Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 254 (2008) 3921–3924
applied surface science
www.elsevier.com/locate/apsusc

Effect of annealing on thermal stability and morphology of pulsed laser deposited Ir thin films

Yansheng Gong [a,b,*], Chuanbin Wang [b], Qiang Shen [b], Lianmeng Zhang [b]

[a] School of Materials Science and Chemical Engineering, China University of Geosciences, Wuhan 430074, China
[b] State Key Laboratory of Advanced Technology for Material Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

Received 3 August 2007; received in revised form 11 December 2007; accepted 13 December 2007
Available online 23 December 2007

Abstract

Iridium (Ir) thin films, deposited on Si (1 0 0) substrate by pulsed laser deposition (PLD) technique using Ir target in a vacuum atmosphere, were annealed in air ambient and the thermal stability was investigated. The crystal structure and surface morphology of Ir thin films before and after being annealed were studied by X-ray diffraction, Raman scattering, scanning electron microscope, and atomic force microscopy. The results showed that single-phase Ir thin films with (1 1 1) preferred orientation could be deposited on Si (1 0 0) substrate at 300 °C and it remained stable below 600 °C, which showed a promising bottom electrode of integrated ferroelectric capacitors. Ir thin films got oxidized to IrO_2 at temperatures from 650 to 800 °C.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Iridium thin films; Annealing; Stability; Morphology; Pulsed laser deposition

1. Introduction

In highly integrated memory devices and high-density ferroelectric memories, the bottom electrodes should remain highly conductive, and the electrode should not be oxidizable or should form a conductive oxide [1,2]. Therefore, noble metals such as platinum (Pt), ruthenium (Ru), and conductive oxides are widely used for this purpose [3,4].

However, Pt deposited directly on Si plugs cannot be used since it readily reacts with silicon to form the silicide, which significantly reduces the properties. Compared with Ru and some conductive oxides, Ir has low oxygen permeability, high chemical stability, and good electric conductivity, which make Ir a potential bottom electrode in ferroelectric memories [5,6]. Moreover, the oxide of Ir is also a good conductive oxide (IrO_2), and the formation of IrO_2 can prevent the permeability of oxygen [7].

As an efficient technique, pulsed laser deposition (PLD) technique could produce higher quality films with better purity and improved adherence [8]. However, only a few reports were focused on the PLD Ir films [9,10], and the effect of annealing on thermal stability and morphology of Ir thin films had been little reported, which was an important property to consider for the applications of electrode materials. In this present work, the effects of annealing on thermal stability and morphology of Ir films deposited on Si (1 0 0) were investigated.

2. Experimental

Ir thin films were deposited by ablating a pure polycrystalline Ir target with a Q-switch pulsed Nd: YAG laser at a substrate temperature of 300 °C. At a repetition rate of 10 Hz, the laser (355 nm, 5 ns) beam of 100 mJ average pulse energy was focused at an angle of 45° onto a rotating target 2 cm in diameter. The substrate temperature was measured using a thermocouple embedded in the substrate holder beneath the substrate mounting area. In order to clean the target surface, 10 min pre-ablating was carried out before the deposition of Ir thin films. The distance between target and substrate was 50 mm and the base pressure of the deposition system was kept at 10^{-5}–10^{-6} Pa during Ir deposition. The annealing was carried out at 600–800 °C for 1 h in air ambient.

The crystal structure of the as-deposited and annealed films was examined by X-ray diffractometer with Cu Kα radiation.

* Corresponding author. Tel.: +86 27 87865674; fax: +86 27 87217002.
E-mail address: gongyansheng@hotmail.com (Y. Gong).

0169-4332/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2007.12.012

Raman scattering was also carried out to assist the identification of the annealed Ir films. Atom force microscopy (AFM) was used to measure the surface morphology and roughness of the films. The thickness was observed by scanning electron microscope (SEM).

3. Results and discussion

Fig. 1 shows the XRD patterns of Ir target and thin films grown on Si (1 0 0) substrate at a growth temperature of 300–400 °C. The θ–2θ scan data of the deposited films at 300 °C exhibited 2θ peaks at 40.86°, 47.45°, 83.68°, and 88.14°, respectively. Comparison of the relative intensities of the (1 1 1), (2 0 0), (3 1 1), and (2 2 2) diffraction peaks with the standard data for cubic iridium (JCPDS-430144) showed the presence of preferred orientation of the Ir planes along (1 1 1) reflection. The result was in agreement with what was previously observed by El Khakani et al. [11]. The (1 1 1) orientation was favoured most likely because the (1 1 1) crystallographic planes were close-packed in the fcc Ir structure. However, when the substrate temperature was increased to 400 °C, there appeared IrSi peaks besides Ir peaks, which was due to the reaction between Si substrate and Ir films at temperature above 400 °C. The result was in agreement with what was previously observed by Demuth et al. [12], who believed that the substrate temperature played an important role in the formation of Ir silicide. This suggests that single-phase Ir thin films with a preponderant (1 1 1) reflection could be obtained at substrate temperature of 300 °C.

The typical AFM plane image of Ir thin films at substrate temperature of 300 °C was shown in Fig. 2. It can be seen that the Ir film consist of closely spaced particles with a nearly dense texture and various shapes. The average particle size in the film was about 20 nm.

To study the thermal stability of Ir thin films, the Ir films deposited at 300 °C on Si (1 0 0) were annealed in air ambient. Fig. 3 shows the X-ray diffraction patterns of Ir thin films at annealing temperatures of 600–800 °C. As can be seen from

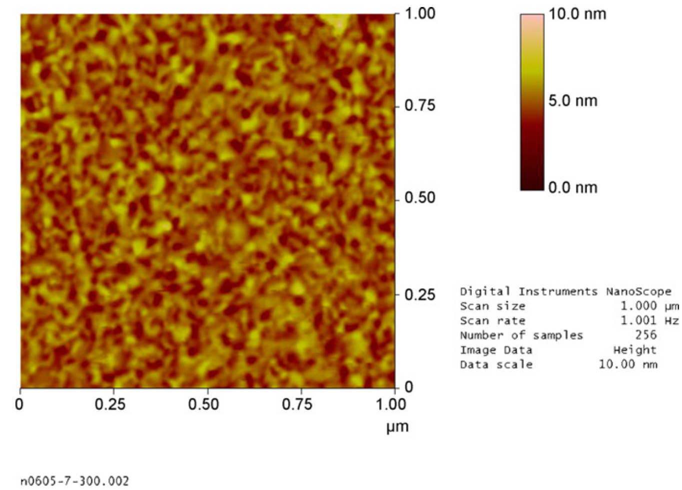

Fig. 2. The typical AFM plane image of Ir thin films at substrate temperature of 300 °C.

Fig. 3, Ir films did not oxidize in air up to 600 °C. Though there was no oxidized phase at 650 °C, the color of the surface of Ir films was different with that of Ir films annealed at 600 °C, which had the same color as the deposited Ir thin films at 300 °C. Raman scattering was carried out to assist the identification of the annealed Ir films. Fig. 4 shows the Raman spectra of Ir thin films at annealing temperatures of 650 and 750 °C for 1h. The three major Raman peaks of single crystal IrO_2 are located at 561, 728, and 752 cm^{-1} [13]. Good agreement between the observed and standard Raman peaks confirms that the deposited Ir films were oxidized to IrO_2 after being annealed at 650 °C for 1 h. This suggests that Ir films remained stable up to 600 °C. When the film was heated to 650 °C above, IrO_2 layer was formed on the surface of the Ir film. However, annealing temperature of 900 °C resulted in almost a total loss of Ir from the substrate due to the sublimation of Ir in the form of IrO_x at high temperature [8]. Though the formation of Ir silicide was found at a deposition temperature of 400 °C and above, the existence of Ir silicide was not detected during the annealing of Ir thin films at 600–800 °C in air

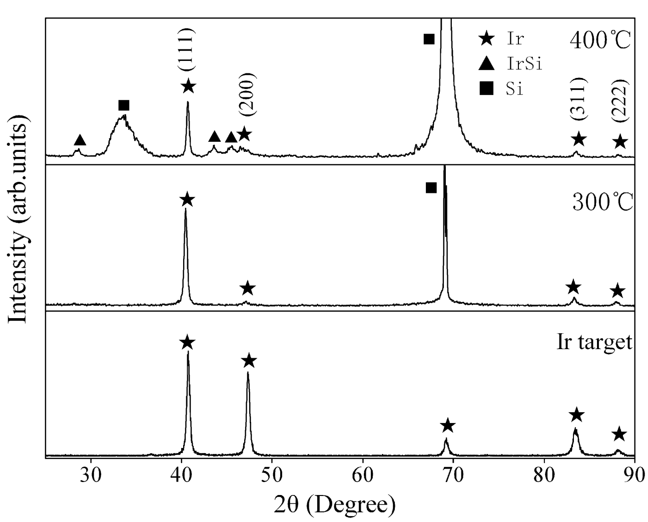

Fig. 1. X-ray diffraction patterns of Ir target and films deposited on Si (1 0 0) substrate at a growth temperature of 300–400 °C.

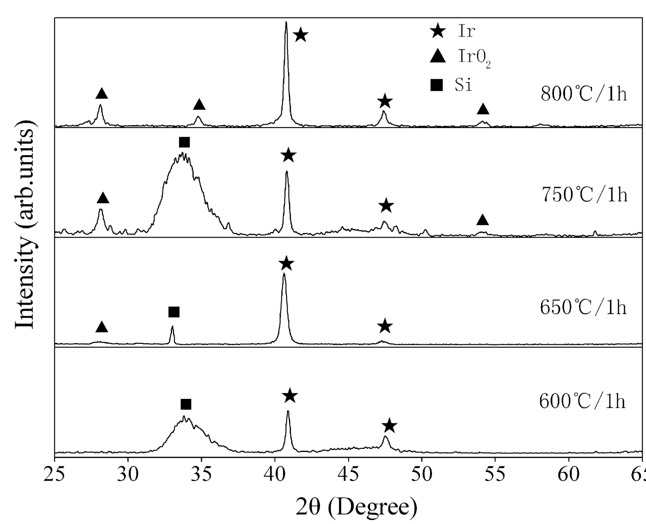

Fig. 3. X-ray diffraction patterns of Ir thin films at different annealed temperatures.

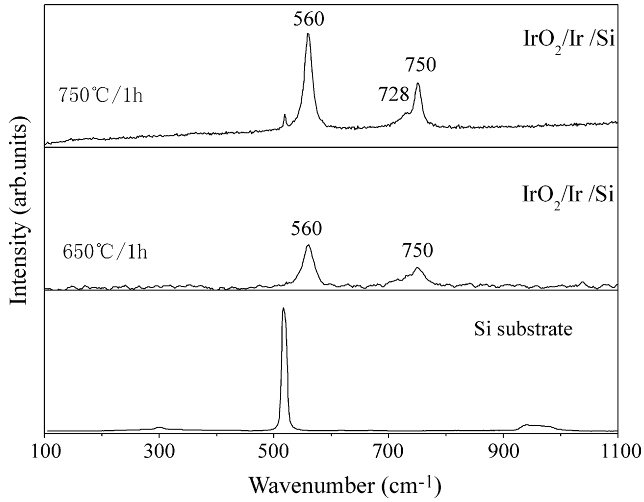

Fig. 4. Raman spectra of Ir thin films at different annealed temperatures.

ambient. In our opinion, the main reason was due to the higher surface mobility of the ablated species during deposition of Ir films than the course of annealing of Ir films. The results were very similar to what was previously observed by Jeon et al. [4].

Changes in the surface roughness as a function of the annealing temperature were determined using AFM. The AFM surface morphology results were showed in Fig. 5. The root mean square roughness (RMS) and surface max height range (low point to high point) of the Ir films as a function of annealed temperature were illustrated in Fig. 6. It is clearly observed that the surface morphology of the Ir films changed with the annealing temperature. The as-deposited Ir film was very smooth, with a RMS of 0.6 nm and a surface max height of 7 nm. The grain size and thus the surface roughness increased with the annealing temperature. The increase in crystallite size resulted from the enhancement of film surface atomic mobility with the increasing of temperature, which enabled the thermodynamically favoured grains to grow [14]. The results were very similar to what was observed by Kohli et al. [15]. From the as-deposited film to annealed film at 650 °C (Fig. 5(b) and Fig. 6), the root mean square roughness and surface max height grew almost linearly, RMS from 0.6 to 8.2 nm, max height from 7 to 17.4 nm. But the film annealed at 750 and 800 °C exhibited large jumps in the RMS and surface max height, which were clearly shown by the AFM images (Fig. 5(c) and (d)) and Fig. 6. The structural changes with annealing

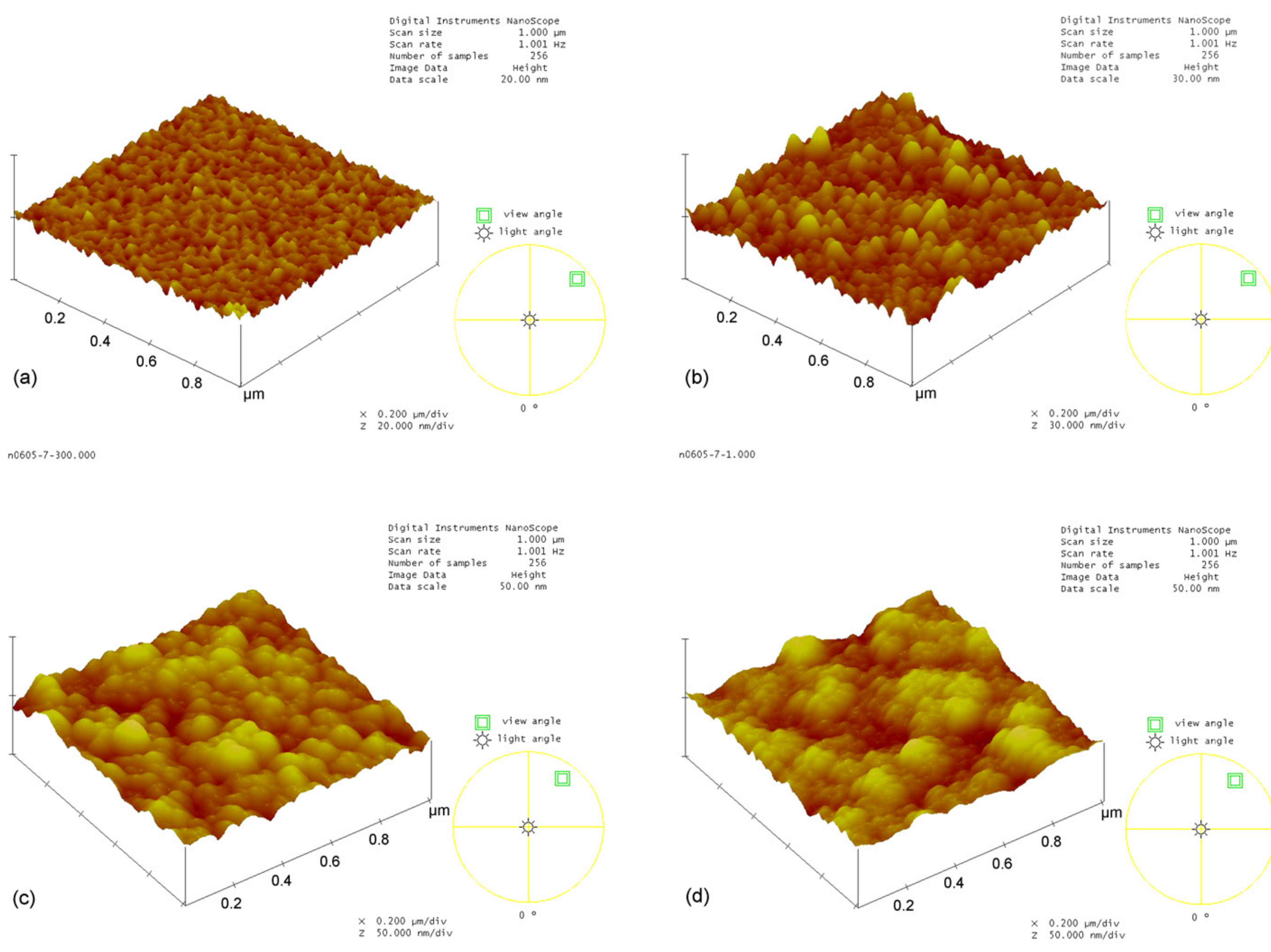

Fig. 5. The AFM stereo images of Ir thin films as a function of the annealed temperatures: (a) as-deposited, (b) 650 °C, (c) 750 °C, and (d) 800 °C.

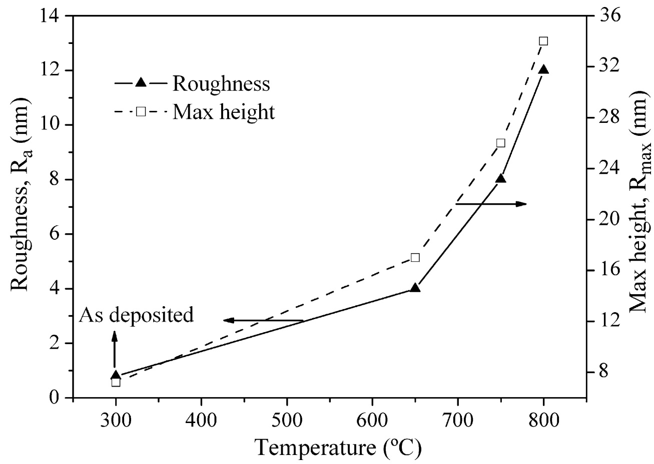

Fig. 6. Root mean square roughness and max height of Ir thin films as a function of annealing temperatures.

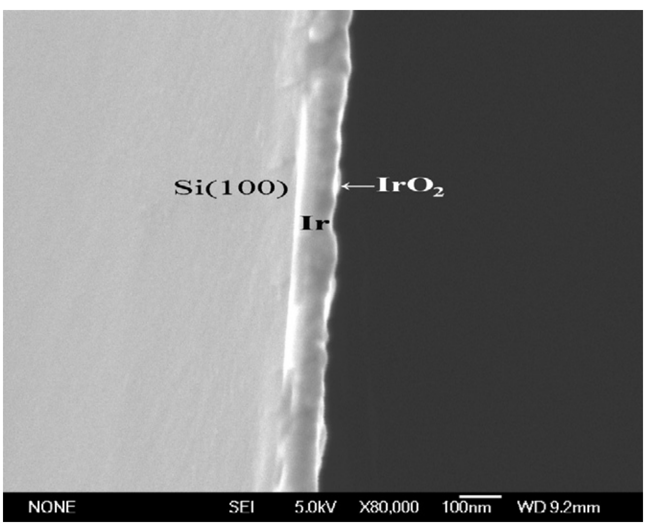

Fig. 7. SEM photographs of the cross-section of Ir films at an annealing temperature of 750 °C.

temperature were a result of the growth of IrO_2 crystalline structure [2], which were consistent with those obtained in XRD patterns (Fig. 3).

Fig. 7 shows the SEM photograph of the cross-section of as-deposited Ir film at an annealed temperature of 750 °C. It can be seen that the Ir film had exhibited good adhesion with the substrate and the thickness of Ir film was fairly homogeneous with the value being about 100 nm. The oxidized layer (IrO_2) was very obvious and the thickness was only about 10 nm. Two reasons were thought to be responsible for the thickness of IrO_2 layer. One is that IrO_2 layer formed on the surface during annealing at 650 °C above may prevent diffusion of oxygen; and the other is that annealing at a high temperature of 650 °C above may make the structure of Ir film dense or make the grain boundary tight for oxygen not to diffuse along (especially for Fig. 5(c) and (d)).

4. Conclusions

Extremely smooth Ir thin films with (1 1 1) preferred orientation were prepared on Si (1 0 0) substrate by PLD technique at substrate temperature of 300 °C. The results of Ir films annealed at different temperature in air ambient showed that the deposited Ir films remained stable up to 600 °C. Ir films began to be oxidized at 650 °C and continuous growth of IrO_2 was observed with increasing temperature up to 750 and 800 °C. AFM measurements show that the films became rougher and the grain sizes became larger as the annealing temperature increased, this was a result of the growth of IrO_2 crystalline structure.

Acknowledgement

The Project was supported by the Research Foundation for Outstanding Young Teachers, China University of Geosciences (Wuhan).

References

[1] D.V. Genechten, G. Vanhoyland, J.D. Haen, J. Johnson, D.J. Wouters, M.K. Van Bael, H. Van den Rul, J. Mullens, L.C. Van Pouck, Thin Solid Films 467 (2004) 104.
[2] B.R. Chalamala, Y. Wei, R.H. Reuss, S. Aggarwal, B.E. Gnade, R. Ramesh, J.M. Bernhard, E.D. Sosa, Appl. Phys. Lett. 74 (1999) 1394.
[3] J.D. Kim, K. Sasaki, T. Hata, Vacuum 59 (2000) 559.
[4] Y.C. Jeon, J.M. Seon, J.H. Joo, K.Y. Oh, J.S. Roh, J.J. Kim, D.S. Kim, Appl. Phys. Lett. 71 (1997) 467.
[5] Z. Dai, C.B. Meinke, R. Loloee, B. Golding, Appl. Phys. Lett. 82 (2003) 3847.
[6] X. Yan, Q.Y. Zhang, X.D. Fan, Mater. Lett. 61 (2007) 216.
[7] S. Thanawala, D.G. Georgiev, R.J. Baird, G. Auner, Thin Solid Films 515 (2007) 7059.
[8] Y.X. Liu, H. Masumoto, T. Goto, Mater. Trans. 45 (2004) 900.
[9] M. Galeazzi, C. Chen, J.L. Cohn, J.O. Gundersen, Nucl. Instrum. Methods Phys. Res. A 520 (2004) 293.
[10] D. Pergolesi, F. Gatti, L. Gastaldo, M.R. Gomes, S. Dussoni, R. Valle, P. Repetto, D. Marréb, E. Bellingeri, Nucl. Instrum. Methods Phys. Res. A 520 (2004) 311.
[11] M.A. El Khakani, B.L. Drogoff, M. Chaker, J. Mater. Res. 14 (1999) 3241.
[12] V. Demuth, H.P. Strunk, D. Wörle, C. Kumpf, E. Burkel, M. Schulz, Appl. Phys. A 68 (1999) 451.
[13] P.C. Liao, C.S. Chen, W.S. Ho, Y.S. Huang, K.K. Tiong, Thin Solid Films 301 (1997) 7.
[14] M.A. ElKhakani, M. Chaker, Thin Solid Films 335 (1998) 6.
[15] S. Kohli, C.D. Rithner, P.K. Dorhout, J. Appl. Phys. 91 (2002) 1149.