JOURNAL OF
Materials
Chemistry
Communication

Low-temperature crystallization of electroceramic thin films at elevated pressure

Chung-Hsin Lu,* Yi-Chou Chen and Yu-Chang Sun

Electronic and Electro-optical Ceramics Laboratory, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, R.O.C. E-mail: chlu@ccms.ntu.edu.tw

Received 1st March 2002, Accepted 22nd March 2002
First published as an Advance Article on the web 9th April 2002

The crystallization of electroceramic thin films derived from amorphous precursor films has been significantly enhanced by using a high vapor-pressure annealing process as low as 350 °C. This method not only considerably reduces the thermal budget and energy consumption during film processing, but also alleviates the interdiffusion between films and substrates.

Electroceramic thin films have attracted considerable interest for applications in nonvolatile ferroelectric random access memories (FeRAM) due to their large reversible spontaneous polarization[1,2] and in dynamic random access memories (DRAM) because of their high dielectric permittivity.[3–5] Usually the formation of well crystallized electroceramic films requires high-temperature annealing (>500 °C);[6–8] however, this will accelerate undesirable interdiffusion at the film–substrate interface, and cause malfunctions in ceramic films. To integrate electroceramic films with silicon ULSI technology, lowering the temperature for the formation of crystallized ceramic films is indispensable. Previously, hydrothermal processing, laser annealing, ion-beam bombardment and electron-beam irradiation were developed for producing crystallized ceramic films at low temperatures.[9–12] In hydrothermal processing, the substrates are immersed into reactive solutions and directly reacted with solutions to form the desired compounds. Because these reactive solutions usually contain acid or alkaline reactants, substrate corrosion or other unfavorable reactions are prone to occur. High excitation energy sources such as lasers, ion or electron beams might produce defects in the ceramic films, thereby impairing their electrical properties. In order to overcome the above shortcomings, we have developed a new high vapor-pressure ($\geqslant 14.6$ MPa) annealing process for crystallizing electroceramic thin films with various crystal structures at low temperatures.

The precursor films of tantalum pentoxide (Ta_2O_5) were prepared using radio frequency (RF) sputtering. (100) n-type silicon wafers with a conductivity of 2.5×10^5 Ω cm were used as the substrates. The substrates were heated to 1050 °C in dry oxygen to form an insulating SiO_2 layer of about 150 nm in thickness, followed by deposition onto a titanium (50 nm)–platinum (150 nm) double layer. The titanium layer was employed to improve the adhesion, and the platinum layer served as the bottom electrode. A chamber pressure of 20 mTorr was maintained during the deposition process using a mixture of argon and oxygen gases at a flow-rate ratio of 4 : 1. The sputtering process was carried out using 100 W of electric power and the substrate temperature was kept at 200 °C. The thickness of the as-deposited films was around 0.15 µm. On the other hand, the precursor films of niobium pentoxide, lead zirconate titanate, and lead niobate were prepared from the respective metal-organic solutions using the spin-coating method. Niobium ethoxide dissolved in 2-methoxyethanol at a weight ratio of 1 : 1 was used as the precursor for Nb_2O_5. To prepare the precursor of $Pb_2Nb_2O_7$, lead 2-ethylhexanoate was first dissolved in toluene at a weight ratio of 1 : 3, and then this lead-containing solution was mixed with the above niobium ethoxide/2-methoxyethanol solution according to the stoichiometric composition of $Pb_2Nb_2O_7$. Mitsubishi Materials Corp provided the lead zirconate titanate (PZT) starting solution prepared from lead acetate, zirconium butoxide, and titanium isobutoxide with a composition of $Pb^{2+} : Zr^{4+} : Ti^{4+} = 1.25 : 0.4 : 0.6$. All of the prepared precursors were spin-coated onto the $Pt/Ti/SiO_2/Si$ substrates at a spinning rate of 3000–4000 rpm. The coated films were first dried at 150 °C using a hot plate, and subsequently pyrolyzed in a furnace at 350 °C for 30 min to evaporate the organic solvent. The thickness of the pyrolyzed films was in the range of 0.15–0.2 µm. The above precursor films were annealed in two types of annealing processes. The first method involved annealing the as-deposited films in a furnace under atmospheric pressure (0.1 MPa) at temperatures ranging from 500 °C to 700 °C for 2 h. The second method was to anneal the films in a closed bomb under high pressure ranging from 12.1–16.5 MPa at 325–350 °C for 30 min–2 h. The bottom of the bomb was filled with distilled water to produce a high vapor-pressure environment at elevated temperatures. The as-deposited films were positioned above the water surface and the pressure in the bomb was determined by the saturated vapor pressure. It should be noted that this process is different from the previous hydrothermal processes,[13,14] since there is no direct contact between the solution and the as-deposited films. The phases of the annealed films were identified by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The surface morphologies of the films were analyzed by scanning electron microscopy (SEM). The composition depth profiles of the prepared films were analyzed *via* secondary ion mass spectroscopy (SIMS). The dielectric properties of annealed Ta_2O_5 films were measured by an impedance analyzer in the metal–insulator–metal (MIM) configuration with platinum as the top electrode.

The as-deposited films of Ta_2O_5 were annealed under atmospheric pressure (0.1 MPa) for 2 h. It was found that no crystallized Ta_2O_5 was formed until the temperature was raised to 700 °C (Fig. 1(a)). Annealing at 325 °C under 12.1 MPa for 2 h yielded only amorphous films; however, annealing at 340 °C under 14.6 MPa slightly triggered the crystallization of Ta_2O_5 films. After annealing at 350 °C under 16.5 MPa, highly crystallized Ta_2O_5 films were obtained (Fig. 1(b)). The observed diffraction peaks corresponding to the (001), (1 11 0) and (1 11 1) planes were characteristic of the orthorhombic Ta_2O_5 phase, consistent with the related ICDD Powder Diffraction File.[15] Accordingly, it is clear that the high-pressure process converted the amorphous films into the crystalline Ta_2O_5 phase with a significant drop in the heating temperature from 700 °C to 350 °C. The relative degree of crystallization was calculated using the integrated intensity of

DOI: 10.1039/b202186m

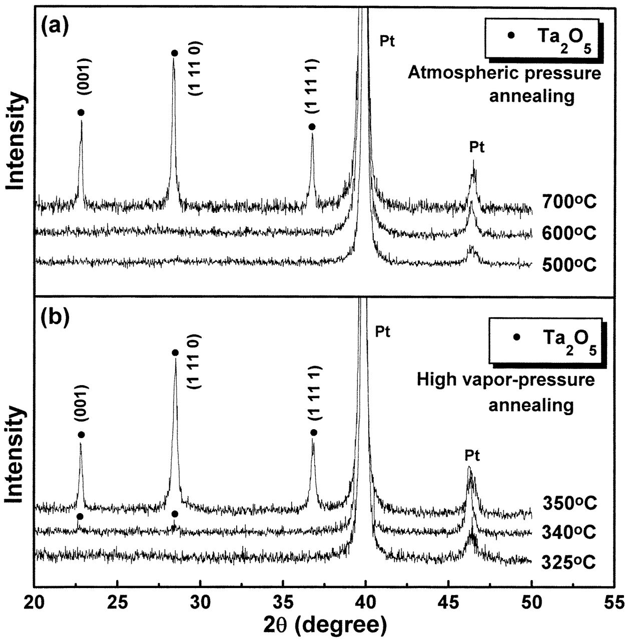

Fig. 1 X-Ray diffraction patterns of the radio-frequency sputtered tantalum pentoxide (Ta_2O_5) precursor films on $Pt/Ti/SiO_2/Si$ substrates treated with (a) atmospheric pressure (0.1 MPa) annealing and (b) high vapor-pressure annealing. The pressures corresponding to annealing temperatures of 325, 340 and 350 °C are 12.1, 14.6, and 16.5 MPa, respectively.

the (1 11 0) peak of the sample annealed at 750 °C as a reference. It was found that the relative degree of crystallization of the films annealed at 350 °C under 16.5 MPa was 93%, which was as high as that of a sample annealed at 700 °C under atmospheric pressure (92%).

The precursor films showed no distinct morphological features. However, upon annealing at 350 °C under 16.5 MPa for 30 min, some rosette-like grains (100–200 nm) were randomly distributed in the films (Fig. 2(a)), indicating the formation of crystalline Ta_2O_5 nuclei. The central nucleus in the rosette structure was clearly identified and the grain growth was observed to be distinctly radial in direction. The crystallization of Ta_2O_5 is considered to be initiated by a primary nucleation center, then proceeding to subsequent radial growth from the central point. After annealing at 350 °C for 2 h, the rosette-like morphology further expanded and the particles coalesced to produce the film surface shown in Fig. 2(b). A similar rosette-like microstructure was observed during the initial nucleation stage in the perovskite lead zirconate titanate films.[16,17]

The bright-field TEM image also confirmed the formation of rosette-like grains after high vapor-pressure annealing (Fig. 2(c)). The corresponding selected-area electron diffraction (SAED) exhibited a spotty pattern, distinctly verifying the crystalline characteristics. The *d*-spacing values calculated from the SAED pattern were in good agreement with the values reported,[15] thereby confirming the formation of the crystalline Ta_2O_5 phase. The SAED pattern for the region corresponding to the matrix region showed a halo structure, revealing the amorphous nature of this region. These observations indicate that high vapor-pressure annealing resulted in the nucleation of the amorphous matrix for the formation of crystalline Ta_2O_5. In principle, the formation of the crystalline phases from amorphous films involves several stages of nucleation and growth. Based on the classical nucleation theory, it is known that the critical nucleation energy for the formation of a stable nucleus depends on the pressure.[18,19] The high vapor-pressure treatment may lead to a decrease in the critical free energy required for the formation of a stable nucleus, thereby promoting the nucleation process at lower temperatures. The other plausible 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[20,21] to produce the crystallized phase at lower temperatures. Further details related to the crystallization process are under investigation.

The depth composition profiles of the annealed Ta_2O_5 films were examined. As illustrated in Fig. 3(a), in the film annealed at 700 °C under normal pressure, titanium from the substrate diffused extensively outward from the intervening layer and tantalum species also diffused into the substrate region. In the film annealed at 350 °C under high-pressure (16.5 MPa), a clear boundary between the Ta_2O_5 thin film and the substrate region was observed (Fig. 3(b)), revealing that both the diffusion of titanium species into the Ta_2O_5 film and the counter-diffusion of tantalum species into the substrate were prevented. This is attributed to the reduced diffusion rate and mobility of the constituent species at low temperatures during the high vapor-pressure annealing process.

The dielectric constants of annealed Ta_2O_5 films were measured using platinum as the top electrode. During annealing under atmospheric pressure at low temperatures,

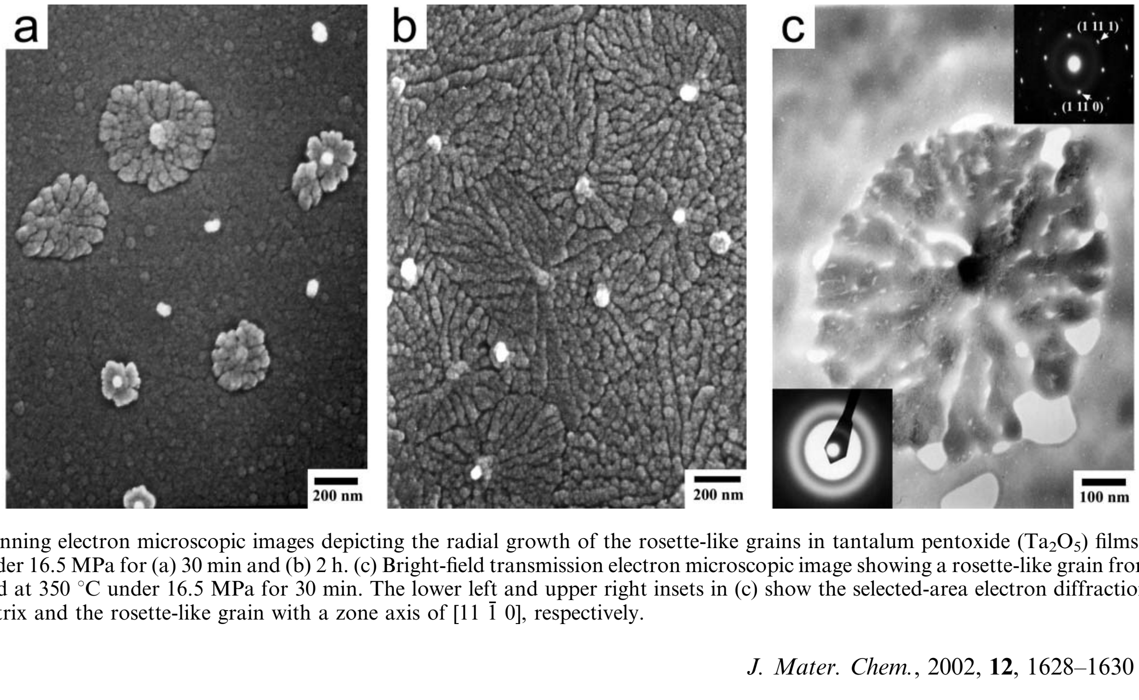

Fig. 2 Scanning electron microscopic images depicting the radial growth of the rosette-like grains in tantalum pentoxide (Ta_2O_5) films heated at 350 °C under 16.5 MPa for (a) 30 min and (b) 2 h. (c) Bright-field transmission electron microscopic image showing a rosette-like grain from a Ta_2O_5 film heated at 350 °C under 16.5 MPa for 30 min. The lower left and upper right insets in (c) show the selected-area electron diffraction patterns of the matrix and the rosette-like grain with a zone axis of [11 $\bar{1}$ 0], respectively.

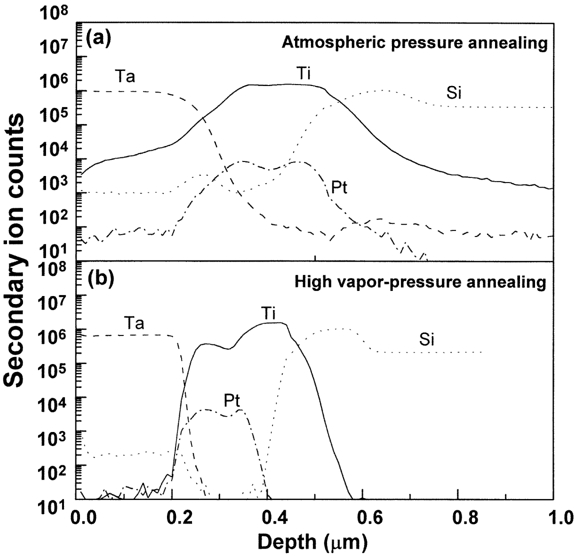

Fig. 3 Secondary ion mass spectroscopic profiles for tantalum pentoxide (Ta_2O_5) films on Pt/Ti/SiO_2/Si substrates treated with (a) atmospheric pressure annealing at 700 °C and (b) high vapor-pressure annealing at 350 °C under 16.5 MPa.

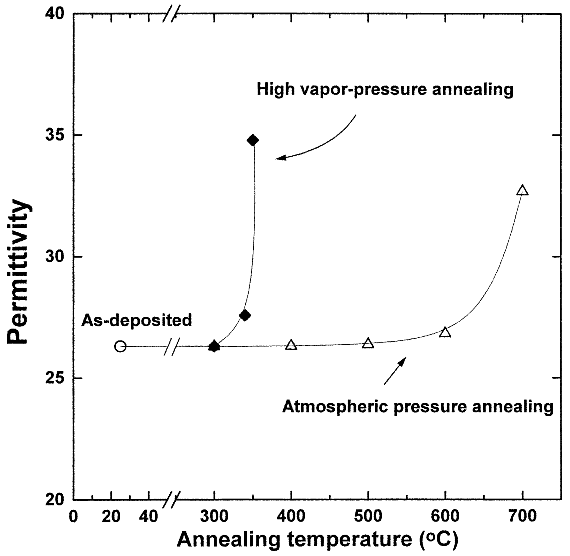

Fig. 4 Relation between the dielectric permittivity and annealing temperatures of tantalum pentoxide (Ta_2O_5) films annealed under atmospheric pressure and high vapor-pressure.

there was no significant changes in permittivity as the precursor films remained amorphous ($\varepsilon \cong 26$) (see Fig. 4). After annealing at 700 °C for 2 h, the outward diffusion of titanium into the Ta_2O_5 film (see Fig. 3) caused serious leakage in the samples. When the annealing time was reduced to 30 min at 700 °C, the dielectric permittivity was measurable and increased to 32.7 due to the film crystallization. Using high-pressure annealing significantly increased the permittivity of Ta_2O_5 films even when the heating temperatures were low. After annealing at 350 °C at high pressure, the dielectric permittivity of the Ta_2O_5 film rose markedly to 34.5. These results demonstrate that Ta_2O_5 films with high dielectric permittivity were obtained at relatively low temperatures using this new approach.

The high vapor-pressure process was also applied to other electroceramic films with disparate physiochemical properties, including niobium pentoxide (structure akin to tantalum pentoxide), lead zirconate titanate (perovskite structure), and lead niobate (pyrochlore structure). For the preparation of the above crystallized films at atmospheric pressure, normally the annealing temperature must be raised to 500–600 °C.[22–24] The precursor films were prepared by spin-coating using metal–organic solutions.

All of the precursor films were found to be amorphous in XRD. With annealing at 350 °C for 2 h under 16.5 MPa, all of the precursor films became crystallized. The obtained XRD patterns were consistent with those reported in the ICDD files.[25] The above preliminary results confirmed that the high vapor-pressure annealing could also enhance the crystallization of the above films at low temperatures. In conclusion, this developed high vapor-pressure annealing process can significantly decrease the thermal budget and energy consumption by greatly lowering the crystallization temperature. It can also alleviate the malfunctions in electroceramic films resulting from interdiffusion of the substrate species into the films, which normally occurs under high-temperature annealing.[26–28] The developed process appears to provide a potential approach to integrate versatile electroceramic films with semiconductor devices.

Notes and references

1 J. F. Scott and C. A. Paz de Araujo, *Science*, 1989, **246**, 1400.
2 Y. Tarui, T. Horai, K. Termoto, H. Koike and K. Nagashima, *Appl. Surf. Sci.*, 1997, **114**, 656.
3 D. E. Kotecki, *Integr. Ferroelectrics*, 1997, **16**, 1.
4 A. I. Kingon, J. P. Maria and S. K. Streiffer, *Nature*, 2000, **406**, 1032.
5 J. F. Scott, *Ferroelectrics*, 2000, **236**, 1.
6 P. C. Joshi and M. W. Cole, *J. Appl. Phys.*, 1999, **86**, 871.
7 T. Hata, S. Kawagoe, W. Zhang, K. Saaki and Y. Yoshioka, *Vacuum*, 1998, **51**, 665.
8 R. D. Dat, J. K. Lee, O. Auciello and A. I. Kingon, *Appl. Phys. Lett.*, 1995, **67**, 572.
9 M. Yoshimura and W. Suchanek, *Solid State Ionics*, 1997, **98**, 197.
10 X. M. Lu, J. S. Zhu, X. F. Huang, C. Y. Lin and Y. N. Wang, *Appl. Phys. Lett.*, 1994, **65**, 2015.
11 N. Yu, P. C. McIntyre, M. Nastasi and K. E. Sickafus, *Phys. Rev. B*, 1995, **52**, 17518.
12 N. Yu, K. E. Sickafus and M. Nastasi, *Mater. Chem. Phys.*, 1996, **46**, 161.
13 J. Zeng, C. Lin, J. Li and K. Li, *J. Mater. Res.*, 1999, **14**, 2712.
14 J. Zeng, M. Zhang, Z. Song, L. Wang, J. Li, K. Li and C. Lin, *Appl. Surf. Sci.*, 1999, **148**, 137.
15 Powder Diffraction File, Card No. 25-922. International Center for Diffraction Data, Newtown Square, PA.
16 A. H. Carim, B. A. Tuttle, D. H. Doughty and S. L. Martinez, *J. Am. Ceram. Soc.*, 1991, **74**, 1455.
17 S. P. Faure, P. Barboux, P. Gaucher and J. Livage, *J. Mater. Chem.*, 1992, **2**, 713.
18 S. C. Liao, W. E. Mayo and K. D. Pae, *Acta Mater.*, 1997, **45**, 4027.
19 B. Yao, F. S. Li, X. M. Lin, B. Z. Ding, W. H. Su and Z. Q. Hu, *J. Non-Cryst. Solids*, 1997, **217**, 317.
20 J. Moon, J. A. Kerchner, H. Krarup and J. H. Adair, *J. Mater. Res.*, 1999, **14**, 425.
21 K. W. Seo and J. K. Oh, *J. Ceram. Soc. Jpn.*, 2000, **108**, 691.
22 S. A. Mansour, G. L. Liedl and R. W. Vest, *J. Am. Ceram. Soc.*, 1995, **78**, 1617.
23 E. M. Griswold, L. Weaver, M. Sayer and I. D. Calder, *J. Mater. Res.*, 1995, **10**, 3140.
24 I. Zhitomirsky, *Mater. Lett.*, 1998, **35**, 188.
25 Powder Diffraction File, Card No. 27-1312, 33-784, and 40-828. International Center for Diffraction Data, Newtown Square, PA.
26 C. H. Lu and B. K. Fang, *J. Mater. Res.*, 1997, **12**, 2104.
27 F. C. Chiu, J. J. Wang, J. Y. M. Lee and S. C. Wu, *J. Appl. Phys.*, 1997, **81**, 6911.
28 C. H. Lu and C. Y. Wen, *J. Appl. Phys.*, 1999, **86**, 6335.