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Growth and characterization of Gd_2O_3 thin film on Si

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Abstract: Gd_2O_3 thin films were deposited on Si (100) substrates by pulsed laser deposition (PLD). The structure, composition and band offset were investigated by X-ray diffraction (XRD), X-ray reflectivity (XRR), X-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). The results show that, the Gd_2O_3 thin film is amorphous when growing at 300 ℃ and is crystallized into monoclinic structure at 650 ℃. The formation of Gd-silicate interfacial layer due to interface reaction is confirmed by XRR and XPS. The valence band offset (ΔE_V) of (-2.28 ± 0.1)eV is obtained by XPS.

Key words: Gd_2O_3 thin film; pulsed laser deposition; high gate dielectric constant

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硅基氧化钆薄膜的生长及结构

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摘要：采用脉冲激光沉积方法(PLD)在不同温度的Si(100)衬底上制备了Gd_2O_3栅介质薄膜，利用X射线衍射、X射线反射率以及光电子能谱等方法对它的结构、组成以及价带偏移等进行了研究. 结果表明：衬底温度为300 ℃时，Gd_2O_3薄膜呈非晶态；当衬底温度为650 ℃时，形成单斜相的Gd_2O_3薄膜. XPS和XRR结果确定其界面主要是由于界面反应形成的钆硅酸盐. 通过XPS分析得到Gd_2O_3与Si之间的价带偏移为(-2.28 ± 0.1)eV.

关键词：Gd_2O_3薄膜；激光脉冲沉积；高介电常数

0 Introduction

With downscaling of device dimensions in complementary metal-oxide-semiconductor (CMOS) technology, the thickness of the gate dielectric must reduce with the decrease of the gate length.

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A major challenge that needs to be overcome is the thickness of the silicon dioxide insulator. Tunneling-induced leakage currents and dielectric breakdown will lead to unacceptable device performance for oxide thickness below ~1.5 nm[1], so the thin silicon dioxide gate-insulated layer must ultimately be replaced by a high-dielectric constant (high-k) material.

As the candidates of SiO_2, high-k materials should meet some strict requirements, including high dielectric constant, moderate band gap, reasonable band alignment to Si, low oxygen diffusivity, thermodynamic stability in contact with silicon at temperatures exceeding 800 ℃, and high-quality interface with silicon with low interfacial state density[2]. Many candidate materials especially ⅢA, ⅢB, and ⅣB metal oxides (Y_2O_3, Al_2O_3, TiO_2, ZrO_2, HfO_2, Lu_2O_3, et al) and their silicate, aluminate[3-10] have been widely investigated. Recently, Gd_2O_3 has attracted people's attention[11-20] because of its dielectric constant (k~16), closest lattice matches to silicon, and thermal stability in contact with Si at 1 000 K. Up to now, the growth and the electrical property of Gd_2O_3 thin film have been studied. For example, Gd_2O_3 thin film has been grown by means of different growth methods such as metal-organic chemical vapor deposition (MOCVD)[21], electron-beam evaporation[22-23], molecular-beam epitaxy (MBE)[24-25], pulsed laser deposition (PLD)[22], etc. These studies indicate that Gd_2O_3 is a promising candidate of SiO_2. Moreover, these studies also show that the structure and components of Gd_2O_3 thin films are strongly dependent on the growth conditions. However, the corresponding study is still not enough. Therefore, it is very important and necessary to study the structure and components of Gd_2O_3 thin film in detail.

In this paper, Gd_2O_3 thin film was grown on Si (100) substrate by PLD method. The structure, interfacial component and band offset are characterized by combining XRD, XRR and XPS.

1 Experiment

Gd_2O_3 thin film was grown on n-type Si (100) substrates by PLD. Gd_2O_3 powder (99.99% purity) was dried and regrinded, and then was pressed into a pellet to prepare a target for laser ablation. Before deposition, the substrate was cleaned via RCA cleaning process and etched using 10% HF solution to obtain an H-terminated Si surface. A Lambda physik LPX200 KrF excimer laser with a wavelength of 248 nm and an energy density of 2 J/cm^2 was used for the film deposition. During the growth, the vacuum of the chamber was kept less than 2×10^{-4} Pa. The target and the substrate were rotated respectively. The Gd_2O_3 thin films were deposited at three substrate temperatures (300, 450 and 650 ℃), and the deposition time was 6 min.

XRD was measured with a level goniometer using the Cu $K\alpha$ radiation ($\lambda=1.540\,6$ Å). XRR measurement was performed at X-ray diffraction beamline (U7B) of National Synchrotron Radiation Laboratory (NSRL). A Si (111) double-crystal monochromator was used to select a wavelength of 1.54 Å. Specular reflection was measured in θ-2θ scanning mode with step 0.002 5°. XPS spectra was taken in the energy ranges for O 1s, Gd 4d and the Si 2p peaks using monochromated Al $K\alpha$ source. UPS experiment was carried out on surface physics beamline (U18) at NSRL. The sample was put in a UHV (~1.33×10^{-8} Pa) chamber equipped with VG ARUPS10 electron energy analyzer. The resolution of the UPS spectra is 0.1 eV, and the incidence energy is 150 eV.

2 Results and discussion

The XRD patterns of Gd_2O_3 thin film grown on Si (100) at different temperatures are shown in Fig. 1. It is obvious that Gd_2O_3 film was amorphous at a low substrate temperature of 300 ℃, and begins to crystallize at a substrate temperature of 450 ℃. With the substrate temperature increasing to 650 ℃, a diffraction peak at $2\theta = 29.4°$ corresponding to (401) diffraction plane of monoclinic Gd_2O_3 phase (401)[26] is observed, which suggests that the Gd_2O_3 thin film can be grown with the predominant (401) orientation on Si (100). The formation of monoclinic structure of Gd_2O_3 thin films on Si substrate was also reported by using magnetron sputtering under different Ar/O_2 ratio. However, cubic phase Gd_2O_3 thin film grown on Si substrate by using CVD was also reported. These results indicate that the structure of Gd_2O_3 thin film are strongly dependent on the growing conditions.

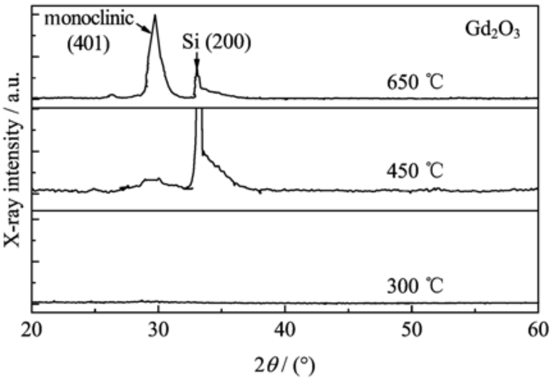

Fig. 1 XRD for the Gd_2O_3/ Si (100) samples as-grown at 300, 450, 650 ℃

The monoclinic structure of Gd_2O_3 appeared at a low substrate temperature, while in general it tends to occur at a higher substrate temperature[18]. Other work groups also obtained the monoclinic structure of Gd_2O_3 thin films. One was deposited on Si (100) substrate at 650 ℃ by a magnetron sputtering system under at Ar/O_2 ratio of 4 : 1[16]. Another was deposited on Si (100) substrate at different temperatures and different ion energies[27].

X-ray reflectivity is an excellent tool to precisely determine the structure parameters, such as thickness, density, roughness of thin films and interface. XRR of the film at 650 ℃ is shown in Fig. 2. To determine the structure parameters quantitatively, the data was fitted using the matrix method. Because the single layer model provided a poor fitting result, the two-layer model, including a Gd_2O_3 layer and an interlayer, was used for fitting and a good result was obtained (shown in Fig. 2). The fitting result indicates that the density of the Gd_2O_3 thin film layer is 7.96 g/cm^3, slightly lower than that of crystal Gd_2O_3 (8.30 g/cm^3). The thickness of Gd_2O_3 thin film and interlayer is 33.0 nm and 1.5 nm respectively. The density of interlayer is 4.75 g/cm^3, which is similar to that of silicate. Therefore, it can be concluded that silicate layer has been formed during deposition. The observed behavior is due to Si reacting with Gd_2O_3 and causes oxygen to diffuse from the top surface towards the film/substrate interface, where it reacts with Si and Gd atoms.

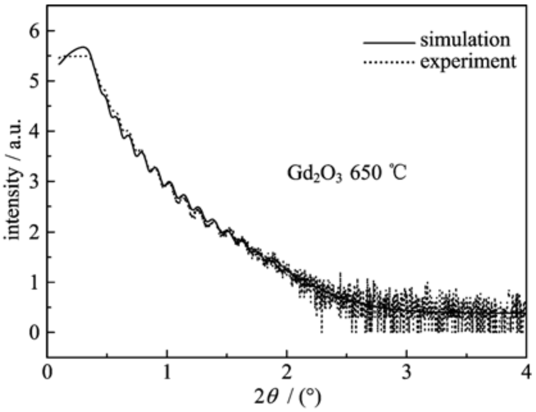

Fig. 2 X-ray reflectivity for as grown Gd_2O_3 film of 650 ℃

XPS is an appropriate method to study the interfacial reaction or diffusion that may occur at the interface layer. A new Gd_2O_3 thin film was deposited for 20 s at 650 ℃ by PLD. Si 2p and O 1s XPS were measured and shown in Fig. 3. The O 1s spectra consist of two peaks, with the main peak with a higher binding energy at 531.42 eV being a little larger than the standard binding energy in the metal oxide, which indicates a low electronegativity caused by oxygen deficiencies[28]. The sub-peak with a lower binding energy of 529.5 eV was supposed to be physisorbed oxygen[29]. For the Si 2p XPS (Fig. 3(b)), the peak at 99.3 eV is due to Si-Si bond from the Si substrate. Two other peaks at 99.8 eV and 101.7 eV, which are lower than Si 2p in SiO_2, can be attributed to Gd-O-Si

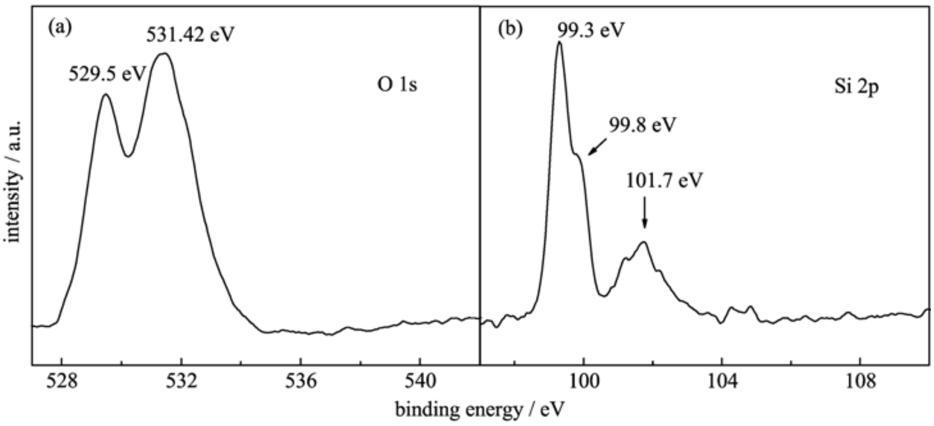

Fig. 3 XPS spectra for the Gd_2O_3 sample of 650 ℃ (a) O 1s and (b) Si 2p

bond. This confirms that the Gd-silicate interlayer is formed, which is consistent with XRR results.

The valence band offset (ΔE_V) is also an important parameter for the gate dielectric. Considering the interfacial layer, the valence band offset of Gd_2O_3 film to Si can be schematized by Fig. 4 and the ΔE_V can be calculated by:

$$\Delta E_V = (E_{Si\,2p} - E_{Gd\,4f}) + (E_{Gd\,4f} - E_{VGd_2O_3}) - (E_{Si\,2p} - E_{VSi}). \quad (1)$$

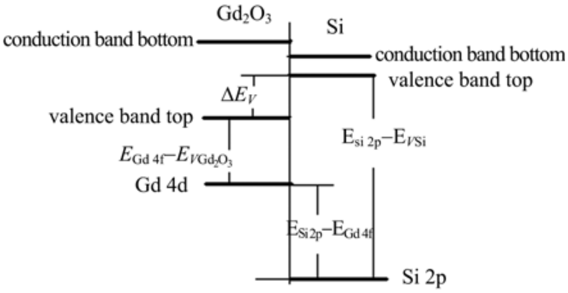

Fig. 4 Schematic energy and band alignment diagram for Gd_2O_3/Si

Fig. 5 gives the XPS of Gd 4f and Si 2p. In order to get the XPS signals from the interface and Si substrate, the as-grown film was etched using Ar^+ ions. Based the XPS, the ΔE_V between Gd_2O_3 film and Si substrate was determined to be (-2.28 ± 0.1)eV, which is consistent with the value of 2.2 eV reported by Hattori[30].

3 Conclusion

In summary, Gd_2O_3 thin films were deposited on Si (100) by PLD. The structure and

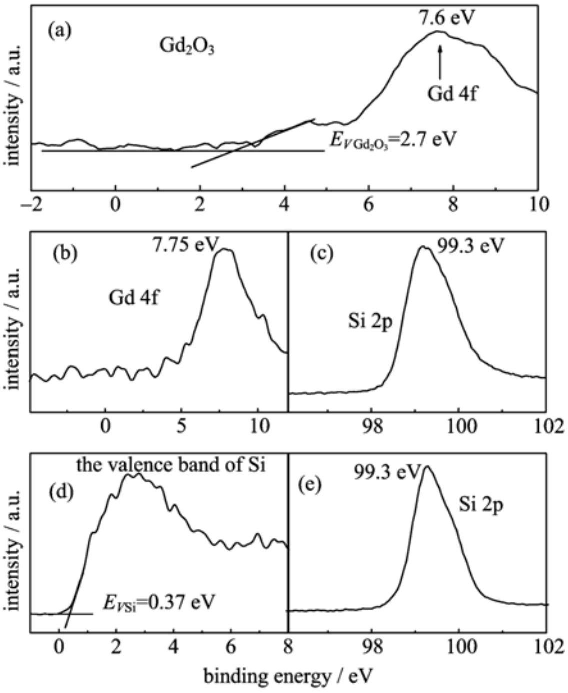

Fig. 5 XPS spectra of (a) Gd 4f peak and the valence band for Gd_2O_3 before Ar^+ sputtering, (b) Gd 4f peak of interface and (c) Si 2p peak of Si substrate after Ar^+ sputtering, (d) valence band of Si and (e) Si 2p peak of Si substrate after deeply sputtering

components of the Gd_2O_3 films were analyzed by XRD, XRR, XPS, and UPS. It was found that the different substrate temperatures strongly influenced the crystal structure of the samples. The XRR spectra and XPS spectra revealed the presence of gadolinium silicate interfacial layer, presumably Gd and Si complex oxides. The valence band offset was obtained by measuring the VBM between the Gd_2O_3 and Si substrate, whose result was (−2.28±0.1)eV.

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