Materials Science-Poland, Vol. 27, No. 2, 2009

Effects of substrate temperature on crystallite orientation of HfO_2 thin films

L. WANG[1,2*], B. FAN[1,3], Z. WANG [1], X. CHENG[1], Y. WU[1], L. CHEN[1]

[1]Institute of Precision Optical Engineering, Department of Physics,
Tongji University, Shanghai, 200092, China

[2]School of Media and Communications Technology, Liaocheng University,
Shandong Province, 252059, China

Optorun Co. Ltd. Kawagoe Shi, Saitama 350-0801 Japan

Hafnium dioxide thin films were deposited on fused silica substrates by reactive electron beam evaporation at three different substrate temperatures. After deposition, hafnium dioxide thin films were annealed in the ambient atmosphere for two hours at 500 °C and 1000 °C, respectively. X-ray diffractometry was used to study physical characterizations of as-deposited and annealed hafnium dioxide. The experimental results showed that hafnium dioxide fabricated at various substrate temperatures had different crystallite orientations after annealing at 500 °C or 1000 °C. These facts suggest that substrate temperature influences not only the crystallization state of as-deposited hafnium dioxide but also crystallite re-orientation after annealing.

Key words: *hafnium dioxide; reactive electron-beam evaporation; crystallite re-orientation*

1. Introduction

Hafnium oxide (HfO_2) has been extensively studied during the last few years due to its relatively high values of the refractive index, bulk modulus, melting point and chemical stability. In particular, it is being considered as a suitable high-*k* material candidate for replacing the gate dielectrics in field effect transistors and dynamic random access memories [1]. HfO_2 is well known as one of the most important oxide thin film materials for interference multilayer coatings down to 250 nm [2, 3]. In general, the dielectric properties of high-*k* materials can be affected by the degree of crystallinity, crystal structure, and crystallographic orientation, in addition to their stoichiometric composition. There have been several reports on the dependences of the dielectric constant upon the crystal structure or crystallographic orientation in high-*k* materials

---

[*] Corresponding author, e-mail: wangyleee@hotmail.com

[4, 5]. HfO_2 may form four crystalline phases (monoclinic, tetragonal, cubic, and orthorhombic) having different dielectric constants [6, 7]. Amorphous layers are generally preferable to gate oxides, but a polycrystalline layer may also be acceptable [8]. Tetragonal and cubic phases can be transformed thermodynamically at approximately 1720 °C and 2600 °C, respectively, whereas the monoclinic phase appears at room temperature [9].

It is therefore important to understand the crystallization kinetics of pure HfO_2 films deposited under various conditions and by various methods and when they are subject to high temperatures. Jiang et al. have demonstrated that the orientation of HfO_2 films is determined by the competition between the surface energy and strain energy by changing fabrication parameters [10]. The morphology and crystallization kinetics of HfO_2 films in function of annealing time or temperature have been previously reported [8, 11, 12]. Until now, however, little work has been done to study the relationship between deposition parameters and annealed HfO_2 crystallization state. In this paper, we report on the solid phase crystallization of HfO_2 films fabricated at various substrate temperatures and on the changes of crystallite orientation after annealing.

2. Experimental

HfO_2 films were prepared by using a box type electron-beam gun coating system (OTFC-1300DBI, Optorun.co., Ltd) at three deposition temperatures, i.e., 100 °C, 200 °C, and 300 °C, on fused silica substrates. The vacuum chamber was baked out prior to deposition for a minimum of 2 h. A programmable temperature controller was used to monitor and control the chamber temperature. Before evaporation, the chamber was evacuated to the pressure lower than 3.0×10^{-4} Pa. Ultrahigh purity O_2 was used to backfill the chamber to the pressure of 1.5×10^{-2} Pa for the deposition. The pressure was monitored by a hot cathode ionization gauge, and it was automatically controlled with a variable leak valve. The evaporation material for HfO_2 films was granular hafnium (of 99.9% purity). The rate approximately of 1 Å/s was maintained for all depositions. Film thickness and deposition rate were monitored by both a crystal monitor and an optical monitor. The crystal monitor was primarily used to control deposition rate, and the optical monitor was used to control film thickness. Table 1 shows the substrate temperatures and the film thicknesses.

Table 1. Films deposited at various substrate temperatures

Sample	Substrate temperature [°C]	Physical thickness [nm]
A	100	756
B	200	739
C	300	735

After deposition, HfO_2 samples were annealed in the ambient atmosphere for 2 h at 500 °C and 1000 °C. The crystal structures of HfO_2 films were investigated using an X-ray diffractometer (XRD Rigaku) in θ–2θ configuration with CuK_α radiation.

3. Results and discussion

The X-ray diffraction diagrams in Fig. 1 demonstrate that HfO_2 films deposited at 100 °C are amorphous, while other samples are polycrystalline.

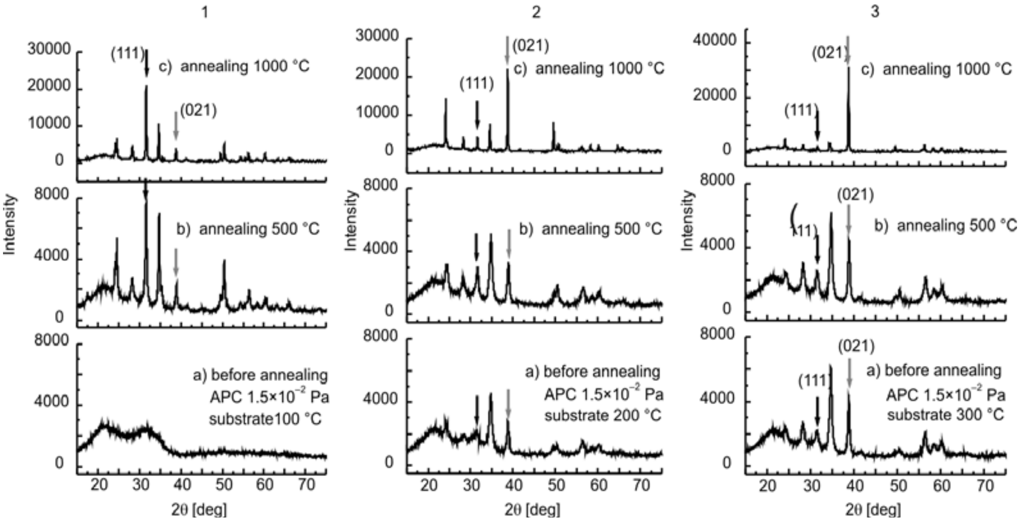

Fig. 1. The influence of substrate temperature to HfO_2 film crystallization state after annealing at: 1) 100 °C, 2) 200 °C, 3) 300 °C

The peak positions and intensities for monoclinic HfO_2 and Hf films from the powder diffraction ICDD card files are shown in Fig. 2.

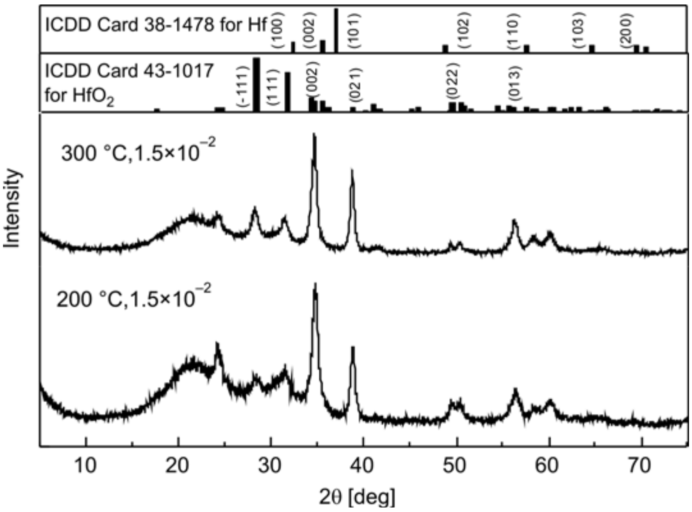

Fig. 2. ICDD card for hafnium and monoclinic hafnia

Each of the resolved peaks in Fig. 1 corresponds to the monoclinic crystal standard and there is no obvious Hf film peak. Around $2\theta = 35°$, there is a strong peak in Fig. 1 (curves 2a and 3a, respectively), which may be enhanced by the superimposed effects of (002), (020) and (200) orientations. The orientations of all the samples changed after annealing and showed different characteristics. After annealing at 500 °C, HfO_2 films deposited at 100 °C follow the transition from amorphous to polycrystalline with strong (111) peak and weak (021) peak, as shown in Fig. 1 (curves 1). As the deposition temperature increases, the (111) peak becomes weak and the (021) peak becomes gradually higher. After being annealed at 1000 °C, the re-orientation of HfO_2 proceeds and the films show the same orientation with stronger (021) peak compared with HfO_2 films annealed at 500 °C. It is obvious that HfO_2 films show preferred orientation during the annealing process. The degree of crystallinity depends strongly on the annealing and deposition temperature, indicating that grain growth in this system is thermally activated.

4. Conclusions

HfO_2 films were deposited at four substrate temperatures and annealed at 500 °C and 1000 °C. The results demonstrate that substrate temperature has great influence on the crystalline state of bpth, as-deposited and annealed HfO_2 films. Sample structure also has important consequences for their optical properties.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (60508018), Committee of Science and Technology Shanghai Municipality (07dz22302) and 863 Project of China.

References

[1] ROBERTSON J., Rep. Prog. Phys., 69 (2006), 327.

[2] TORCHIO P., GATTO A., ALVISI M., ALBRAND G., KAISER N., AMRA C., Appl. Opt., 41 (2002), 3256.

[3] DAVID R., PAUL B., KENNETH J., Appl. Opt., 39 (2000), 1589.

[4] JOSHI P., COLE M., J. Appl. Phys., 86 (1999), 871.

[5] ZHAO X., VANDERBILT D., Phys. Rev. B, 65 (2002), 075105.

[6] LEGER J., ATOUF A., TOMASZEWSKI P., PEREIRA A., Phys. Rev. B, 48 (1993), 93.

[7] PARK P., KANG S., Appl. Phys. Lett., 89 (2006), 192905.

[8] HO M., GONG H., WILK G., BUSCH B., GREEN M., VOYLES P., MULLER D., BUDE M., LIN W., SEE A., J. Appl. Phys., 93 (2003), 1477.

[9] WANG J., LI H., STEVENS R., J. Mater. Sci., 27 (1992), 5397.

[10] JIANG B., REN C., ZHENG Z., LIU X., FAN H., YAO L., LI Y., SU X., Nucl. Instr. Meth. B, 215 (2004), 413.

[11] BOHRA F., JIANG B., ZUO J., Appl. Phys. Lett., 90 (2007), 161917.

[12] MODREANU M., PARRAMON J., CONNELL D., JUSTICE J., DURAND O., SERVET B., Mater. Sci. Eng., 118 (2005), 127.

Received 30 October 2008
Revised 25 March 2008