and dielectric layers was effectively suppressed by employing the HPC process due to lowering of the required crystallization temperatures.

The dielectric properties of Ta_2O_5 thin films crystallized via atmospheric pressure annealing and the HPC process were determined. The dielectric constant of Ta_2O_5 thin films annealed at 700 °C under atmospheric pressure was 27.5. After annealing at 850 °C, the constant was reduced to 11. The decrease in the dielectric constant of Ta_2O_5 thin films was considered to relate to the diffusion of silicon species. The diffused silicon species formed SiO_2 at the interface

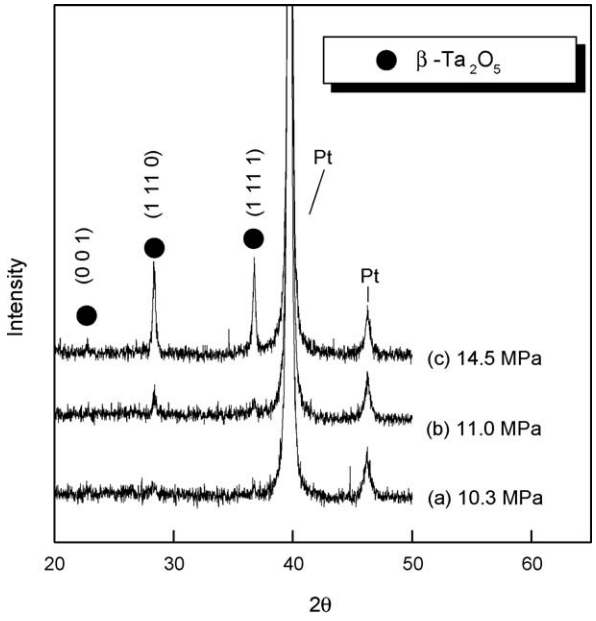

Fig. 5. X-ray diffraction patterns of Ta_2O_5 thin films annealed at 340 °C under (a) 10.3 MPa, (b) 11.0 MPa, and (c) 14.5 MPa.

between Ta_2O_5 and Pt layers and resulted in reduced dielectric constant of dielectric layers.[22] On the other hand, the dielectric constant of Ta_2O_5 thin films crystallized at 350 °C via the HPC process was 30.0. The greater dielectric constant of Ta_2O_5 thin films crystallized via the HPC process was ascribed to the low crystallization temperature that effectively suppressed the diffusion of silicon species. The HPC process was confirmed to not only lower the crystallization temperature of Ta_2O_5 thin films, but also improve their dielectric properties.

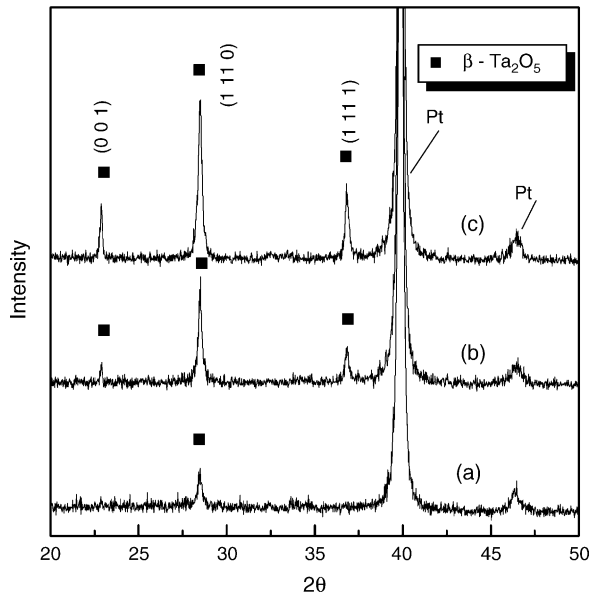

Fig. 6. X-ray diffraction analysis for Ta_2O_5 thin films crystallized via HPC process at 350 °C for (a) 15 min, (b) 30 min, and (c) 60 min.

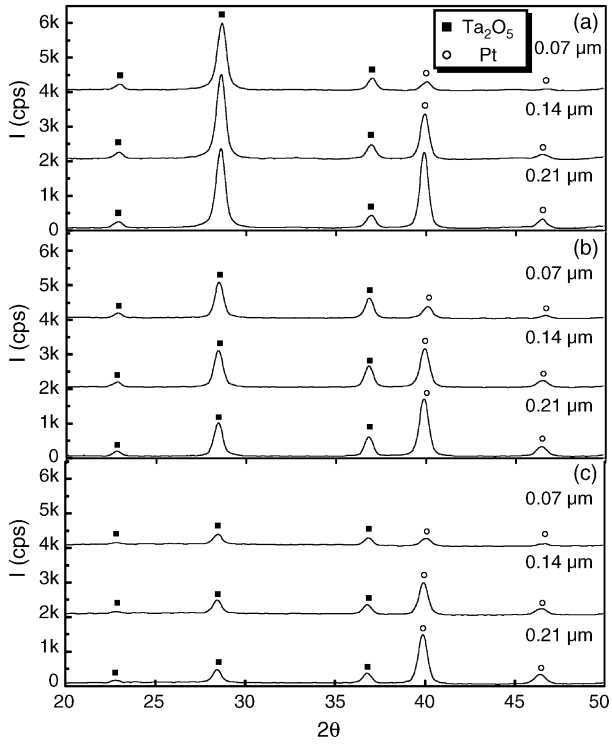

Fig. 7. GIXRD diffraction patterns of Ta_2O_5 thin films annealed at (a) 700 °C under atmospheric pressure, (b) 350 °C under 16.5 MPa, and (c) 320 °C under 11.3 MPa.

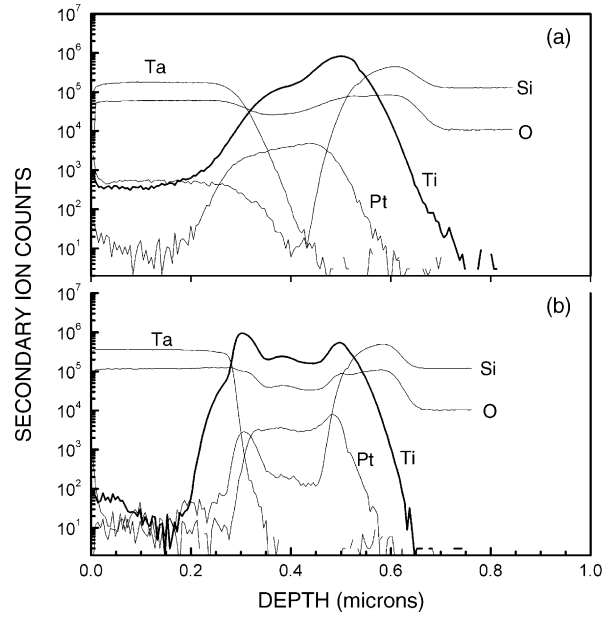

Fig. 8. Secondary ion mass spectroscopic profiles of Ta_2O_5 thin films on $Pt/Ti/SiO_2/Si$ substrates. The films were annealed at (a) 700 °C under atmospheric pressure and (b) 350 °C under 16.5 MPa.

4. Conclusions

The crystallization process of Ta_2O_5 thin films deposited via a metal-organic decomposition process was investigated

in this study. When Ta_2O_5 films were annealed under atmospheric pressure, the crystallization of the films started to take place at 700 °C. As the HPC process was adopted and annealing at 16.5 MPa was performed, the crystallization temperature of Ta_2O_5 films was substantially lowered to 350 °C. The development of crystallized Ta_2O_5 during the HPC process was related to the applied pressure and heating durations. According to SIMS analysis, crystallized Ta_2O_5 phase was found to homogeneously distribute within the films prepared via the HPC process. During high-temperature annealing under atmospheric pressure, the silicon species diffused from the substrates into Ta_2O_5 layers, and the dielectric constants of the prepared films were decreased. On the other hand, the interdiffusion between the substrates and dielectric layers was suppressed during the HPC process by lowering the heating temperatures, and the dielectric constants of Ta_2O_5 thin films were increased. The HPC process was confirmed to not only effectively reduce the thermal budget and energy consumption during film processing, but also improve the dielectric properties of Ta_2O_5 thin films.

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